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Probing Magnetism at the Atomic Scale: Non-Equilibrium Statistical Mechanics Theoretical Treatise

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Abstract

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Here, I present a theoretical study, based on non-equilibrium quantum statistical mechanics and on the non-equilibrium extension to the RKKY intveraction,where I investigate the emergence of magnetism at the atomic scale in adsorbed molecular complexes hosting localized spin moments, at the stake of being probed with scanning tunneling microscopy tip, and being driven by a temperature gradient and gated by an electric field. The scanning tunneling microscopy set up is modeled as a molecular junction with a magnetic molecule embedded within it, where the molecule consists in a set of electronic levels resembling the typical s-p orbitals of a metal hydride or an organometal, and a localized spin moment resembling the magnetic unit hosted by the latter and former type of molecules mentioned. The electronic levels and the magnetic units are coupled via the Kondo interaction. One of the electrodes in the junction plays the role of an scanning tunneling microscopy tip, and the other one, does it for the metal in which the molecule is adsorbed, and a bias voltage and a temperature gradient is applied across both metals, giving rise to the effect of the above mentioned experimental set up and producing electrical, spin, energy and heat currents as a response, providing the possibility to predict experimentally observed quantities such as differential conductivities. Throughout the thesis, I present first a comprehensive introduction to the topic pointing out its relevance, the experimental context in which the work I append lies and I as well present the formal structure of the work I present. The upcoming chapters, lead the audience to the discussion of the non-equilibrium formalism in atomic, molecular and condensed matter physics, paying special attention on the subject on magnetism, and putting in to context the molecular system where the interplay, among electrons, spins and phonons is relevant. To wrap up the theoretical discussion I described the state of the art progress on quantum coherence and interferometry in molecular junctions and locate my contribution into this context. Then I conclude and summarize. My contribution promises to pave the way to more robust spin based quantum engineered technology.

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Dedicated to ELOHIM, G-D of Israel, blessed be His Holy name, Yeshua Ha'Mashiach, salvation is your name.

To my Supporting and Beautiful Wife Laura,

To my Mother Martha, My Father Gustavo,

My Siblings Daniel and Laura, Maricela, Angela, Eliana Marcela, David Ricardo and Matthew, always in my heart and mind,

To all of Those in the Department of Science, Technology and Innovation in the Colombian Government - Colciencias and in Colfuturo (Academic Operator),

Specially to Constanza, Juaninta, Fabio Iguavita, Laura, Ronald Guzman, for all the support and great effort you made to help me to move forward and to make progress,

To the Sephardic Diaspora, my prayers and love always with you.

To the Memory of my mentor in the Torah and Colleague Andrew Murray Knott (1962-2015)

List of papers

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

   I   *Charge Transport and Entropy Production Rate in Magnetically Active Molecular Dimer* , *J. Phys. Chem. C 121, 49, 27357-27368*,

  II   *Electronically Mediated Magnetic Anisotropy in Vibrating Magnetic Molecules* , *Accepted for publication in ACS-Omega*,

 III   *Quantum Coherence Driven Magnetic Ordering in Biased Three Level Organometallic Molecules* , *Manuscript*,

 IV   *Spin-dependent heat signatures of single-molecule spin dynamics* , *Manuscript*.

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Contents

Part I:
Background and Context

Besides introducing the background and context in which my research contributes to the advance and progress of the fields of molecular magnetism and non-equilibrium statistical mechanics, in this part I want to empower former colleagues from schools of electrical and electronic engineering, and related audience with the tools to understand the investigations presented here, and then possibly to motivate them to dive into this amazing field.

1. Introduction

How old is really the first reference to Magnetism?

And G-d said, Let there be light and there was light.

Genesis 1:3.

1.1 Context of This Thesis

Very often in science, crucial progress is made when the historical background and how different efforts converged to achieve it are known. This line of thought is representative of the way many fields have evolved, including electrodynamics, general relativity and optics, where in the moments in which sufficient convergence was achieved, great progress was made as in the case of Maxwell laws for electrodynamics, and the historical progress made from Oersted to Faraday, gave Maxwell an enlightening intuition about the correspondence between light and electromagnetic waves. Condensed matter physics is not an exception to this rule, and the quantum theory of magnetism is an excellent sample representative of this population, in which, the convergence of different philosophies/schools and the knowledge of how the thought about the magnetic manifestations of matter change through the centuries played a crucial role, if not, unambiguously dominated the fundamental knowledge we posses nowadays, about magnetic interactions at the atomic level in condensed matter. The path that went From the perception of magnetic effects in Iron ores to the magic of the Earth's magnetic soul, to the majesty of Maxwell's electrodynamics to the striking result of Bohr-Van Leewuen theorem that settle the basic questions yet to be solved by Heisenberg, Landau, Pauli, Anderson, Wannier, Kondo among others, and that brought the scientific knowledge to the awareness of the development of localized magnetic moments in impure metallic compounds, is what brought the work that I will present in the next few chapter about magnetic interactions at the atomic level, and how can they be engineer from the convergence of the current research and understood from the contributions of the great scientists of the past century that never let their guard down when the manifestations of magnetic matter broke the schemes and paradigms they knew and had built.

In this thesis, I will elaborate on how spin-spin interactions can be engineered from the manipulation of host materials and probed using schemes

corresponding to Scanning Tunneling Microscopy (STM) experiments. Along the way, I have considered, as well, how to detect spin states formed when magnetic impurities are adsorbed on a host, and rather to manipulate and tune this interactions, I am interested in measuring them for the purpose to contribute in the interpretation and study of ground breaking experiments [1, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14] that will lead to quantum state preparations using spin degrees of freedom, envisioning their integration in to systems of quantum information, quantum communication, but more importantly, of quantum metrology.

In the next few sections, I will try to convince you that the study of magnetism ever since known, shaped the way we live and the way we survive, and I will lead you to the ground where engineering magnetic interactions at the atomic level became important, mainly due to the progress made in science physics in the past two centuries.

1.2 Relevance of the Study of Magnetism in our Society

Magnetism, such a mysterious phenomena for many, magical for others, attractive for fewer, has driven the curiosity of the latter since the times of the Greeks in magnesia with the load stone and the Chinese with the compass. At such an early stage of human civilization, Magnetism had already revolutionized the life style of the inhabitants of the earth by becoming an essential mechanism for human navigation, and at a latter stage, it will become the cornerstone of human progress providing the necessary means for understanding energy conversion, for making radio-communication a reality and for enabling the storage large amounts of information, among others.

Moreover, leaving technical progress aside, that evolved intimately linked with the understanding of electricity and magnetism and their consequences in matter, the latter has been proven unappealingly important for life on our planet, as the Earth's magnetic field is a powerful shield against cosmic rays as well as a useful lighthouse for animal navigation specially birds and turtles, but as well for bacteria and

$$\vec{\nabla} \cdot \vec{D} = \rho$$
$$\vec{\nabla} \cdot \vec{B} = 0$$
$$\vec{\nabla} \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t}$$
$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$
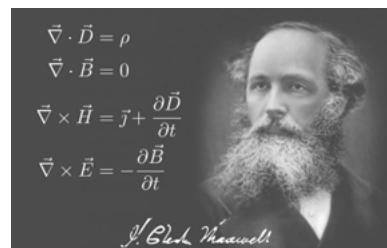
Figure 1.1. James Clerk Maxwell

related micro-organisms[1].

This amazing phenomena, can be attributed to the currents of molten iron in the Earth's outer core, what William Gilbert in 1600 called the Earth's magnetic soul, and its manifestations will later, in the 19th century, give rise to observations that shaped what we now know as Maxwell's laws, which became of capital importance in the technological progress of human kind [15], [16]. These suggests that if all of the sudden, the laws of physics will change, most probably cars, radios, phones, fridges will not exist, but what is certain, is that life as we know it, will disappear from our planet, making the study of magnetism not only important for the technological and economical progress, but crucial for the survival of humans on Earth [16].

1.3 Perception Mechanisms of Magnetism at the Microscopic Scale

The perception mechanisms used to observe the ability of macroscopic matter to exhibit magnetism, nowadays are quite robust, and serve to test very well established knowledge in the field, such as the Biot-Savart law, the Ampere-Maxwell Law, the Faraday-Lenz law, the Gauss law for charge density, part of the family of Maxwell laws for electrodynamics [15], [16].

Nonetheless, in the times where James Clerk Maxwell was investigating the mathematical unification of the above mentioned laws, little clarity about how magnetism emerged from matter was given, even though the different magnetic manifestations in different compounds were known, namely *Paramagnetism*, *Diamagnetism* and *Ferromagnetism* (See reference [17] for details), their explanation from a more fundamental point of view was still a great chal-

Figure 1.2. Recognition to J. C. Maxwell at King's College

lenge. It was only until Niels Bohr in 1911 and Hendrika Johanna Van Leeuwen in 1919, both on their *Doctoral Dissertation*, that through the consistent application of statistical mechanics and classical mechanics, it was proven that the thermal average of magnetization will always be zero [18], hence, suggesting that the phenomenon of magnetism was purely

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[1]A very nice dive in, into magnetism is found on the second volume of Lectures on Physics by Richard Feynman

quantum mechanical, result reported in [19]. In the coming years, several attempts to understand ferromagnetism were made by E. Ising [20] and W. Heisenberg [21], setting the basis of what we know know as *effective fields* and *exchange interactions*, concepts of radical relevance in the description of the manifestations of magnetism in material systems. On the counterpart, *Paramagnetism* and *Diamagnetism* was studied by Pauli, Landau and Langevin respectively [17], settling the foundations of the field of magnetism in condensed matter as we know it nowadays, but in the coming decades a new problem in this field will emerge as a consequence of doping metals with magnetic impurities, and great amount of new physics will drive the fascination of young and old [22].

1.4 Emergence of Quantum Magnetism: Magnetic Moments

As early as the 1930's, scientists were already aware that, the basic manifestations of magnetism in matter, namely ferro-para-dia-magnetism were of quantum origin. From the perspective of Schrödinger equation, this statement was understood by considering a Hamiltonian of the form [18]:

$$H = \frac{(-i\hbar\boldsymbol{\nabla} - e\boldsymbol{A})^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{e^2|\boldsymbol{A}|^2}{2m} + \frac{ie\hbar}{2m}\left(\boldsymbol{A}\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\boldsymbol{A}\right) + V(r),$$

where m represents the mass of the electron, e is the electron charge, $\hbar$ is the normalized Planck's constant and $\boldsymbol{A}$ is the magnetic vector potential, which is given by $\boldsymbol{A} = \frac{1}{2}r \times \boldsymbol{B}$, being $\boldsymbol{B} = (0,0,B_0)$ the magnetic field aligned with the z-axis. In terms of B_0, the Hamiltonian for the electron in the Magnetic field $\boldsymbol{B}$ reads now as:

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{e^2}{8m}\left(x^2 + y^2\right)B_0^2 + \frac{ie\hbar}{2m}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)B_0 + V(r).$$

Going one step further in arranging the above Hamiltonian, let's recall that the z–component of the angular momentum $\boldsymbol{L}$ reads $L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$, which can be used to arrive at a final form for the Hamiltonian $\boldsymbol{H}$:

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{e^2}{8m}\left(x^2 + y^2\right)B_0^2 - \frac{eB_0L_z}{2m}B_0 + V(r). \tag{1.1}$$

Now, the question that L. Landau asked was, how can paramagnetism emerge from quantum mechanics?. The answer to this question, that can be asked for the phenomenon of diamagnetism as well, is related to how sensitive the energy of the electron $\epsilon_e = \boldsymbol{\mu}\cdot\boldsymbol{B}$ is to the applied magnetic field, that is, is related to the magnetic moment of the electron $\boldsymbol{\mu} = \frac{\partial H}{\partial \boldsymbol{B}}$.

Calculating the magnetic moment component μ_z from expression 1.1, one arrives at the following important result:

$$\mu_z = -\frac{e^2}{4m}\left\langle\left(x^2+y^2\right)\right\rangle B_0 + \frac{eL_z}{2m} = \mu_{dia} + \mu_{para}, \qquad (1.2)$$

where μ_{dia} and μ_{para} are the diamagnetic contribution to the total moment and the paramagnetic contribution, respectively, and are independently given by:

$$\mu_{dia} = -\frac{e^2}{4m}\left\langle\left(x^2+y^2\right)\right\rangle B_0 = -\frac{e^2}{6m}\left\langle r^2\right\rangle B_0, \qquad (1.3)$$

$$\mu_{para} = \frac{eL_z}{2m}. \qquad (1.4)$$

On the same front, W. Heisenberg also used the concept of local magnetic moment in his pioneer work on ferromagnetism [21], but it was only until the late 1950's when the mechanism of local moment formation was unveil from a theoretical point of view, which was motivated by ground breaking experiments performed during the 1930's, where W. J. de Haas, J. H de Boer, and G. J van den Berg observed a resistance minimum in Gold, Copper and Lead, which was not completely understood until scientists developed novel techniques to control the level of purity in metals [22], [23], [24], [25], [26], [27]. Once the concentration of individual magnetic impurities in metals ranged in parts per million, Al Clogston and collaborators showed different conditions under which a local magnetic moment can be formed in metals, and hence, at low enough temperatures, a resistance minimum will emerge [28]. This deep understanding about the localized magnetic moments from impurities in metals, motivated two bright scientists to deliver a contribution on this direction, namely, Philip W. Anderson in 1959 [29] and 1961 [30] and Jun Kondo in 1962 [25] and in 1964 [26]. J. Kondo considered a series of metallic materials doped with magnetic impurities, and from previous experiments he came to the conclusion that the resistance minimum observed previously was related to the presence of a localized magnetic moment, what drove him to used the s-d exchange model previously considered in the work by Zener [24], Kasuda [31] and Yosida [32], based on the argument that the resistance minimum was exclusively related to the interaction between the localized spin and the conduction electrons, giving rise to the effective field Hamiltonian known as the **Kondo model** (For details see chapter 5):

$$\boldsymbol{H}_{spin} = J\boldsymbol{s}_e \cdot \boldsymbol{S}, \qquad (1.5)$$

where J is the exchange constant between the localized spin and the conduction electrons in the metal, s_e is the spin operator for the conduction electrons and S is the spin operator for the localized magnetic moment.

Kondo's conclusion with regards to the temperature at which the resistance minimum happens and how deep is that resistance minimum is irrelevant for the work presented in this thesis, however, the Kondo model given by expression 1.5, became of capital importance to understand the spin-spin interactions at the atomic level, being signatures of the latter, the modulation of the electrical properties of the metal that hosts the magnetic impurity. These discoveries will then pave the way to engineer spin-spin interactions at the atomic level when a metal is doped with magnetic impurities, through the conduction electrons of the host, enhancing the understanding of spin ordering with just few degrees of freedom, and therefore creating the context to explore magnetism at the atomic level [2]. This new world that the pioneer fathers of the field will never have envisioned with, promises to change our society in similar ways that magnetism at larger length and energy scales did.

1.5 Perception Mechanisms of Magnetism at the Atomic Scale

With the development of Scanning Tunneling Microscopy (STM) by Binnig and Rohrer in the 1980's, the perception mechanisms, meaning the instrumentation useful to manipulate and control matter at the nanometer scale were noticeably enhanced [33]. Combined with the control of purity in metal thing films and with the study and further progress in conducting polymers and molecular electronics first by Ratner's proposal of the molecular rectifier [34] and then by the revolutionary discoveries Heeger and Marmid [35], [36], [37], [38], [39], STM experiments showed its usefulness and electrical detection of atomistic quantum mechanics became real, when Xenon atoms were deposited in to a single crystal Nickel surface [40] and subsequently imaged (See image 3 in Ref. [40]). The latter, pave the way for new and novel experiments of manipulation of atoms adsorbed on surface [13].

In the last decade, experiments showing the capability of STM measurements to resolve magnetic structure [2], [3], to study the strength and orientation of magnetic anisotropies of individual Iron and Manganese atoms adsorbed on Copper Nitride [41], [42] and to tailor nanomagnets (Using Spin-Resolved Scanning Tunneling Microscopy) going from atom manipulation to engineer complex 2D arrays of magnetic ad-atoms interacting through the RKKY interactions [2], [43], [44], as well as antiferromagnetic nanostructures from spin-polarized STM where the magnetic states designed can be switched among with all electric control, technique that as showed to provide usefulness in tuning the nature of the interaction [45], as well by applying a temperature gradient across the STM tip and the substrate [46]. Manipulation of few spin degrees of freedom has triggered

interest in the community of magnetism in the condensed phase due to the increasing interest in designing and controlling spin states and tuning spin-spin interactions [8], [47], [48], [49], for potential applications in quantum information technology, in spintronic devices and in quantum engineering applications, more punctually in quantum metrology designs. More specifically, experimental systems of interest, include supramolecular spin valves where a single [9] or a dimer of spins is grafted into a carbonnanotube driven by nonmagnetic electrodes [50], showing outstanding magnetoresistance ratios [9]. Switching devices where the behavior between a spin pair of Cobalt atoms adsorbed on Copper substrates exhibiting different transport signatures for triplet and singlet pairing were tested and its applicability demonstrated [10]. Moreover, the coherent control of three-spin states in a triple quantum dot, where the desired behavior is to persist in coherence while the exchange coupling of one spin in increase with respect to another one and is decreased with respect to the remaining one, hence, fulfilling one of the criteria for spin-qubit architectures, demonstrated for first time [51], [52].

Moreover, an increasing interest in the effect of molecular vibrations coupled to single magnetic units as in the experiment reported in [50] has seen a dramatic increase, both from the experimental [53], [54] and theoretical point of view [55], [56]. In [50], a single molecule magnet is drafted onto a carbon-nanotube with discrete phonon density of states, opening the possibility to study the effect of individual phonon modes on the magnetism of the SMM. This work was based on the proposal of a vibrating carbon nanotube pending from two metallic electrodes, where precise magnetometry was predicted based on the sensitivity of the vibrational frequency of the Carbon nanotube to an applied magnetic field [57]. In nanomagnets, the renormalization of the phonon frequency by the magnetic exchange interactions has been observed and demonstrated [53], and theoretical predictions have been made on how vibrations also modulate the tunneling magnetoresistance [55], [56]. This outstanding progress on the study of phonons and spins in few molecule-condensed matter physics, and the experimental observation of more flexible and robust single ion magnets with large single ion anisotropies [58], [59], [60], on top of the scarcity of investigations aiming at making theoretical predictions on the strength and orientation of the single ion magnetic anisotropy, motivated the study appended in this thesis in paper II.

On the theoretical ground, STM measurements have fuel a broad range of studies where a model Hamiltonian representing the microscopic mechanisms giving rise to the interactions within a specific molecule, constitute the basic ingredients of a theory used to make useful predictions based, mainly on transport calculations [61], [62], [63], [64], [65], [66], [67]. This

theory, which is based on how strongly or weakly the former molecule couples to metallic leads, representing the STM tip and a metallic substrate, captures essential pieces of physics from the molecule in the calculated electrical currents, differential conductivities and transmission probabilities, resembling the experimental set ups where molecules adsorbed on surfaces are probed by an STM tip. Some studies of relevance using this theoretical formulation have been put forward by Prof. Jonas Fransson [68] where by calculating differential conductivities, essentials of inelastic transport processes are picked up as signatures from the predictions, and the magnetic structure of a sample is also resolved from this formalism. Recently, motivated by experiments by Jens Wiebe [2] and by Heiko Webber [10] on effective spin-spin interactions in magnetic ad-atoms, it was shown that signatures of the formation of spin singlet and triplet states were observed in the charge current. In this thesis, I extend this formulation in paper I to the problem of entropy production within the magnetic molecule, and correlate the results obtained with the formation of a triplet and singlet states, aiming at distinguishing coherent and incoherent transport processes from the knowledge about the spin-state. On paper III, the investigation of molecules with more complex spin structure are considered, among which, particular interest is put into Triradical Trianion of a Naphthalenediimide molecular triangle, which exhibits both all ferromagnetic interactions and spin frustration [69], and reference is made to similar studies on molecular frustration [70], [14], [71], from where a set of open questions in non-collinear molecular magnetism emerge, that can be approached from the viewpoint of non-equilibrium statistical mechanics.

1.6 Research Questions and Contributions in This Thesis

In the present thesis I approached the following scientific questions and related issues:

1. All Electro-Thermal Control on Molecular Machines: How can a bias voltage, a gate field and a temperature gradient across a molecular junction serve as a control signal for spin states formation? and how coherent and incoherent transport processes can be used as a detection mechanism to sense the former states?
2. Single Ion Anisotropy Modulation: What is the interplay between electron correlation energy and vibrational degrees of freedom in the stability and control of the direction and strength of magnetization of a single molecule magnet?
3. Interplay Between Quantum Coherence and Magnetism at the Molecular Scale: What is the effect of the degree of quantum interference in a molecular complex hosting magnetic units on their RKKY spin-spin

interactions? What is the effect of the spin back-action on the degree and nature of quantum interference in the molecular complex hosting the magnetic units giving rise to the former?

4. Detection of Time Scales in Spin Dynamics Driven Energy Current?

1.7 How to read This Thesis

This thesis is segmented in 3 parts: Introduction, theoretical background and contributions and outlook. Throughout the first *chapter*, I expose chronologically, the scientific progress that lead to manipulation of magnetic matter at the atomic scale and how it became reasonable to detect the associated interactions electrically, and perhaps thermally. In *chapter 2*, I briefly discuss the logic behind scanning tunneling microscopy, a simple scheme is detailed and how to look at an STM experiment from the perspective of a tunneling junction. To wrap up part I, chapter 3 discusses the formal structure of this thesis, introducing the basic philosophy of the many body problem, the common language of quantum mechanics and the crucial relationships deriving from the theory of quantum mechanical angular momentum, these mainly to put readers with background in electrical engineering in context with the content of the investigations presented here. Moving forward, you will encounter Part II, which deals with the theoretical background that the work I present here embraces, and is constructed for three different type of audiences: electrical engineers with basic knowledge on electrodynamics and no-knowledge on quantum mechanics, physicists and chemists with some background in quantum mechanics but with discrete knowledge on statistical mechanics and quantum optics, and lastly, to the audience that is rather familiar with the problem of molecular magnetism and non-equilibrium statistical mechanics, and this is just a mere formality to provide details and context with respect to my doctoral investigation. As such, feel free to skip any section of the theoretical background in which you feel a good degree of comfort or which you find irrelevant for the discussion of the work presented here. Firstly, chapter 4, leads to reader to the concept of non-equilibrium Green's function from the basic notions about the Green's function in classical electrodynamics and zero-temperature quantum mechanics. For experts in the usage of Green's functions in quantum mechanics, I strongly suggest to skip chapter 4, and if the reader is rather familiar withthe concept of Green's functions, but not with its usage in non-equilibrium statistical mechanics, I suggest to skip the chapter in mention until section 4.2. In Chapter 5, I fully derive, from an effective spin action theory, the expressions for RKKY exchange in the context of systems out of equilibrium, putting the results into context by settling the zero temperature theory of effective RKKY effective exchange, and by comparing the latter and the former with the phenomenological Heisen-

berg Hamiltonian for classical spins. Moreover, a very exciting chapter in my personal opinion, chapter 6, elaborates on the physics of the electron-phonon interaction, how it emerges in different types of condensed matter systems, how to put the latter into the context of molecular junctions, and I briefly discuss the interplay between vibrational degrees of freedom and electron correlation energies in the context of quantum dots and molecular junctions. In this chapter, I also present a detailed derivation of the phonon correlation function and the correction to the electronic Green's function by the vibrational induced renormalization of the electronic parameters such as energy of the electronic level and the associated electron-electron interaction energy, in a similar fashion as presented in [68]. In chapter 7 I present a detailed derivation of a generalized framework for obtaining the non-equilibrium Green's function for multilevel molecular systems with arbitrary coupling to electron reservoirs, given an original model Hamiltonian that results from the Bosonic-Fermionic decoupling emerging from the application of the Lang-Firsov Transformation. In the rest of the chapter I used the derived formalism to analize, and furthermore derive the electronic Green's functions characterizing the dynamics of each of the systems analyzed in this thesis. The last chapter of this part, namely chapter 8, is related to the phenomenon of quantum interference in molecular junctions, and its interplay with magnetic ordering in such amazing systems. I give an overview of the main questions asked, the relevance of the field and the theoretical methods used and how to merge them. Moreover, I discuss the well established knowledge in relation to single photon interferometry and how to extend this paradox to single electron interferometry in molecular junctions. Lastly, I discuss electron interferometry in molecular junctions from the view point of the Aharonov-Bohm effect and available models in the literature, such as, quantum coherence in two level systems, with dephasing and without dephasing. The last part of this thesis deals with the description of the appended papers, with a brief overview of the results and contribution. Then, the remaining chapters are devoted to conclusions, future work, acknowledgments, summary in Swedish, summary in Spanish and appendices.

2. Scanning Tunneling Microscopy: Probing at the Atomic Scale

"If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms â little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied."

And,

"Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy."

Richard Feynman.

2.1 Scanning Tunneling Microscopy - STM

Invented by Binnig and Rohrer and implemented by the latter and the former in addition to Gerber and Weibel, scanning tunneling microscopy (STM) gave light to understanding, manipulating and controlling matter at the atomic scale, that is, probing matter at the atomic scale [33]. The essential elements of an STM are the scanning tip usually made of W or $Pt - Ir$ alloy; and a piezo drive, which consists in three mutually perpendicular piezoelectric transducers (labeled as x, y and z piezo in [33]). By applying a voltage the piezoelectric transducer expands or contracts. The form of this voltage determines how the XY plane of the sample is scanned, where the latter can be performed by applying a sawtooth like voltage to the x-piezoelectric and a ramp like voltage on the y-piezoelectric. The z-piezoelectric along with a coarse positioner are used to approach the STM tip towards the sample, until both of them are set to be few Ångströms

apart, and as a consequence, the wave-functions in the tip and in the sample surface overlap. As a consequence of this interference phenomena, purely quantum mechanical, electron current flows from the tip to the surface, current known as tunneling current, which is distinguished from other transport phenomena as its nature is purely quantum mechanical, originating from the overlap among wave-functions.
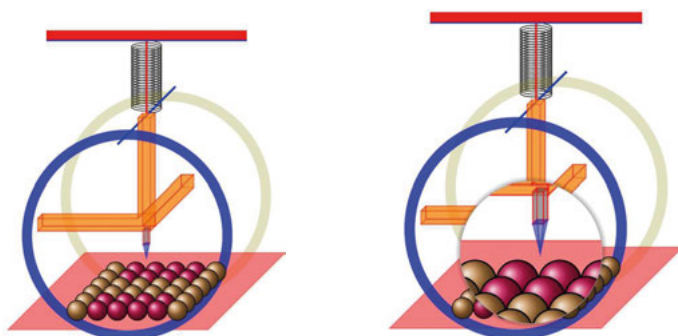
Figure 2.1. **Left-Panel**: The typical configuration of an STM experiment is shown. The tip is painted in blue, and the piezo-electric transducers painted in orange. The substrate is a plane painted in red, and the surface of atoms to scan are painted in brown and in purple. The chamber of the STM lies between the blue and light green rings.
Right-Panel: The region where the tip approaches the sample is magnified. Recall that the sample and the tip are just few Ångströms apart

2.2 STM and Molecular Electronics

Probing molecular interactions at the atomic scale provides great insight on the interplay between structure and function, a crucial understanding that leads to the enhancement of the perception mechanisms of electronic, optic, thermal, magnetic and mechanical properties among others, of the molecule being interrogated. Among two of the most important manifestations of microscopic matter that can be probed using electro-thermal measurements are quantum coherence and magnetism, both of which hold a strong correlation with the molecular structure of the unit under test. This

is where molecular electronics and probing techniques at the atomic scale converge in the concept of molecular junctions.
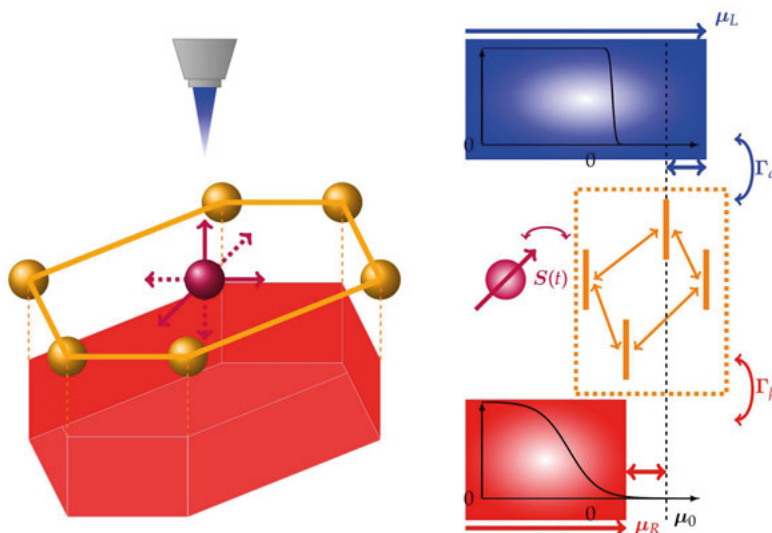
Figure 2.2. Schematic Of Scanning Tunneling Microscopy as a Tunneling Junction: The STM tip painted in blue is represented in the molecular junction by a electrode in the same color, with an associated Fermi-function f_L, chemical potential μ_L and temperature T_L. Likewise, for the metallic substrate which is represented by a plane painted in red, there is an equivalent metallic electrode in the molecular junction shown to the right side, with an associated Fermi-function f_R, chemical potential μ_R and temperature T_R. The Fermi-functions associated with each electrode are sketch on top of them, with the convention of blue for colder and red for hotter, therefore giving $T_R > T_L$. This situation can be reversed, that is, $T_R < T_L$, the convention adopted here is just an exemplifying one. The coupling between the STM tip and the molecule is represented by parameter Γ_α, and the coupling between the molecule and the substrate is represented by Γ_β. The molecule is described by a set of orange atoms linked with orange bonds. To the right, in the molecular junction, this is represented by a set of levels and a set of couplings or hybridizations among these levels. Lastly, the magnetic unit within the molecule painted in purple is shown in the molecular junction coupled to the molecule, this via the Kondo interaction.

Molecular electronics as opposed to scanning probes, is concern with the design of molecules and polymers that will give a desired electrical, magnetic or thermal response. On the other hand, techniques such as scanning tunneling microscopy are more concern with studying the structure and discerning the function of molecular assembles from the electric,

magnetic or thermal response to a metallic probing tip. As they converge in the concept of molecular junction, it is useful to describe the STM experiment with the use of a junction associated with the experiment as shown in Fig. 2.2. Throughout the thesis, I explore few types of systems that can be accurately, at least to some reasonable point, described by a set up as the one described in Fig. 2.2, and in a more didactic way, as shown in Fig. 2.3, where some spin structure in the surface of the substrate is shown. In chapter 7, these set-ups will be explained and fully developed from the perspective of Non-equilibrium Green's functions, and some of them will be discussed in chapter 8, and all of them in chapter 9 to some level of detail, as a prelude to the appended papers to the thesis.
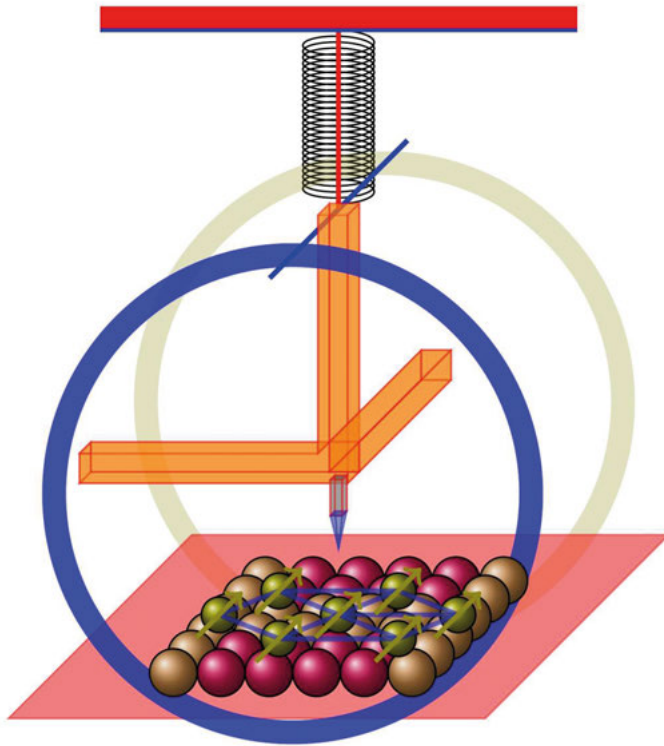
Figure 2.3. Engineering Atom-by-Atom Exchange Interactions in an STM experimental Set-Up: Typical system considered in the investigation of this doctoral thesis.

3. Formal Structure of the Thesis

"The aim of science is to make difficult things understandable in a simpler way; the aim of poetry is to state simple things in an incomprehensible way. The two are incompatible".

Paul Adrien Maurice Dirac

3.1 Contextualization

Quantum theory is built in a rather axiomatic fashion, building a representation for quantum mechanical eigenvalue problems in an infinite dimensional Hilbert space. The Stern-Gerlach experiment, made manifest the intrinsic magnetic nature of the electron, which was later clarified by Paul Dirac presenting the theory of the magnetic moment of the electron. From Dirac's equation it became obvious, that, the Hilbert space spanning the possible spin states of a spin $\frac{1}{2}$ particle is bidimensional, what was then known as isospin space, since it could serve as a representation for any two level system. Moreover, the explanation of the anomalous Zeeman effect set the basis for understanding the conservation of the total angular momentum of the electron.

In this chapter, I review some of the axiomatic representations in quantum mechanics, mainly for multiple degrees of freedom, the basic notions of a many body state and the basics of the conservation of total angular momentum. The discussion of Spin Hamiltonians in the upcoming chapters will be heavily based on the discussion presented below.

3.2 Introduction to the Many-Body Problem

The behavior of large and complex aggregations of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of the properties of few particles. Instead, at each level of complexity entirely new properties appear, and the understanding of new behaviors requires research which I think is as fundamental in its nature as any other.

Philip W. Anderson.

3.2.1 Where is Many Body Quantum Theory?

Many body physics in condensed matter deals, with the basic question of what principles and laws emerge as time and length scales go from their characteristic values at the microscopic scale to the ones at the macroscopic scale [72]. At the microscopic scale, time is of the order of $10^{-15}s$ when energy ranges around $1eV$, and $10^{-8}cm$ characterizes the length scale. At present, I am not interested in going beyond few nanometers in length scale and the physics emerging is spanned around the meV range, which makes the many body challenge much more practical as compare with the cases in which the desire of the study is to understand the emergent properties in materials with a macroscopic number of electrons (of the order of 10^{23}). One of those properties that emerge as a consequence of many body interactions is the pressure in a gas. Although pressure was studied at an early stage by Bernoulli and Pascal from a phenomenological point of view, it was James Clerk Maxwell the one who actually understood pressure from a statistical description by considering an ensemble of particles responsible for the emergence of such macroscopic observable in gases, showing the impossibility to understand it from a single particle view point [73], [72]. In general, many body interactions at the microscopic level, govern the ruling principles of materials such as metals, semiconductors, minerals and even insulators. Chemistry and life, in general, is a consequence of many body interactions at the most fundamental level and areas such as quantum biology have emerged as a rather necessity to explain emergent phenomena in life sciences in terms many particle interactions [17], [74], [72]. More importantly, in the context of this thesis, I will develop the concept of molecular magnetism, that emerges purely from a quantum many body phenomenology such as the Coulomb interaction, what makes the development of the many body terminology crucial for me and the reader to communicate properly during this journey throughout molecular magnetism driven out of equilibrium.

3.2.2 The Many Body Problem

The many body problem deals with the basic aspect of determining the quantum state of a many particle system, that is, to solve Schrödinger equation for a many particle system. To make sense of it, let's recall that the Schrödinger equation for a single particle problem is given by [75]:

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}), \qquad (3.1)$$

where the wave function $\psi(\boldsymbol{r})$ represents the state of a quantum mechanical particle located at position $\boldsymbol{r}$, E is the energy of the particle, m its mass and $\hbar = \frac{h}{2\pi}$ is a constant, referred to as the normalized Planck's constant.

In a similar way, the two particle Schrödinger's equation given by:

$$-\frac{\hbar^2}{2m}\nabla^2_{r_1}\psi(r_1,r_2) - \frac{\hbar^2}{2m}\nabla^2_{r_2}\psi(r_1,r_2) + V(r_1,r_2)\psi(r_1,r_2) = E\psi(r_1,r_2),$$
(3.2)

can be thought as the simpler many particle model in quantum mechanics, where the state of the two particle system is determined by the two particle wave function $\psi(r_1,r_2)$, in which particle 1 is located at r_1 and particle 2 is located at r_2. In general, what one pursues in the many body problem, is to solve Schrödinger's equation for a system of N particles whose state is determined by the wave function $\psi(r_1,r_2,\cdots,r_N)$ [75]. The solution to this problem becomes impractical for systems, for instance, encompassing a number of particles of the order of 10^{23}. Density functional theory provides a way out to this problem, and is an exact when what is known as the exchange correlation functional is known. For details see ref. [17].

Throughout the thesis, I am more interested in at most two particle systems, describing electron-electron interactions at the most. For simplicity, I will illustrate some fundamental concepts and convey some important points that will lead to defining a proper language to communicate my work with a variety of audience. For a two particle system of indistinguishable units, weather electrons (Fermions), protons (Fermions), phonons (Bosons), when the units are interchanged in position, their wave function might pick up a minus sign, leading to:

$$\psi(r_1,r_2) = \pm\psi(r_2,r_1),$$
(3.3)

and since the indistinguishability of the constituents of the system will bear no observable account, the probability to find a particle in a given position will be the same:

$$|\psi(r_1,r_2)|^2 = |\psi(r_2,r_1)|^2.$$
(3.4)

The above result, expressed through equations 3.3 and 3.4 is known as the symmetry condition of the wave function, that upon particle permutation picks up a minus sign for the case of Fermions (Antisymmetric Wave Functions) and remains unchanged for the case of Bosons (Symmetric Wave Functions). I will focus mainly in the case of electrons, which is more relevant to the work presented here, but full details can be found in references such as [75], [76], [77]. Now let's go deeper in the structure of quantum mechanics, and let's recall that a state of the electron depends both on its position in space as well as its spin coordinate, whether spin up or spin down electron, and as a consequence the wave function $\psi(r_1,r_2)$ has to be, by obligation expressed as the product of a spatial wave function $\phi(r_1,r_2)$ and a spin wave function $\chi(s_1,s_2)$, looking like:

$$\psi(r_1,r_2) = \phi(r_1,r_2)\chi(s_1,s_2).$$
(3.5)

As a direct consequence of Pauli's exclusion principle [1] the Fermion wave function given by expression 3.5, is antisymmetric upon particle permutation as said earlier, and as such, if its spatial part is symmetric (S), then the spin part should be antisymmetric (A), and conversely, if its spatial part is antisymmetric (A), then the spin part should be symmetric (S), statement that is better illustrated through the following set of expressions [75], [77], [76], [72], [74], [17]:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \phi^{(S)}(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi^{(A)}(\boldsymbol{s}_1, \boldsymbol{s}_2), \qquad (3.6)$$

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \phi^{(A)}(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi^{(S)}(\boldsymbol{s}_1, \boldsymbol{s}_2). \qquad (3.7)$$

In Quantum mechanics literature such as [75], [77] the antisymmetric spin state is known as a singlet state which has zero total magnetic quantum number, and the symmetric spin state is known as a triplet state with total magnetic quantum equal to one, and are respectively given by:

$$\chi^{(A)}(\boldsymbol{s}_1, \boldsymbol{s}_2) = \chi_{singlet}(\boldsymbol{s}_1, \boldsymbol{s}_2) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \qquad (3.8)$$

$$\chi^{(S)}(\boldsymbol{s}_1, \boldsymbol{s}_2) = \chi_{triplet}(\boldsymbol{s}_1, \boldsymbol{s}_2) = \begin{array}{c} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \end{array}. \qquad (3.9)$$

This is my first attempt to discuss the physics of a system consisting of more than one particle, more specifically, two particles. One more aspect about the discussion I am putting forward is the absence of spin in the Schrödinger description of quantum mechanics. The existence of spin was first predicted from a relativistic version of Schrödinger equation, namely, Dirac equation, though for the purpose of introducing quantum formality in this thesis, I feel that the discussion about Dirac's theory is unnecessary to convey the point I want, which is to provide some basic vocabulary to dive through my contributions, mainly for audience with a background in electrical and electronic engineering. From the latter formalism, a representation and notation that is crucial for quantum mechanics derives, which is, Dirac's notation. The wave function $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ represents the state of the particle or particles, each of them with a definite number of degrees of freedom, for instance, for one electron, the spin degrees of freedom are spin up and spin down (two degrees of freedom), hence the dimension of the

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[1] Pauli's exclusion principle dictates a restriction on the occupation of an electron in a given state per spin coordinate, that is, a given quantum state, characterized by a principle quantum number n, angular momentum quantum number ℓ and azimuthal quantum number m, can only be occupied by two electrons with different spin, one spin up electron and one spin down electron. This principle excludes the occupation of such energy level by two electrons with the same spin.

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problem is the number of particles times the number of degrees of free-
dom for each particle. Moreover, the wave function, which is the state of
the system independent of its representation, whether it is represented in
in spherical basis, rectangular basis, or any other, and from this view point,
the state of the system can be represented as an N-dimensional vector in
the Hilbert space, where the N-dimensions represent the product of the di-
mension of the Hilbert space for each particle, being each Hilbert space
composed by the number of degrees of freedom each particle posses.
This N-dimensional state, denoted as $|\psi\rangle$ is related to the wave function
by the operation $\langle r|\psi\rangle = \psi(r)$, and the state $|\psi\rangle$ is called a *ket* state and
since the nature of this state is complex, its conjugate $\langle\psi|$ is called a *bra*
state. This bra-ket notation is known in physics as *Dirac* notation, and is
completely new as representation for electrical engineers, though is unap-
pealingly necessary and fundamental to dive into quantum mechanics and
more specifically into condensed matter related problems nowadays. From
this construction, the many body problem can be then stated in terms of
this quantum state $|\psi\rangle$ as an eigen-value problem of the form:

$$A|\psi\rangle = a|\psi\rangle, \tag{3.10}$$

where A is an operator applied into the state $|\psi\rangle$ and a is the associated
eigen-value to that operator. Eq. 3.10 represents an experiment, where a
measurement on the system $|\psi\rangle$ is represented by operator A, and the re-
sult of the experiment is the eigen-value a. As an example consider a sys-
tem whose state is $|\psi\rangle$ and the task is to measure its energy. The operator,
whose associated eigen-value is the energy E is the Hamiltonian $\mathcal{H}$. This
eigen-value problem is exactly the same as the one for the Schrödinger
equation, but now written as:

$$\mathcal{H}|\psi\rangle = E|\psi\rangle. \tag{3.11}$$

Moreover, the last question on might want to ask is, if the state of the sys-
tem is represented by an N-dimensional state-vector, then, in the eigen-
value problem given by Eq. 3.10, how should the operator A be repre-
sented? The answer is, if the state of the system is an N-dimensional state
vector, the operator A is an $N \times N$ matrix, whose structure contains the
symmetries of the physical system under study.
In the next section I will introduce the terminology used in this thesis.

3.3 Second Quantized Terminology

Second quantization refers to the fact that, the number of particles for a
given system configuration is quantized. For example, in an atomic orbital
characterized by the quantum numbers (See chapter 4 of ref. [75]) n, ℓ and

m can be at most occupied by two electrons, one pin up and the other one spin down. This particle number restriction refers to second quantization, and its notation refers to, extracting the number of particles that a particular system contains. The latter can be written as an eigen-value problem in the following way:

$$\mathcal{N}|\psi\rangle = n|\psi\rangle, \tag{3.12}$$

where $\mathcal{N}$ is the particle number operator and n is the number of particles in the system, that is, the associated eigen-value of the particle number operator. In the second quantized formulation, the Hamiltonian is formulated in terms of what is known as second quantized operators, and the notation is as follows: the state $|\psi\rangle$ contains the number of particles for each set of quantum numbers. For example, for two particles spin up and spin down, the state $|\psi\rangle$ contains 4 positions, $n_{1\uparrow}$, $n_{1\downarrow}$, $n_{2\uparrow}$ and $n_{2\downarrow}$. On the other hand, second quantized operators adopt the following form: $b_{i,m}$ is an operator that annihilates one particle in the sub-state i with quantum number m, and the operator $b_{j,n}^{\dagger}$ creates one particle in the sub-state j with quantum number n. As an example consider the two particle state defined above, and the applied the annihilation operator $b_{1\downarrow}$, which gives:

$$b_{1\downarrow}|\psi\rangle = b_{1\downarrow}|n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow}, n_{2\downarrow}\rangle = |n_{1\uparrow}, n_{1\downarrow} - 1, n_{2\uparrow}, n_{2\downarrow}\rangle, \tag{3.13}$$

and now, there is one particle less in the system, and since for spin up and spin down particles each substate can be occupied by maximum one particle, that particular sub-state has now zero particles:

$$b_{1\downarrow}|\psi\rangle = b_{1\downarrow}|n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow}, n_{2\downarrow}\rangle = |n_{1\uparrow}, 0, n_{2\uparrow}, n_{2\downarrow}\rangle. \tag{3.14}$$

To illustrate the application of a creation operator, now consider a state with three sub-states, and each one of the is labeled with a quantum number n. In principle, I will not consider any particle number restriction in this case, so by applying $b_{j,n}^{\dagger}$ to the state $|\psi\rangle$ it gives:

$$b_{2n}^{\dagger}|\psi\rangle = b_{2n}|n_{1n}, n_{2n}, n_{3n}\rangle = |n_{1n}, n_{2n} + 1, n_{3n}\rangle, \tag{3.15}$$

and hence, sub-state 2 has one more particle. The notation presented in this section constitutes the basic vocabulary that I will use to communicate my doctoral investigation, which can be counter intuitive for electrical and electronic engineers, part of the audience at which I aimed my PhD thesis to.

3.4 Hilbert Spaces in Multiple Degrees of Freedom

To construct an arbitrary many body operator for a multi-partite state, I consider here a simple example of a bipartite system, with a bipartite state,

namely, the Heisenberg Hamiltonian (See Chapter 5):

$$\mathcal{H}_{spin} = \mathcal{J}_{AB}\boldsymbol{S}_A \cdot \boldsymbol{S}_B, \tag{3.16}$$

where the state $|s\rangle = |\uparrow,\downarrow\rangle \otimes |\uparrow,\downarrow\rangle = |\uparrow\uparrow,\uparrow\downarrow,\downarrow\uparrow,\downarrow\downarrow\rangle$ obeys an eigenvalue problem of the form $\mathcal{H}_{spin}|s\rangle = \mathcal{E}_{spin}|s\rangle$. Operators $\boldsymbol{S}_A$ and $\boldsymbol{S}_B$ are monopartite operators acting on either $|\uparrow\rangle$ or $|\downarrow\rangle$, given by:

$$S_{ix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad S_{iy} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad S_{iz} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

where index i labels coordinate of either spin $\boldsymbol{S}_A$ or $\boldsymbol{S}_B$.

The idea in constructing the arbitrary bipartite operator, is to consider that the latter acts on a bipartite state state which is 4−dimensional of the form:

$$\begin{bmatrix} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{bmatrix}$$

hence, the product $\boldsymbol{S}_A \cdot \boldsymbol{S}_B$ has to be represented by a 4×4 matrix. The formal logic behind this is the following: The Hilbert space in which the state $|s\rangle$ lives, denoted as $\mathbb{H}_{ab}$, combines the Hilbert space for spin $\boldsymbol{S}_A$ which is $\mathbb{H}_a = (\uparrow,\downarrow)$, with the Hilbert space for spin $\boldsymbol{S}_B$ which is $\mathbb{H}_{b=(\uparrow,\downarrow)}$, in the following way (tensor product):

$$\mathbb{H}_{ab} = \mathbb{H}_a \otimes \mathbb{H}_b, \tag{3.17}$$

then the product $\boldsymbol{S}_A \cdot \boldsymbol{S}_B$ can be written, using the same logic, as follows:

$$\boldsymbol{S}_A \cdot \boldsymbol{S}_B = S_{Ax} \otimes S_{Bx} + S_{Ay} \otimes S_{By} + S_{Az} \otimes S_{Bz}. \tag{3.18}$$

Moreover, the effective Hamiltonian $\mathcal{H}_{spin}$, in matrix form, then reads from Eq. 3.18:

$$\mathcal{H}_{spin} = \begin{bmatrix} \mathcal{J}_{AB} & 0 & 0 & 0 \\ 0 & -\mathcal{J}_{AB} & 2\mathcal{J}_{AB} & 0 \\ 0 & 2\mathcal{J}_{AB} & -\mathcal{J}_{AB} & 0 \\ 0 & 0 & 0 & \mathcal{J}_{AB} \end{bmatrix}. \tag{3.19}$$

From expression 3.19, the spin eigen-value problem is solved by calculating $|\mathcal{H}_{spin} - \lambda\mathbb{I}| = 0$, in the following way:

$$|\mathcal{H}_{spin} - \Lambda\mathbb{I}| = \begin{vmatrix} \mathcal{J}_{AB} - \lambda & 0 & 0 & 0 \\ 0 & -\mathcal{J}_{AB} - \lambda & 2\mathcal{J}_{AB} & 0 \\ 0 & 2\mathcal{J}_{AB} & -\mathcal{J}_{AB} - \lambda & 0 \\ 0 & 0 & 0 & \mathcal{J}_{AB} - \lambda \end{vmatrix} = 0,$$

$$= (\mathcal{J}_{AB} - \lambda)^2 (\mathcal{J}_{AB} + \lambda)^2 - 4\mathcal{J}_{AB}^2(\mathcal{J}_{AB} - \lambda)^2 = 0. \tag{3.20}$$

Denoting $\mathcal{E}_{spin} = \lambda$ as the eigen-energies of the spin Hamiltonian $\mathcal{H}_{spin}$, we write:

$$\mathcal{E}_{spin} = \{\mathcal{J}_{AB}, \mathcal{J}_{AB}, \mathcal{J}_{AB}, -3\mathcal{J}_{AB}\}. \tag{3.21}$$

There are three degenerate spin energies corresponding to a triplet state $\mathcal{E}_{spin} = \{\mathcal{J}_{AB}, \mathcal{J}_{AB}, \mathcal{J}_{AB}\}$ with spin wave function (eigen-state of the spin Hamiltonian) $\chi_{triplet}$ given by:

$$\chi_{triplet} = \begin{cases} |\uparrow\uparrow\rangle, & E_{spin} = \mathcal{J}_{AB}, \\ |\downarrow\downarrow\rangle, & E_{spin} = \mathcal{J}_{AB}, \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), & E_{spin} = \mathcal{J}_{AB}, \end{cases}$$

and another spin energy $\mathcal{E}_{spin} = -3\mathcal{J}_{AB}$ corresponding to a singlet state $\chi_{singlet}$ given by:

$$\chi_{singlet} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \quad E_{spin} = -3\mathcal{J}_{AB}. \tag{3.23}$$

In paper III, I consider a tripartite spin state, with an associated spin Hamiltonian given by:

$$\mathcal{H}_{spin} = \mathcal{J}_{AB}S_A \cdot S_B + \mathcal{J}_{AC}S_A \cdot S_C + \mathcal{J}_{BC}S_B \cdot S_C, \tag{3.24}$$

in which case the total Hilbert space given by:

$$\mathbb{H}_{abc} = \mathbb{H}_a \otimes \mathbb{H}_b \otimes \mathbb{H}_c. \tag{3.25}$$

Since in Hamiltonian given by Eq. 9.22 all operators appear not in every term, to keep track of the position of each operator in the Hilbert space representation of Hamiltonian $\mathcal{H}_{spin}$, an identity operator $\mathbb{I}_i$ is introduced in Eq. 9.22 as follows:

$$\mathcal{H}_{spin} = \mathcal{J}_{AB}S_A \cdot S_B \cdot \mathbb{I}_C + \mathcal{J}_{AC}S_A \cdot \mathbb{I}_B \cdot S_C + \mathcal{J}_{BC}\mathbb{I}_A \cdot S_B \cdot S_C. \tag{3.26}$$

Here, I use this formalism to solve the 8-dimensional problem of a tripartite spin state in chapter 9. See Eqs. 9.16, 9.17 and 9.18 for a reference.

3.5 Review of Angular Momentum and Related Representations

3.5.1 Spin Algrebra

In this thesis, to understand the spin representation in the Lie algebra, is of capital importance as seen in chapter 9. In this case, the eigen-value problem reads:

$$s^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle, \quad s_z|s,m\rangle = \hbar m|s,m\rangle, \tag{3.27}$$

$$s_{\pm}|s,m\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)}|s, m \pm 1\rangle, \qquad (3.28)$$

$$\left[s_x, s_y\right] = i\hbar s_z, \quad \left[s_y, s_z\right] = i\hbar s_x, \quad \left[s_z, s_x\right] = i\hbar s_y, \qquad (3.29)$$

where:

$$s_{\pm} = s_x \pm i s_y. \qquad (3.30)$$

Now, I will get busy during the rest of the chapter in deriving spin matrix representations as the ones used for the bipartite Hamiltonian above, which will be later used in papers I, II and III.

3.5.2 $\frac{1}{2}$ Spin Matrices

To derive the spin operators for spin $\frac{1}{2}$ representations, let's consider a spinor χ given by:

$$\chi = \begin{bmatrix} a \\ b \end{bmatrix} = a\chi_+ + b\chi_-, \qquad (3.31)$$

being, χ_+ and χ_- represented by:

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \qquad (3.32)$$

Now, we proceed by considering the result $s^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle$, with $|s,m\rangle = \chi_+, \chi_-$, where the spin operator s^2 is represented by:

$$s^2 = \begin{bmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{bmatrix}. \qquad (3.33)$$

By using eq. 3.33 and replacing it into expression 3.27, I now write the following set of expressions:

$$s^2\chi_+ = \begin{bmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \lambda_{11} \\ \lambda_{21} \end{bmatrix} = \frac{3\hbar^2}{4}\begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$s^2\chi_- = \begin{bmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} \lambda_{12} \\ \lambda_{22} \end{bmatrix} = \frac{3\hbar^2}{4}\begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

from where, we obtained an specific representation for operator s^2 given by:

$$s^2 = \frac{3\hbar^2}{4}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \qquad (3.34)$$

where I have invoked the result $s^2\chi_{\pm} = \frac{3\hbar^2}{4}\chi_{\pm}$ [sakurai]. To proceed, now I will consider the operator s_z represented by:

$$s_z = \begin{bmatrix} \kappa_{11} & \kappa_{12} \\ \kappa_{21} & \kappa_{22} \end{bmatrix}, \qquad (3.35)$$

obeying the relations $s_z\chi_+ = \frac{\hbar}{2}\chi_+$ and $s_z\chi_- = -\frac{\hbar}{2}\chi_-$. By using a similar procedure as for operator s^2, I cast the following two expressions:

$$s_z\chi_+ = \begin{bmatrix} \kappa_{11} & \kappa_{12} \\ \kappa_{21} & \kappa_{22} \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$s_z\chi_- = \begin{bmatrix} \kappa_{11} & \kappa_{12} \\ \kappa_{21} & \kappa_{22} \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = -\frac{\hbar}{2}\begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

arriving at the following result for the matrix representation of operator s_z:

$$s_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{3.36}$$

Now, proceeding with the representations for s_x and s_y, the matrix representing s_+ and s_+ has to be determined, to then be replaced in expression 3.30. First, considering s_+, looking at expression 3.28, the following relations are obtained:

$$s_+\chi_+ = s_+|\frac{1}{2},\frac{1}{2}\rangle = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1)}|\frac{1}{2},\frac{1}{2}+1\rangle = 0, \tag{3.37}$$

$$s_+\chi_- = s_+|\frac{1}{2},-\frac{1}{2}\rangle = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) + \frac{1}{2}(-\frac{1}{2}+1)}|\frac{1}{2},\frac{1}{2}\rangle = \hbar\chi_+. \tag{3.38}$$

From expressions 3.37 and 3.38, the following set of equations can be cast in representation form:

$$s_+\chi_+ = \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = 0$$

$$s_+\chi_- = \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix}\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \hbar\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \hbar\chi_+,$$

and by combining the above expressions, the $\frac{1}{2}$ representation for s_+ gives:

$$s_+ = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}. \tag{3.39}$$

Following the same logic, the spin $\frac{1}{2}$ representation for s_- gives then:

$$s_+ = \hbar\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}. \tag{3.40}$$

By manipulating expression 3.30, representations for s_x and s_y give:

$$s_x = \frac{1}{2}(s_+ + s_-) = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{3.41}$$

$$s_y = \frac{1}{2i}(s_+ - s_-) = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}. \tag{3.42}$$

From the representations for s_z, s_x and s_y, it can be observed the appearance of some 2×2 matrices known as *Pauli* or σ matrices, such that

$$s_x = \frac{\hbar}{2}\sigma_x, \quad s_y = \frac{\hbar}{2}\sigma_y, \quad s_z = \frac{\hbar}{2}\sigma_z, \tag{3.43}$$

and are given by:

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{3.44}$$

σ matrices constitute the core of the Hilbert space representation for spin $\frac{1}{2}$ magnetism, and throughout the thesis I will continuously refer to this representations. One more aspect about the Pauli matrices that will come in handy, mainly in chapter 5, is the following identity:

$$(A \cdot \sigma)(B \cdot \sigma) = A \cdot B + i A \times B \cdot \sigma, \tag{3.45}$$

where A and B are regular vectors and σ is a vector with σ matrix components given by $\sigma = (\sigma_x, \sigma_y, \sigma_z)$. Note that to derive expression 3.45, it is useful to express all vectors in component form and the apply relation:

$$\sigma_i \sigma_j = i\epsilon_{ijk}\sigma_k,$$

where i, j, k index a given component of a σ matrix and ϵ_{ijk} is the levi-chivita tensor. For details about the derivation of expression, see this multimedia source[2].

3.5.3 Spin 1 Matrices

For a spin 1 system three spin states are defined:

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \chi_0 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \chi_- = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \tag{3.46}$$

obeying the following eigenvalue axioms with respect to the operator s_z:

$$s_z\chi_+ = \hbar\chi_+ \quad s_z\chi_0 = 0 \quad s_z\chi_- = -\hbar\chi_-, \tag{3.47}$$

that follow from:

$$s_z|s,m\rangle = \hbar m|s,m\rangle. \tag{3.48}$$

Following the line of reasoning applied for spin $\frac{1}{2}$ representations, it is straightforward to derive the following representation for operator s_z:

$$s_z|s,m\rangle = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \tag{3.49}$$

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[2]Youtube Channel: Juan David Jaramillo, Video: Pauli's Identity for Sigma Matrices.

From expression 3.28, the following relations for operators s_+ and s_- are given:

$$s_+\chi_+ = 0, \quad s_+\chi_0 = \sqrt{2}\hbar\chi_+, \quad s_+\chi_- = \sqrt{2}\hbar\chi_0, \quad (3.50)$$

$$s_-\chi_+ = \sqrt{2}\hbar\chi_0, \quad s_-\chi_0 = \sqrt{2}\hbar\chi_-, \quad s_-\chi_- = 0, \quad (3.51)$$

and following the same procedure presented in the section for spin $\frac{1}{2}$ representation, then, operators s_+ and s_- can be represented in the following way:

$$s_+ = \sqrt{2}\hbar \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} \quad s_- = \sqrt{2}\hbar \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}. \quad (3.52)$$

With a bit of manipulation of expression 3.30, I write operators s_x and s_y in the following way:

$$s_x = \frac{\hbar}{\sqrt{2}}\hbar \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad s_y = \frac{\hbar}{\sqrt{2}}\hbar \begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix}. \quad (3.53)$$

3.6 Final Comments

Now that matrices s_x, s_y and s_z have been specified, both for spin $\frac{1}{2}$ and spin 1 systems, the physics emerging from a single spin degree of freedom can be determined. In this thesis, we deal with one spin degree of freedom in paper II and in paper IV where single magnetic site - single molecule magnets are addressed. For the case of two spin degrees of freedom, see the work from paper I, and for three spin degrees of freedom see paper III. Notice that to solve Hamiltonians containing more than one degree of freedom, one requires to construct a Hilbert space spanning a representation for a multipartite state, hence, the dimension of a Hamiltonian matrix increases exponentially with the number of degrees of freedom. More detail calculations about the spin models used in the papers appended, are given in chapter 9.

Once formal structure of quantum theory is acknowledged, one identifies the main ingredients of a theory based on model Hamiltonians. This statement is very important to be adsorbed, now, in this chapter, as the model Hamiltonian is the soul of the work I present in this thesis, and therefore, to conclude the chapter, I give the following items to recall about the subject:

1. Wave functions have a symmetry depending on the particle they represent, be it Bosons or Fermions. Electrons are Fermions and Phonons are Bosons, which are the particle and the excitation I refer to in this thesis.

2. Wave functions are a product of a spatial part and spin part. For a Fermionic wave function, that is anti-symmetric, if the spatial part is anti-symmetric, the spin part is symmetric, and on the other hand, if the spatial part is symmetric, the spin part should be anti-symmetric.

3. When the wave function or the quantum state is expanded in a particle number basis, or other relevant basis, the Schrödinger equation or the Dirac equation, becomes a matrix eigenvalue problem of the dimension of the representation of the quantum state in the Hilbert space.

4. Within this formalism, the operators either create or destroy particles in a many-body state. These operators can be single particle or many particle operators.

5. In the formal structure used in this thesis, the single particle operators are the ones extensively used, and their role is to create or destroy a single particle at the time according to a rule, that we have identified earlier as the Pauli exclusion principle.

6. Remember this rule - Pauli Exclusion Principle: A quantum mechanical state can only be occupied at most by one particle per spin degree of freedom, that is, a given state, including the spin degree of freedom, can either have one or zero particles.

7. Consequence of the Rule: An operator attempting to destroy a particle in an empty state, will annihilate the state ($a|0\rangle = 0$), and an operator attempting to create a particle in an occupied state will as well annihilate the state ($a^{\dagger}|1\rangle = 0$).

With this I conclude this chapter and the part on contextualization.

Part II:
Theoretical Background

Here, I will combine, a comprehensive summary for the theory around which my contribution is built, with a detailed overview of the of the basic assumptions and procedures that led to the most representative theoretical results such as the Keldysh Green's functions, Meir-Jauho-Wingreen formalism, the RKKY interaction, the Non-equilibrium version of the RKKY interaction, phonon correlation functions among others. This, with the aim to lead audience with background in electrical and electronic engineering to identify that, the way non-equilibrium statistical mechanics is built from the Keldysh-Schwinger theory, can be completely natural to those coming from the latter and the former schools.

4. Non-Equilibrium Molecular Green's Functions

"It is the glory of G-d to conceal a matter; to search out a matter is the glory of kings".

Proverbs 25:2

The study of the fundamental physics to account for the dynamics, given a system of interest, has been focused on the description of reversible and deterministic systems, which evolve unitarily. Although commonly approached, this type of systems are a rare exception as most processes in nature are not reversible, and the question of how irreversibility arises from reversibility is posed as the knowledge of quantum mechanical evolution is re-examined once reversibility vanishes in the system of study [78]. From the classical perspective, the fundamental question of how irreversibility emerges from reversibility has been extensively asked, pointing out at dissipation having to do with irreversibility and asking the question of how the steady state dynamics is reached. Concerning quantum mechanical systems, the concept of dissipation can be exemplify by considering an electron in a two level atom. Once the electron has reached the excited state, after some energy dissipation, the electron state relaxes back to its ground state.

In this context, it is understood that the two level atom is a system with few degrees of freedom, that absorbs and dissipates energy from and to a system with thermodynamically large number of degrees of freedom known as reservoir or environment. These type of systems, that evolve under the effect of an environment with which entropy is interchanged, are known as open quantum systems, which is characterized by a non-unitary evolution, meaning, that the ground state decays proportional to the strength of the coupling between the physical system and environment. Moreover, an important question that arises in the open quantum systems paradigm, is, once the system is allowed to evolved quantum mechanically driven by its coupling to an environment, what are the time scales of the correlations between the system and the environment? does the system eventually reach thermodynamic, chemical or electrical equilibrium with the reservoir? If the system is originally in equilibrium with a toy reservoir, how do the quantum

mechanical observables evolved as the correlations between the systems and an an arbitrary drive are turned on?

These questions were approached by Julian Schwinger and by Leonid Keldysh [79], and as a result of these considerations, the formalism of the Non-equilibrium Green's functions was born, what is more often known in the transport, magnetism and statistical mechanics literature as the Keldysh Green's functions or the Green's functions on the Keldysh contour. In this chapter, I will lead a discussion through the more relevant aspects of the theory of Green's functions, aiming at convincing the audience that the Keldysh Green's functions are the building blocks of the work that will be discussed in the following chapters.

4.1 Green's Functions in Physics

Green's functions in physics have a long and successful tradition, in areas ranging from theoretical mechanics, to classical electrodynamics, to quantum mechanics/statistical mechanics and lately to quantum field theory [80], [81], [82]. Originally, George Green in his 1828 essay studied the theory of potentials in electrodynamics and their influence on the theory of electricity [16]. Following up the work of Dennis Poisson, George Green thought that, any physical system that is exposed to a perturbation or excitation will respond according to its natural characteristics, and the relationship between the response and the excitation, determines unambiguously the intrinsic physical properties of the system, which later will be known as the **Green's Function**. The latter, is also known as the transfer function or the impulsive response in the community of systems dynamics and control theory [83], due to the particularity that, when the duration of the excitation is infinitesimally small, that is, when the excitation is a delta impulse, the response will be then the Green's function itself which is widely known, as referred above as the impulse response [83].

In the next few sections, I will give a brief overview of the use of Green's functions in electrodynamics [80] and quantum mechanics [75], leading to the discussion of their use in *Non-Equilibrium Statistical Mechanics*, and their potential use in magnetism at the atomic scale and in transport calculations in molecular junctions.

4.1.1 Green's Functions in Electrodynamics

I now invite, to consider the wave equation for the electric scalar potential $\phi(r,t)$ written as [80]

$$\nabla^2 \phi(r,t) - \frac{1}{c^2}\frac{\partial^2 \phi(r,t)}{\partial t^2} = -4\pi\rho(r,t). \tag{4.1}$$

which can be written in operator form as follows:

$$\mathcal{D}(r,t)\psi(r,t) = S(r,t), \tag{4.2}$$

where $S(r,t)$ is known as the source of the wave equation and here, the charge density $\rho(r,t)$ plays this role. The operator $\mathcal{D}(r,t)$ is known as the D'lambertian operator and is given by:

$$\mathcal{D}(r,t) = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}. \tag{4.3}$$

Now, solutions to equation 4.2 have the form:

$$\psi(r,t) = -\frac{1}{4\pi}\int d^3r' \frac{S(r',t-|r-r'|/c)}{|r-r'|}, \tag{4.4}$$

and the solution to expression 4.1, is written as well using expression 4.3 in the following way:

$$\phi(r,t) = -\frac{1}{4\pi}\int d^3r'(-4\pi)\frac{\rho(r',t-|r-r'|/c)}{|r-r'|} = \int d^3r' \frac{\rho(r',t-|r-r'|/c)}{|r-r'|}. \tag{4.5}$$

Both expressions 4.4 and 4.5, that specify solutions to eqs. 4.1 and 4.2, have the form:

$$\psi(r,t) = \int d^3r' dt' G(r,r',t,t') S(r',t'), \tag{4.6}$$

where the correlation function $G(r,r',t,t')$, is known as the Green's function, and it fully determines the response $\psi(r,t)$ of the system to the excitation or perturbation $S(r',t')$. As commented in the introduction to the chapter, this correlation function is also known as the impulse response. Expression 4.6 will be derived with the use of the Green function later in the document.

To proceed with the task, deriving the Green's function for expression 4.2, I re-express the latter as:

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\Psi(r,t) = S(r,t), \tag{4.7}$$

where now, I take the freedom to identify $\Psi(r,t)$ as the wave, and $S(r,t)$ known as the source or excitation. Expression 4.7 has a general solution of the form:

$$\Psi(r,t) = \Psi_h(r,t) + \Psi_p(r,t),$$

where $\Psi_h(r,t)$ is the solution to the homogeneous part of equation 4.7 ($S(r,t) = 0$) and $\Psi_p(r,t)$ is the solution given the particular source $S(r,t)$, and through the linear response expression is given by:

$$\Psi_p(r,t) = \int \int d^3r' d\tau G(r - r', t - \tau) S(r', \tau), \qquad (4.8)$$

and this expression has the form of eq. 4.6, with the differentiating factor is that, the Green's function here, $G(r - r', t - \tau)$ depends on the difference of times and positions, that is, linear and time invariant LTI, what is refer to throughout the thesis as stationary response. Moreover, to completely determine the solution $\Psi_p(r,t)$, besides the knowledge of the source $S(r',t')$, the Green's function $G(r - r', t - t')$ is required. To determine the Green's function $G(r - r', t - t')$, the following equation must be solved:

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) G(r - r', t - t') = \delta^3(r - r') \delta(t - t'), \qquad (4.9)$$

from where, the logic behind the attribute *impulse response*, given to the Green's function, becomes obvious. Therefore, the Green's function $G(r - r', t - t')$ can be seen as a wave generated by an impulse at the origin, and hence $\Psi_p(r,t)$ is a superposition of these waves as described by expression 4.8, and the source $S(r,t)$ it is seen as a superposition of point sources of the form:

$$S(r,t) = \int \int d^3r' d\tau \delta^3(r - r') \delta(t - \tau) S(r', \tau). \qquad (4.10)$$

Moreover, to solve for $G(r - r', t - t')$, consider the Fourier transform:

$$G(k,\omega) = \int \int d^3r d\tau G(r, \tau) e^{-i(k \cdot r - \omega \tau)}. \qquad (4.11)$$

From the above expression, it is quite clear that by multiplying expression 4.9 with the factor $e^{-i(k \cdot (r - r') - \omega(t - t'))}$ as follows:

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) G(r - r', t - t') e^{-i(k \cdot (r - r') - \omega(t - t'))}$$

$$= \delta^3(r - r') \delta(t - t') e^{-i(k \cdot (r - r') - \omega(t - t'))},$$

then integrating the above expression with respect to r and t and applying expression 4.20, the Green's function in the Reciprocal domain reads:

$$G(k,\omega) = \frac{c^2}{\omega^2 - c^2 k^2} = \frac{c^2}{(\omega - ck)(\omega + ck)}. \qquad (4.12)$$

To evaluate $G(r, \tau)$, the inverse Fourier transform should be calculated from:

$$G(r, \tau) = \int \int \frac{d^3 k d\omega}{(2\pi)^4} G(k, \omega) e^{-i(k \cdot r - \omega \tau)}, \tag{4.13}$$

which can be written as two contour integrals written below:

$$G(r, \tau) = \lim_{\Omega \to +\infty} \frac{c^2}{(2\pi)^4} \int d^3 k e^{ik \cdot r} \int_{C_+} d\omega \frac{e^{-i\omega\tau}}{(\omega - ck)(\omega + ck)}, \quad \forall \, \tau < 0, \tag{4.14}$$

$$G(r, \tau) = \lim_{\Omega \to +\infty} \frac{c^2}{(2\pi)^4} \int d^3 k e^{ik \cdot r} \int_{C_-} d\omega \frac{e^{-i\omega\tau}}{(\omega - ck)(\omega + ck)}, \quad \forall \, \tau > 0, \tag{4.15}$$

where C_+ and C_- are the contours as defined in figure 4.1 and 4.2, and Ω is the radius of the contours $C_{+,\Omega} \in C_+$ and $C_{-,\Omega} \in C_-$.

To evaluate expressions 4.14 and 4.15, recall that the Cauchy theorem for the integral:

$$f(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} f(\omega) e^{-i\omega\tau}, \tag{4.16}$$

reads:

$$f(t) = 2\pi i \sum_{k}^{N} Res \left[\frac{1}{2\pi} f(\omega) e^{-i\omega\tau} \right]_k, \quad \Im m(\omega) > 0, \tag{4.17}$$

$$f(t) = -2\pi i \sum_{k}^{N} Res \left[\frac{1}{2\pi} f(\omega) e^{-i\omega\tau} \right]_k, \quad \Im m(\omega) < 0. \tag{4.18}$$

To apply the above theorem, the poles of $G(k, \omega)$ must be specified. The poles of $G(k, \omega)$ are found to be $\omega = \pm ck$, both of them laying on the real axis. Furthermore, to impose causality on the Green's function $G(r, \tau)$, two new objects must be defined: The **Retarded Green's Function** $G^+(r, t)$ and The **Advanced Green's Function** $G^-(r, t)$. As the aim of this discussion is to lead, readers more familiarized with classical electrodynamics (i.e: electrical and electronic engineers), to the application of Green's functions in the context of statistical mechanics, note that the typical notation for retarded and advanced Green's functions used throughout our discussion in non-equilibrium statistical mechanics, respectively are: $G^R(r, t)$ and $G^A(r, t)$. For causality, choose the retarded Green's function $G^+(r, t)$ to have the poles only in the lower ω-plane, that is, $\Im m(\omega) < 0$, which as a consequence of the latter gives:

$$G^+(r, t) = 0, \quad \tau < 0, \quad G^-(r, t) = 0, \qquad \tau > 0.$$

Moreover, to completely construct the above objects $G^+(r, t)$ and $G^-(r, t)$, the poles $\omega = \pm ck$, must be placed off the real axis by the transformation (analytical continuation) $\omega \to \omega \pm i\epsilon$, which implies that $\omega = \pm ck \pm i\epsilon$, where it has been taken $\omega_1^+ = ck - i\epsilon$ and $\omega_2^+ = -ck - i\epsilon$ as the poles of the Retarded

Green's function, and $\omega_1^- = ck + i\epsilon$ and $\omega_2^- = -ck + i\epsilon$ as the poles of the Advanced Green's function (see figures 4.1 and 4.2).
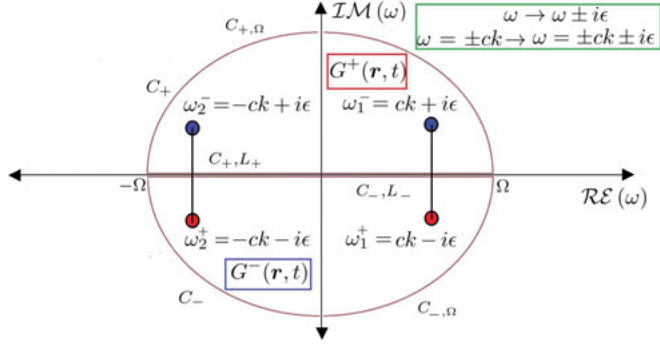
Figure 4.1. Poles location for the Retarded and Advanced Green's Functions $G^+(r,t)$ and $G^-(r,t)$ respectively.
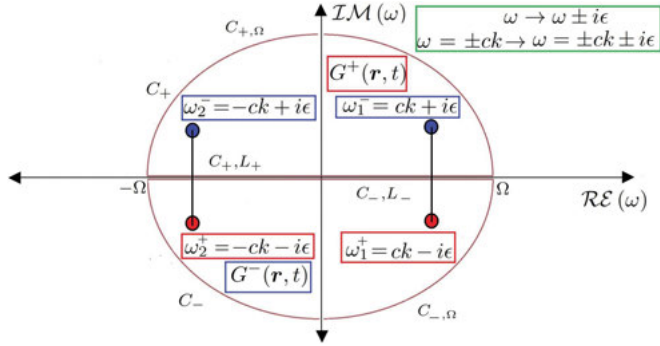
Figure 4.2. Poles location for the Retarded and Advanced Green's Functions $G^+(r,t)$ and $G^-(r,t)$ respectively. Associate colors of boxes surrounding $G^+(r,t)$ and $G^-(r,t)$ respectively and $\omega_{1,2}^{+,-}$, with the colors of the circles representing the poles.

Finally, $\forall\, \tau > 0$, the retarded Green's function reads:

$$G^+(r,\tau) = \lim_{\epsilon \to 0}\lim_{\Omega \to +\infty} \frac{c^2}{(2\pi)^4} \int d^3k\, e^{ik\cdot r} \int_{C_-} d\omega \frac{e^{-i\omega\tau}}{(\omega - ck - i\epsilon)(\omega + ck - i\epsilon)},$$
(4.19)

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and the integral present in the above expression:

$$\lim_{\Omega \to +\infty} \int_{C_-} d\omega \frac{e^{-i\omega\tau}}{(\omega - ck - i\epsilon)(\omega + ck - i\epsilon)},$$

can be calculated using the Cauchy's theorem as announced in expression 4.17 and evaluates to:

$$\lim_{\Omega \to +\infty} \int_{C_-} d\omega \frac{e^{-i\omega\tau}}{(\omega - ck - i\epsilon)(\omega + ck - i\epsilon)} = -2\pi \frac{sin(ck\tau)}{ck} e^{-\epsilon\tau}, \qquad (4.20)$$

and replacing the above expression back in equation 4.19, $G^+(r,\tau)$ finally reads:

$$G^+(r,\tau) = -\frac{c}{4\pi|r|}\delta(|r| - c\tau) = -\frac{1}{4\pi|r|}\delta(t - |r|/c), \qquad (4.21)$$

note the notation $r = |r|$.

From the above expression, the solution to equation 4.7, can be written in the form specified by expression 4.8 as follows:

$$\Psi_p(r,t) = \int \int d^3r' d\tau \left(-\frac{1}{4\pi|r-r'|}\delta(t - \tau - |r-r'|/c)\right) S(r',\tau), \qquad (4.22)$$

and by implementing the delta-function in expression 4.22, the solution to expression 4.7 finally reads:

$$\Psi_p(r,t) = -\frac{1}{4\pi}\int d^3r \frac{S(r',t - |r-r'|/c)}{|r-r'|} = -\frac{1}{4\pi}\int d^3r \frac{S(r',t - t_{ret})}{|r-r'|}, \qquad (4.23)$$

where $t_{ret} = |r-r'|/c$.

In the section that I conclude here in the next following lines, I aimed at, showing that, the concept of Retarded and Advanced Green's functions, is a concept that it should be already familiar in the context of classical electrodynamics, quite common discussion in electrical and electronic engineering study plans, and that through an arbitrary expression for calculating the response of the system to a perturbation or excitation, the Green's function is a useful object to characterize the physics of a given system, containing precise information about the time scales spanning the phenomenon of interest, this resolved by analyzing the poles in the complex plane. In the next section, I will show, that for the more fundamental equation of Quantum Mechanics, meaning the Schrödinger equation, a similar logic can be applied, and as a result, a Green's function for this case can be derived. All of these, keeping in mind the final goal: Understand the implications of the Green's function theory in statistical mechanics by developing the concept of propagator, and showing its connection with the previous knowledge about Green's functions, known much before Quantum Field Theory.

4.1.2 Green's Functions in Quantum Mechanics

Consider the typical one particle Schrödinger equation given by [75], [77]:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(r) + V(r)\Psi(r) = E\Psi(r), \tag{4.24}$$

which re-organizes as follows:

$$\left(\nabla^2 + k^2\right)\Psi(r) = Q(r), \tag{4.25}$$

where $k^2 = \frac{2mE}{\hbar^2}$ and $Q(r) = \frac{2mV(r)}{\hbar^2}\Psi(r)$. Do note that in expression 4.25, $Q(r)$ depends itself on $\Psi(r)$, so let's assume that there exists a function $G(r)$ (Green's Functions) such that:

$$\left(\nabla^2 + k^2\right)G(r) = \delta^3(r), \tag{4.26}$$

from where the solution to expression 4.25 can be cast in linear response form as follows:

$$\Psi(r) = \int d^3r' G(r - r')Q(r'),$$

where $Q(r)$ can be express as:

$$Q(r) = \int d^3r'\delta^3(r - r')Q(r') = \int d^3r'\left(\nabla^2 + k^2\right)G(r - r')Q(r'), \tag{4.27}$$

and it plays the role of a source, as $S(r,t)$ in the context presented for electrodynamics.

To calculate $G(r)$, expression 4.26 is multiplied by a factor of $e^{iq\cdot r}$, and then integrated with respect to d^3r as follows:

$$\int \left(\nabla^2 + k^2\right)G(r)e^{iq\cdot r}d^3r = \int \delta^3(r)e^{iq\cdot r}d^3r = 1,$$

therefore, giving the following expression for $G(q)$:

$$G(q) = \frac{1}{k^2 - q^2} = \frac{1}{(k-q)(k+q)}. \tag{4.28}$$

From expression 4.28, and using the inverse Fourier transformation, $G(r)$ reads:

$$G(r) = \frac{i}{8\pi^2 r}\left[\oint_{C_+} dq\frac{qe^{iqr}}{(q-k)(q+k)} - \oint_{C_-} dq\frac{qe^{-iqr}}{(q-k)(q+k)}\right],$$

where the contours C_+ (anti-clockwise orientation) and C_- (clockwise orientation) are defined as in figure 4.3. By using the residue theorem as in expressions 4.17 and 4.18, $G(r)$ can be calculated as follows:

$$G(r) = \frac{i}{8\pi^2 r}\left[2\pi i\left(\frac{qe^{iqr}}{(q+k)}\right)_{q=k} - (-2\pi i)\left(\frac{qe^{-iqr}}{(q-k)}\right)_{q=-k}\right],$$

giving:

$$G(\boldsymbol{r}) = \frac{i}{8\pi^2 r} 2i\pi e^{ikr} = -\frac{e^{ik|\boldsymbol{r}|}}{4\pi|\boldsymbol{r}|}. \tag{4.29}$$
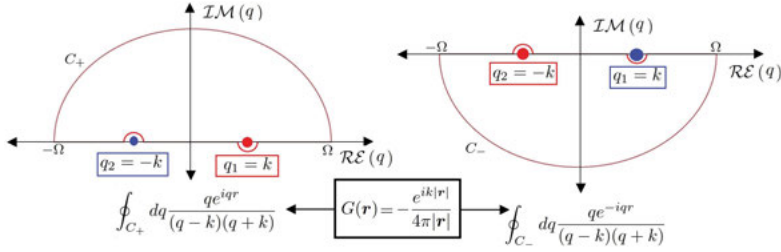
Figure 4.3. Definitions of the contours C_+ and C_-, to evaluate the contour integrals appearing in the evaluation of the Green's function $G(\boldsymbol{r})$.

Knowing $G(\boldsymbol{r})$, the particular solution to expression 4.25 gives:

$$\Psi_p(\boldsymbol{r}) = \int d^3 r\, G(\boldsymbol{r} - \boldsymbol{r}') Q(\boldsymbol{r}') = \int d^3 r \left(-\frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|} \right) \frac{2mV(\boldsymbol{r}')}{\hbar^2} \Psi(\boldsymbol{r}'),$$

$$= -\frac{m}{2\hbar^2\pi} \int \frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} V(\boldsymbol{r}')\Psi(\boldsymbol{r}')d^3 r. \tag{4.30}$$

As for the solution to the homogeneous part of expression 4.25, that is $\Psi_h(\boldsymbol{r})$, it can be obtained from:

$$\left(\boldsymbol{\nabla}^2 + k^2 \right) \Psi_h(\boldsymbol{r}) = 0. \tag{4.31}$$

As for the problem considered from classical electrodynamics in the previous section, the total solution to expression 4.25 can be express as a superposition of the form:

$$\Psi(\boldsymbol{r}) = \Psi_h(\boldsymbol{r}) - \frac{m}{2\hbar^2\pi} \int \frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} V(\boldsymbol{r}')\Psi(\boldsymbol{r}')d^3 r. \tag{4.32}$$

To conclude, let's think about the following question: what is the most relevant result of the present section, with regards to the proposed goal? I would say that the answer, is, that the Green's function derived in this section satisfies the Schrödinger equation as given in expression 4.26, from where the wave function can be obtained as a convolution integral given

by expression 4.30 and 4.32. Now, the following question emerges: Is it possible to derive a theory of quantum mechanical transitions, such that, an object derived from that theory, satisfies an equation of the type of expression 4.26? and if so, can I argue (and would you be convinced?) that this object is a Generalized Green's function for a many particle problem? I will lead to some satisfactory answer to this question in the next section.

4.1.3 Path Integrals and Green's Functions

Solution to the time independent Schrödinger equation given by expression 4.24, gives information about the state of a quantum mechanical particle in its fundamental state, that is, its state in the absence of energy exchange, what is known in physics as *ground state*. When energy is put into the quantum system of interest, and is absorbed, the state of the particle transitions from its ground state to a given excited state [77]. This transitions can be of different nature, an many of them might be allowed and some other forbidden, like the so called *dipole allowed selection rules*, just to give one example from quantum mechanics [75]. It is often useful, to develop a theory to analyze these transitions and their properties such as the life times of these excited states. Richard Feynman, develop a formalism, which goal was to find an alternative way to compute the time evolution operator as compare with the time dependent Schrödinger equation (for detailed discussion see [75], [77], [84], [85]), defined by:

$$|\psi, t\rangle = \mathbb{U}(t, t')|\psi, t'\rangle, \tag{4.33}$$

where $\mathbb{U}(t, t') = e^{-\frac{i}{\hbar}\mathcal{H}(t-t')}$ is the time evolution operator for a given Hamiltonian $\mathcal{H}$.

From expression 4.33, the following elaboration can be made:

$$\langle x, |\psi, t\rangle = \langle x|\mathbb{U}(t, t')|\psi, t'\rangle = \langle x|\mathbb{U}(t, t')\int dx'|x'\rangle\langle x'|\psi, t'\rangle,$$

$$= \int dx'\langle x|\mathbb{U}(t, t')|x'\rangle\langle x'|\psi, t'\rangle,$$

$$= \int dx'\langle r, t|\mathbb{U}(t, t')|r', t'\rangle\langle x'|\psi, t'\rangle, \tag{4.34}$$

where the term $\langle r, t|\mathbb{U}(t, t')|r', t'\rangle$ in the above expression is known as the Feynman propagator, and it may be specified as follows:

$$\langle r, t|\mathbb{U}(t, t')|r', t'\rangle = \langle x, x'\rangle = \langle r, t|e^{-\frac{i}{\hbar}\mathcal{H}(t-t')}|r', t'\rangle. \tag{4.35}$$

Note the following about the above realization: the operator $\int dx'|x'\rangle\langle x'|$ is an identity operator, so no harm is done when introduced.
The simplified notation for this propagator is written as $\langle x, x'\rangle$, and it gives

the probability amplitude for a quantum mechanical transition, of a particle initially located at r at time t, that after the transition is located at r'. Feynman, cleverly though about this problem, and came up with an idea that is, to consider a classical action and consider all possible ways in which a particle can transit in the phase space from its initial to final point, and add all the probability amplitudes for that particle to undergo the transition between the two points, which corresponds to all possible paths this particle can take in the phase space, and as such defined the propagator [85] and its form to calculated as a Feynman path integral, which is given by [77], [84], [86]:

$$\langle x, x' \rangle = \int \mathcal{D}[x(t)] e^{-\frac{i}{\hbar} S[x(t)]}, \qquad (4.36)$$

where $x(t)$ is the path taken by the particle in the phase space and the symbol $\mathcal{D}[x(t)]$ denotes integration over all possible paths in the phase space. It can be shown that, expression 4.37, fulfills an Schrödinger type equation of the form [77], [85]:

$$\left(i\hbar \frac{\partial}{\partial t} - \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \right) \langle x, x' \rangle = 0, \qquad (4.37)$$

what makes $\langle x, x' \rangle$ a quantum mechanical object with the properties of a Green's function, suitable for solving problems where a quantum system is driven to make a transit from a fundamental to an excited state [74], [17]. In quantum theory, one refers to the propagator considered in this section as Zero-Temperature Green's functions as they lack or are temperature independent [74].

4.1.4 Zero-Temperature Green's Functions From Path Integrals

Propagators calculated in the form of a Feynman path integral satisfy Schrödinger equation as shown in [85]. This form of quantum mechanics is more useful when thinking about processes that are triggered at a quantum level, than when one desires to determine the state of the system of interest as in the case of the Schrödinger formulation [87]. To motivate the formulation of propagator based quantum mechanics let's consider a single electron state $|k\sigma\rangle$, in the ground state $|\Omega(t)\rangle$ (see full discussion in chapter 5 of Ref. [17]). The occupation fraction of this ground state is denoted as $\langle \Omega(t) | c_{k\sigma}^\dagger c_{k\sigma} | \Omega(t) \rangle$, which can be further elaborated as follows:

$$\langle \Omega(t) | c_{k\sigma}^\dagger c_{k\sigma} | \Omega(t) \rangle = \langle \Omega(0) | e^{\frac{i}{\hbar} \mathcal{H} t} c_{k\sigma}^\dagger c_{k\sigma} e^{-\frac{i}{\hbar} \mathcal{H} t} | \Omega(0) \rangle,$$

$$= \langle \Omega(0) | e^{\frac{i}{\hbar} \mathcal{H} t} c_{k\sigma}^\dagger e^{-\frac{i}{\hbar} \mathcal{H} t} e^{\frac{i}{\hbar} \mathcal{H} t} c_{k\sigma} e^{-\frac{i}{\hbar} \mathcal{H} t} | \Omega(0) \rangle,$$

hence, the occupation fraction of the ground state of interest reads:

$$\langle \Omega(t)|c^{\dagger}_{k\sigma}c_{k\sigma}|\Omega(t)\rangle = \langle \Omega|c^{\dagger}_{k\sigma}(t)c_{k\sigma}(t)|\Omega\rangle, \qquad (4.38)$$

where $|\Omega(0)\rangle = |\Omega(0)\rangle$, and do note that we have made use of the result $|\Omega(t)\rangle = e^{-\frac{i}{\hbar}\mathcal{H}t}|\Omega(0)\rangle$. Now let's discuss the interpretation of the above formulation. The occupation fraction of the single electron state $|k\sigma\rangle$ can be interpreted as the probability of finding one electron in the single electron state $|k\sigma\rangle$ at time t, which can be seen from the following relation:

$$\langle \Omega|c^{\dagger}_{k\sigma}(t)c_{k\sigma}(t)|\Omega\rangle = (c_{k\sigma}(t)|\Omega\rangle)^{\dagger}\, c_{k\sigma}(t)|\Omega\rangle = |c_{k\sigma}(t)|\Omega\rangle|^{2}\,.$$

Now, following the same logic, one can guess the amplitude of a process that consists in finding an electron in a single particle state $|k\sigma\rangle$ at time t, and an instant later at t' will be found in the same single particle state. This amplitude can be written as: $\langle \Omega|c^{\dagger}_{k\sigma}(t')c_{k\sigma}(t)|\Omega\rangle$. This transition amplitude represents the kinematics of the electron in the system, then it accounts for the processes that this one undergoes. Conversely, the process consisting of not finding one electron in the single particle state $|k\sigma\rangle$ at time t' and at a later time t will not be found in the same single particle state, is represented through the amplitude $\langle \Omega|c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\rangle$. Notice that $\langle \Omega|c^{\dagger}_{k\sigma}(t')c_{k\sigma}(t)|\Omega\rangle$ for $t' > t$ can be written as $\langle \Omega|c^{\dagger}_{k\sigma}(t')c_{k\sigma}(t)|\Omega\rangle\theta(t'-t)$, and $\langle \Omega|c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\rangle$ for $t > t'$ can be written as $\langle \Omega|c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\rangle\theta(t-t')$. These two processes reveal important properties of the system as they represent the annihilation of an electron at a single particle state $|k\sigma\rangle$ at time t and its posterior creation at time t in the same single particle state; and the creation of an electron in the single particle state $|k\sigma\rangle$ at time t' and its subsequent destruction at time t respectively. It makes sense to look at this processes using the time ordered propagator given by:

$$\left\langle \Omega|\mathcal{T}\,c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\right\rangle$$
$$= \left\langle \Omega|c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\right\rangle\theta(t-t') - \left\langle \Omega|c^{\dagger}_{k\sigma}(t')c_{k\sigma}(t)|\Omega\right\rangle\theta(t'-t). \qquad (4.39)$$

In the above expression, $\mathcal{T}$ denotes the time ordering operator, which orders the applied operators in decreasing order from left to right. To express the above propagator in a form that will satisfy a Schrödinger like equation such as:

$$\left(i\hbar\frac{\partial}{\partial t} - \mathcal{H}\right)G_{k\sigma}(t,t') = \delta(t-t'),$$

the propagator $\left\langle \Omega|\mathcal{T}\,c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\right\rangle$, and the time order Green's function must be related through the following expression:

$$G_{k\sigma}(t,t') = -\frac{i}{\hbar}\left\langle \Omega|\mathcal{T}\,c_{k\sigma}(t)c^{\dagger}_{k\sigma}(t')|\Omega\right\rangle. \qquad (4.40)$$

This is the definition to which I will refer from now on when discussing quantum mechanical Green's functions.

4.2 Contour Ordered and Anti-Ordered Non-Equilibrium Green's Functions

When the thermodynamic limit breaks, new methods of analysis that rely not in the concepts of equilibrium statistical mechanics are required. Leonid V. Keldysh, back in 1965 in his work ***Diagram Technique for Nonequilibrium Processes*** [79], proposes a graph technique analogous to that one proposed by R. Feynman[85], for the case in which the transition (propagator) between quantum states in a system under the action of a drive is required. The latter, drives the system such that it ***deviates to any arbitrary extent from the state of thermodynamic equilibrium***, as claimed by L. V Keldysh in his work. Commonly, Keldysh graph technique is known as Keldysh field theory, as it is represented through a field theory parametrized with a set of Green's functions defined in a time contour known as the Keldysh contour, and the action representing this field theory is typically know as the Schwinger-Keldysh action [86]. These Green's functions are typically known as Keldysh propagators, or Green's functions defined in the Keldysh contour [88], [68], and I refer to them as *Non-Thermal Green's Functions*, suggesting that an equilibrium thermodynamic state cannot be defined for the system of study.

The Keldysh formulation is concerned with the time evolution of quantum mechanical observables under the effect of the time dependent drive under which the system is to evolve, without any specific reference to the thermodynamic state of the system during this evolution (that is, after the drive is turned on [79]), except at the moment infinitesimally before the external field is switched on. At this moment (typically $t \to -\infty$), before the field, interactions and other correlations are turned on, the thermodynamic state of the system can be described by the grand=canonical density matrix, and from there it evolves deviating from this thermodynamic state and therefore transiting to a non-equilibrium situation [79], [86], [88].

Subsequently, a contrast between equilibrium and non-equilibrium conditions in matter will be made [86], definitions will be established [79] and the Keldysh formulation will be explained and the Green functions as derived for the Keldysh contour will be specified [79]. Moreover, this formulation will be applied to the problem of charge and energy transport in nanostructures as presented in [89], [88].

4.2.1 Defining Non-Equilibrium

To properly account for the dynamics of systems operating in a far from equilibrium regime, it is important to understand what it means to be in equilibrium from the perspective of the system. It comes natural to define non-equilibrium as opposite to thermodynamic equilibrium as claimed in [86], for which throughout this document, reference will be made to the following equilibrium definition (conditions) [86, 73]:

Thermodynamic Equilibrium

1. An equilibrium system is characterized by a unique set of extensive and intensive thermodynamic variables, invariant over time.
2. After isolation of the system from its environment (refer to the discussion on the quantum master equation), all variables remain unchanged (After isolation, the system should relax back to equilibrium. Refer to the discussion on the time relaxation approximation for the transport Boltzmann equation) [17].
3. Distinction between equilibrium and stationary non-equilibrium must be made [86].

To illustrate the last condition (3) on the definition of thermodynamic equilibrium given above, in [86] it is mentioned that when an electronic conductor is subjected to a strong time independent voltage bias, the particle distribution function will be time independent, different from Gibbs distribution function given by:

$$p(x=y) = \frac{1}{z(\beta)} exp(-\beta E(y)), \qquad (4.41)$$

where β is typically refer to as the *inverse temperature*, and the Gibbs distribution function is a stationary non-equilibrium distribution function. Once the bias voltage connected through leads (serving as reservoirs) has been removed, the electronic particle distribution function for the conductor will relax back to the Gibbs form given by expression 4.41, and not relax back to an equilibrium form as expected for thermodynamic equilibrium. This implies that the system remains out of equilibrium after isolation [86], [68]. From the conditions above mentioned, that a system in thermodynamic equilibrium must fulfill, it can be argued that the former conditions are rather rarely met [73], [90], [86], making equilibrium in matter a perfectly strange condition [86], and a useful formalism to work under such conditions must be acknowledged [91], [79], [88]. To proceed with the conceptual development of why and how of the non-equilibrium Green's functions, I know take a step forward from the formulation presented in the previous section, where the model was temperature independent, that is, zero temperature, and define a propagator where the transitions in quantum states are triggered by changes in temperature, making this formalism still an equilibrium description, which is normally refer to as the Matsubara formalism (For details see Ref. [74], [17]).

4.2.2 Finite-Temperature Green's functions: Matsubara Formalism

To extend the definition of the Green's function for zero temperature given in expression 4.40 into a finite temperature formalism, I put into consideration that the density matrix in the grand-canonical representation ρ_0, can be written as a time evolution operator in the imaginary-time formalism as [17]:

$$\rho = exp[-\beta\mathcal{K}] = exp\left[-\frac{i}{\hbar}\mathcal{K}t\right],\qquad(4.42)$$

where $t = -i\hbar\beta$ is the evolution parameter and $\mathcal{K} = \mathcal{H} - \mu$ is known as the grand-canonical Hamiltonian. Often, the term it in the above expression is referred to as the imaginary time τ, whose value depends on the temperature T defined through $\beta = \frac{1}{k_B T}$. Under these conceptions, the tools defined for time evolution such as the generator for time translations given by:

$$\mathbb{U}(t, t') = exp\left[-\frac{i}{\hbar}\int_t^{t'} \mathcal{H}(t'')dt''\right],\qquad(4.43)$$

can be used to evolve in temperature the system under study.

Within this formalism, i.e, the imaginary-time formalism or the *Matsubara* formalism [17], [74], the Schrödinger equation can be re-written in terms of imaginary time as follows:

$$-\hbar\frac{\partial}{\partial\tau}|\psi(\tau)\rangle = \mathcal{K}|\psi(\tau)\rangle,\qquad(4.44)$$

and the imaginary time evolution operator can be written as:

$$\mathbb{U}(\tau, \tau') = exp\left[-\frac{1}{\hbar}\int_{\tau'}^{\tau} \mathcal{H}(\tau'')d\tau''\right].\qquad(4.45)$$

Moreover, the Green's function within this formalism can be also determined and it follows the same properties in imaginary time as it analogously did in real time, which is given by:

$$\mathscr{G}_{k\sigma, k'\sigma'}(\tau, \tau') = -\frac{1}{\hbar}\left\langle \mathcal{T}_\tau \psi_{k\sigma}(\tau)\psi_{k'\sigma'}^\dagger(\tau')\right\rangle.\qquad(4.46)$$

Analogously to the case specified in expression 4.37, the above expression satisfies the imaginary time Schrödinger equation of the form:

$$\left(-\hbar\frac{\partial}{\partial\tau} - \mathcal{K}\right)\mathscr{G}_{k\sigma, k'\sigma'}(\tau, \tau') = \delta_{\sigma\sigma'}\delta_{kk'}\delta(\tau - \tau'),\qquad(4.47)$$

where the expectation value in expression 4.46 is the thermal average and $\mathcal{T}_\tau$ is the time ordering operator in imaginary time. This imaginary time

propagator given by expression 4.46, has the properties of propagator and expectation value, as for the case of real time Green's functions [90], [17]. Moreover, the imaginary time Green's functions represent a probability amplitude of going from state $|k'\sigma'\rangle$ to state $|k\sigma\rangle$ when the change in temperature ΔT is equivalent to the change in imaginary time $\Delta\tau = \tau - \tau'$. Following the same logic as Feynman's path integral, a coherent state path integral can be defined for imaginary time [81], [87] from where the partition function in this formalism can be defined as:

$$\mathcal{Z} = Tr\left(e^{-\beta\mathcal{K}}\right) = \int\int \mathcal{D}\bar{\psi}\mathcal{D}\psi e^{-S[\psi,\bar{\psi}]}. \tag{4.48}$$

This definition for the partition function in the Grand-Canonical ensemble, is rather suitable for a context in which the action of the system is classical and the quantum mechanics is taken care of by integrating through all possible paths, as for the Feynman path Integrals. Accordingly, the imaginary time Green's function namely, the Matsubara Green's function reads:

$$\mathcal{G}_{k\sigma,k'\sigma'}(\tau,\tau') = -\frac{1}{\hbar}\left\langle \mathcal{T}_\tau \psi_{k\sigma}(\tau)\psi^\dagger_{k'\sigma'}(\tau')\right\rangle$$

$$= \int\int \mathcal{D}\bar{\psi}\mathcal{D}\psi \psi_{k\sigma}(\tau)\psi^\dagger_{k'\sigma'}(\tau')e^{-S[\psi,\bar{\psi}]}. \tag{4.49}$$

In this very case, the action $S[\psi,\bar{\psi}]$ is given by:

$$S[\psi,\bar{\psi}] = \int d\tau\left(x(\tau)\cdot p(\tau) - \mathcal{H}\right). \tag{4.50}$$

Note that this formalism is based on the calculation of a thermal expectation value which implies that there is a well defined thermodynamic state, situation from which I want to deviate. Next, I will start discussing the Keldysh formalism, which allows non-equilibrium conditions for the system under observation.

4.2.3 Evolution of the Density Matrix

Consider a set up that consists in a thermodynamic reservoir, with a huge number of degrees of freedom governed by Hamiltonian $\mathcal{H}_B$. This bath, is allowed to exchange entropy with a quantum system governed by $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i$, for a time $t > t_0$ (see figure 4.4), time at which the time evolution of the degrees of freedom in the quantum system of study do not evolve unitarily anymore, but evolve under the effect of a time dependent drive, correlations and interactions all specified by $\mathcal{H}_B$. The Hamiltonian that describes the entropy exchange (that is, the exchange of particles and heat) between the thermodynamic reservoir and the system is denoted as $\mathcal{H}_T$ [92].
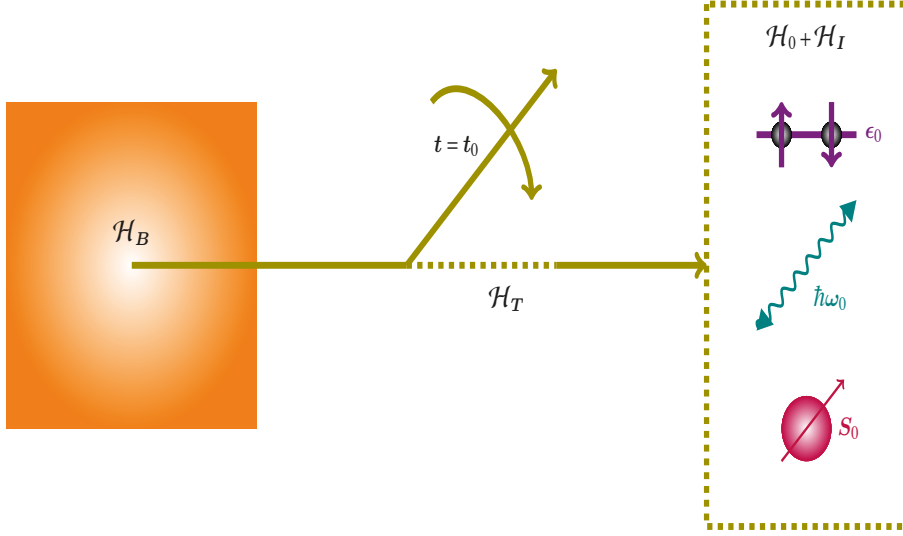
Figure 4.4. Example of the Type of Systems Considered in the Derivation of the Keldysh Formalism Presented in [79]: A bath represented by the model Hamiltonian $\mathcal{H}_B$ is connected for $t > t_0$ with a system containing few degrees of freedom, for instance, phonons, electrons and spins. This connection is represented by a commutator drawn in green, and the system with its few degrees of freedom in enclosed by a dashed box drawn in green, to resemble the flow of entropy through the green path, from the reservoir into the syste.

At some time instant t_0, the quantum system shown in figure 4.4, can be described through the density matrix $\rho_0 = \rho(\mathcal{H}(t_0))$ given by:

$$\rho_0 = \rho(\mathcal{H}(t_0)) = e^{(F_0 - \mathcal{H}(t_0))/k_B T}, \tag{4.51}$$

where F_0 is the initial free energy.
Once the quantum system is put into contact with the thermodynamic reservoir (for $t > t_0$), the time evolution of the density matrix $\rho(t)$ is completely governed by the time dependent Hamiltonian $\mathcal{H}(t) = \mathcal{H}_0(t) + \mathcal{H}_i(t)$, which includes the effect of a time dependent drive on the system. Before these interactions, correlations and drives are turned on (for $t < t_0$), the time evolution of the density matrix is trivial. After Commutation, the model Hamiltonians, $\mathcal{H}_0(t)$ and $\mathcal{H}_i(t)$ are given by:

$$\mathcal{H}_0(t) = \int dr \psi^\dagger(r,t) \left(\epsilon(p) \left[-i\hbar \nabla - \frac{e}{c} A(r,t) \right] + e\Phi(r,t) \right) \psi(r,t), \tag{4.52}$$

$$\mathcal{H}_i(t) = g \int \psi^\dagger(r,t) \psi(r,t) \phi_0(r,t), \tag{4.53}$$

where $\mathcal{H}_i(t)$ can represent electron-electron correlations or electron-phonon interactions; g is a dimensionless coupling constant, $\{\Phi(r,t), A(r,t)\}$ is an

external electromagnetic field (which is zero for $t < t_0$), $\epsilon(p)$ is the dispersion law for the electrons, and the quantum fields $\psi(r,t)$ and $\psi^\dagger(r,t)$ obey the following expansion law:

$$\psi(r,t) = \sum_p a_p \phi_p(r,t), \quad \psi^\dagger(r,t) = \sum_p a_p^\dagger \phi_p^*(r,t). \qquad (4.54)$$

The operator coefficients a_p and $a_p^\dagger$ follow an anti-commutation relation of the form $\{a_p, a_{p'}^\dagger\} = \delta_{pp'}$. The complete set of functions $\phi_p(r,t)$ can be obtained by solving the eigenvalue problem:

$$\left(\epsilon(p) \left[-i\hbar\nabla - \frac{e}{c}A(r,t) \right] + e\Phi(r,t) - i\hbar\frac{\partial}{\partial t} \right) \phi_p(r,t) = 0,$$

which yields:

$$\phi_p(r,t) = e^{i(p\cdot r - \epsilon(p)t)}, \qquad (4.55)$$

and as a consequence of expression 4.55, the quantum fields $\psi(r,t)$ and $\psi^\dagger(r,t)$ obey the following anti-commutation relation:

$$\{\psi(r,t), \psi^\dagger(r,t)\} = \delta(r - r')\delta(t - t'). \qquad (4.56)$$

Moreover, in the interaction representation, the time evolution of the quantum field $\psi(r,t)$ and the density matrix $\rho(t)$ are respectively given by:

$$i\hbar\frac{\partial\psi(r,t)}{\partial t} = [\psi(r,t), \mathcal{H}_0(t)], \qquad (4.57)$$

$$i\hbar\frac{\partial\rho(t)}{\partial t} = [\mathcal{H}_i(t), \rho(t)], \qquad (4.58)$$

where the solution to the density matrix reads:

$$\rho(t) = S(t,t_0)\rho_0 S^\dagger(t,t_0) = S(t,t_0)\rho_0 S(t_0,t), \qquad (4.59)$$

being $S(t,t_0)$ the scattering matrix, which is given by:

$$S(t,t_0) = \mathcal{T} \cdot exp\left[-\frac{i}{\hbar} \int_{t_0}^t \mathcal{H}_i(\tau)d\tau \right], \qquad (4.60)$$

and typically t_0 is taken as $t_0 \to -\infty$.

4.2.4 Expectation Value of Time Dependent Operators

Once the time evolution of the density matrix is known, the expectation value of an operator in the interaction representation can be calculated as follows:

$$\langle L(t) \rangle = Tr(\rho(t)L(t)), \qquad (4.61)$$

where the time evolution of operator $L(t)$ is given by:

$$ i\hbar \frac{\partial L(t)}{\partial t} = [L(t), \mathcal{H}_0], \tag{4.62} $$

and the density matrix $\rho(t)$ is also defined in the interaction representation. Moreover, when dealing with correlation functions of several field operators at different instants of time, it is more convenient to work in the Heisenberg representation. The density matrix in this representation scheme, carries no time dependence while the operators carry all time dependence. The above statement is followed by the expression shown below:

$$ i\hbar \frac{\partial L_H(t)}{\partial t} = [L_H(t), \mathcal{H}_0]. \tag{4.63} $$

The time-invariant density matrix $\rho_0^{(ss))}$, is just the density matrix evaluated at an arbitrary time t_{ss} at which $\rho(t)$ has undergone all changes due to the external fields after the switching process. By taking $t_0 \to -\infty$, $\rho(t_{ss})$ can be constructed using expression 4.59 as follows:

$$ \rho(t_{ss}) = S(t_{ss}, -\infty) \rho_0 S(-\infty, t_{ss}). \tag{4.64} $$

On the other hand, the Heisenberg representation of the field operator reads:

$$ \psi_H(r, t) = S(t_{ss}, t) \psi(r, t) S(t, t_{ss}). \tag{4.65} $$

Then by using the property described in expression 4.64, the time order expectation value $\langle \mathcal{T} A(t_1) B(t_2) C(t_3) \ldots \rangle$ gives:

$$ \langle \mathcal{T} A(t_1) B(t_2) C(t_3) \ldots \rangle $$
$$ = Tr[\rho_0 \mathcal{T} S(-\infty, t_1) A_H(t_1) S(t_1, t_2) B_H(t_2) S(t_2, t_3) \cdots S(t_n, -\infty)]. \tag{4.66} $$

Figure 4.5. Keldysh Contour: The Keldysh contour labeled as $C_\gamma = C_\gamma^{++} \bigcup C_\gamma^{--}$.

In Eq. 4.66, the the time order operator $\mathcal{T}$, orders the times t_1, t_2, t_3, $\cdots$ t_n along the time contour C_γ as shown in figure 4.5 and defined by:

$$ C_\gamma = \{-\infty, t_1, t_2, t_3, \cdots, t_i, t_{i+1}, \cdots, t_n, -\infty\}, \tag{4.67} $$

and the time ordering operator that orders along C_γ is denoted by $\mathcal{T}_C$, hence in expression 4.66 $\mathcal{T} \to \mathcal{T}_C$. From now on, this contour will be refer

to as the Keldysh contour. Expression 4.66, then, formulates the expectation value of a time ordered product of operators evaluated at different times in terms of a density matrix ρ_0, that represents the state of the quantum mechanical system in figure 4.4 before the interactions, drives and correlations are switched on at $t = t_0$.

According to [79], the time order in contour C_γ should be understood as follows: the time points in the return part of the contour (C_γ^{--}) correspond to later times then those points lying in the direct branch (C_γ^{++}) , and any two points on the return branch, the latter is the one closest to $-\infty$. When considering integrals in the contour C_γ, there might be complications (For instance, see Langreth rules in [68], [89], [88]). To go around this issue, Leonid Keldysh proposed a trick in [79] that consists in replacing the identity $S(t', +\infty)S(+\infty, t') = 1$ between the terms $S(t_n, t_{ss})$ and $S(t_{ss}, -\infty)$ in the elaboration presented above for the expectation value of the time ordered product given by expression 4.66. Posterior to the application of this procedure, the contour C_γ becomes C_K, known as the Schwinger-Keldysh contour [86], [79].

4.2.5 Keldysh Formalism: Contour Equations

Here I will go through the definitions of the Green's functions as defined for the Keldysh contour, as well as the Kedysh rotation [79]. As starting point, let's consider a two operator time order product written as:

$$\langle T\boldsymbol{L}(t)\boldsymbol{M}(t')\rangle = Tr\left[\rho_0 \mathcal{T}_{C_K}\left(S_C \boldsymbol{L}(t_-)\boldsymbol{M}(t'_+)\right)\right], \qquad (4.68)$$

where $\mathcal{T}_{C_K}$ is the time ordering operator along the Keldysh contour and S_C is the scattering matrix in the Keldysh contour. The time points in expression 4.68, with sub-index "$-$" denote those lying in the return branch C_K^{--}, and those with sub-index "$+$", denote those lying in the direct branch C_K^{++}.

Moreover, it becomes of capital importance to identify the type of Green's functions defined in the contour. To do so, consider a line that goes from the first time argument t' to the second time argument t as shown in figure 4.6. Moreover, by considering the relative position between these two time points, four types of Greens functions can be defined.

Figure 4.6. Two Time points in the Keldysh Contours: Time t' lies on the upper branch of the Keldysh contour, while time t lies on the lower or return branch of the Keldysh. Both of these time points can either lie on opposite sides of the contour or on the same side, be it in the upper or lower branch. Depending on the branch where they lie, the Kernel $G(t,t')$ can be evaluated in four different ways.

As such, as stated in [79], I summarize some useful rules to identify these Kernels:

1. If the line goes from $t' \in C_K^{--}$ to $t \in C_K^{++}$, it is set in correspondence with the Green's function $G^{-+}(r,t_+,r',t'_-)$ given by:

$$
G^{-+}(r,t_+,r',t'_-) =
$$
$$
-i\operatorname{Tr}\left[\rho_0 \mathcal{T}_{C_K}\left(\psi(r,t_+)\psi^\dagger(r',t'_-)\right)\right] = i\left\langle \psi^\dagger(r',t'_-)\psi(r,t_+)\right\rangle_0, \quad (4.69)
$$

where the symbol $\langle\rangle_0$ denotes averaging using density matrix ρ_0.

2. If the line goes from $t' \in C_K^{++}$ to $t \in C_K^{--}$, it is set in correspondence with the Green's function $G^{+-}(r,t_-,r',t'_+)$ given by:

$$
G^{+-}(r,t_-,r',t'_+) =
$$
$$
-i\operatorname{Tr}\left[\rho_0 \mathcal{T}_{C_K}\left(\psi(r,t_-)\psi^\dagger(r',t'_+)\right)\right] = -i\left\langle \psi(r,t_-)\psi^\dagger(r',t'_+)\right\rangle_0. \quad (4.70)
$$

3. If the line goes from $t' \in C_K^{++}$ to $t \in C_K^{++}$, it is set in correspondence with the Green's function $G^{++}(r,t_+,r',t'_+)$ given by:

$$
G^{++}(r,t_+,r',t'_+) =
$$
$$
-i\operatorname{Tr}\left[\rho_0 \mathcal{T}_{C_K}\left(\psi(r,t_+)\psi^\dagger(r',t'_+)\right)\right] = -i\left\langle \mathcal{T}_{C_K}\psi(r,t_+)\psi^\dagger(r',t'_+)\right\rangle_0,
$$
$$
(4.71)
$$

often, this Green function is denoted as $G^C(r,t_+,r',t'_+)$, making reference to the fact that both time points at which this function is evaluated lie on the upper part of the contour C_K.

4. Lastly, if the line goes from $t' \in C_K^{--}$ to $t \in C_K^{--}$, it is set in correspondence with the Green's function $G^{--}(r,t_-,r',t'_-)$ given by:

$$
G^{--}(r,t_-,r',t'_-) =
$$
$$
-i\operatorname{Tr}\left[\rho_0 \mathcal{T}_{C_K}\left(\psi(r,t_-)\psi^\dagger(r',t'_-)\right)\right] = -i\left\langle \bar{\mathcal{T}}_{C_K}\psi(r,t_-)\psi^\dagger(r',t'_-)\right\rangle_0,
$$
$$
(4.72)
$$

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where $\bar{\mathcal{T}}_{C_K}$ is known as the anti-time ordering operator which is defined through:

$$\bar{\mathcal{T}}_{C_K}\psi(r,t)\psi^\dagger(r',t') = \begin{cases} \psi(r,t)\psi^\dagger(r',t') & \text{if } t < t', \\ \psi^\dagger(r',t')\psi(r,t) & \text{if } t > t'. \end{cases} \tag{4.73}$$

Often, this Green function is denoted as $G^{\bar{C}}(r,t_-,r',t'_-)$, making reference to the fact that both time points at which this function is evaluated lie on the lower part of the contour C_K.

These functions as defined above, can be written as a matrix G as:

$$G = \begin{bmatrix} G^C(r,t_+,r',t'_+) & G^{+-}(r,t_-,r',t'_+) \\ G^{-+}(r,t_+,r',t'_-) & G^{\bar{C}}(r,t_-,r',t'_-) \end{bmatrix} = \begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix}. \tag{4.74}$$

In [79], matrix G is rotated using the transformation:

$$G \rightarrow \left(\frac{\sigma_0 - i\sigma_y}{\sqrt{2}}\right) G \left(\frac{\sigma_0 - i\sigma_y}{\sqrt{2}}\right) = \frac{1}{2}\left(G + iG\sigma_y - i\sigma_y G + \sigma_y G\sigma_y\right)$$

$$= \frac{1}{2}\begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix} + \frac{i}{2}\begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$
$$- \frac{i}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix},$$

$$= \frac{1}{2}\begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix} + \frac{1}{2}\begin{bmatrix} -G^{+-} & G^C \\ -G^{\bar{C}} & G^{-+} \end{bmatrix}$$
$$+ \frac{1}{2}\begin{bmatrix} -G^{-+} & -G^{\bar{C}} \\ G^C & G^{+-} \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} iG^{+-} & -iG^C \\ iG^{\bar{C}} & -iG^{-+} \end{bmatrix}$$

$$= \frac{1}{2}\begin{bmatrix} G^C + G^{\bar{C}} - G^{+-} - G^{-+} & (G^{+-} - G^{-+}) + (G^C - G^{\bar{C}}) \\ (G^{-+} - G^{+-}) + (G^C - G^{\bar{C}}) & (G^{+-} + G^{-+}) + (G^C + G^{\bar{C}}) \end{bmatrix},$$

where σ_0 denotes the identity matrix and σ_y denotes the y–component of the Pauli matrices. From the above, it can be seen that the matrix G transforms as:

$$G = \begin{bmatrix} G^C & G^{+-} \\ G^{-+} & G^{\bar{C}} \end{bmatrix} \Rightarrow \begin{bmatrix} \frac{G^C + G^{\bar{C}} - (G^{+-} + G^{-+})}{2} & \frac{(G^{+-} - G^{-+}) + (G^C - G^{\bar{C}})}{2} \\ \frac{(G^{-+} - G^{+-}) + (G^C - G^{\bar{C}})}{2} & \frac{(G^{+-} + G^{-+}) + (G^C + G^{\bar{C}})}{2} \end{bmatrix} = \bar{G}, \tag{4.75}$$

where $\bar{G}$ is the transformed matrix.

The transformed Green's function $\bar{G}$ can be simplified by checking that $G^C + G^{\bar{C}} = G^{+-} + G^{-+}$. On the other hand, it is useful to also verify that $G^C - G^{\bar{C}} = G^R + G^A$. In the context developed throughout the chapter, G^R is known as the retarded or causal Green's function and G^A is known as the advanced Green's function and they are respectively given by:

$$G^R = (-i)\left\langle \psi(\boldsymbol{r},t)\psi^\dagger(\boldsymbol{r}',t') + \psi^\dagger(\boldsymbol{r}',t')\psi(\boldsymbol{r},t)\right\rangle \theta(t-t'), \qquad (4.76)$$

$$G^A = (i)\left\langle \psi(\boldsymbol{r},t)\psi^\dagger(\boldsymbol{r}',t') + \psi^\dagger(\boldsymbol{r}',t')\psi(\boldsymbol{r},t)\right\rangle \theta(t'-t). \qquad (4.77)$$

Moreover to compute the terms $\bar{G}_{12}$ and $\bar{G}_{21}$ from matrix $\bar{G}$, it is necessary to consider the expressions $(G^{+-} - G^{-+}) + \left(G^C - G^{\bar{C}}\right)$ and $(G^{-+} - G^{+-}) + \left(G^C - G^{\bar{C}}\right)$. First:

$$(G^{+-} - G^{-+}) + \left(G^C - G^{\bar{C}}\right) = (i)\left\langle \{\psi(\boldsymbol{r},t), \psi^\dagger(\boldsymbol{r}',t')\}\right\rangle + G^R + G^A,$$

$$= \begin{cases} 0 & \text{if } t > t', \\[2mm] 2G^A & \text{if } t' > t, \end{cases}$$

Similarly, for $(G^{-+} - G^{+-}) + \left(G^C - G^{\bar{C}}\right)$ it gives:

$$(G^{-+} - G^{+-}) + \left(G^C - G^{\bar{C}}\right) = (-i)\left\langle \{\psi(\boldsymbol{r},t), \psi^\dagger(\boldsymbol{r}',t')\}\right\rangle + G^R + G^A,$$

$$= \begin{cases} 2G^R & \text{if } t > t', \\[2mm] 0 & \text{if } t' > t, \end{cases},$$

hence, giving the following matrix $\bar{G}$:

$$\bar{G} = \begin{bmatrix} 0 & G^A \\ G^R & G^C + G^{\bar{C}} \end{bmatrix}. \qquad (4.78)$$

To wrap up the discussion about the Keldysh formalism, do note that in the transport literature the Green's functions G^{+-} and G^{-+} are typically refer to as the lesser $G^<$ and greater $G^>$ Green's functions [89], [88], which will be extensively used in the formulations encounter in this thesis.

4.3 Review of the Meir-Jauho-Wingreen Formalism

The Meir-Jauho-Wingreen (MJW) formalism was introduced in 1994 in a paper called *"Time-Dependent Transport in Interacting and Non-Interacting*

Mesoscopic Systems" [89], [88]. Here in this section I want to briefly high-light three fundamental results from this formalism, which will be often refer to in the development of the work of this thesis, namely, the general expression for contour Green's functions in terms of Retarded and Advanced Green's functions (Eq. 4.87), the Meir-Jauho-Wingreen non-interacting particle current (Eq. 4.94) and the close form for contour Green's functions in terms of the contour self-energies (Eq. 4.109 and Eq. 4.110). First, I will consider the expression for lesser Green's function.

4.3.1 Langreth Equation for the Contour Order Green's Functions

The system considered in [jauho], for instance, can be described by the following set of modeling equations:

$$\mathcal{H} = \sum_{\alpha} \mathcal{H}_{\alpha} + \mathcal{H}_{Q,D} + \sum_{\alpha} \mathcal{H}_{T,\alpha}, \tag{4.79}$$

$$\mathcal{H}_{\alpha} = \sum_{k,\sigma} \epsilon_{k\alpha}(t) c^{\dagger}_{k\sigma,\alpha}(t) c_{k\sigma,\alpha}(t), \tag{4.80}$$

$$\mathcal{H}_{mol} = \sum_{m,\sigma} \epsilon_m(t) d^{\dagger}_{m\sigma}(t) d_{m\sigma}(t), \tag{4.81}$$

$$\mathcal{H}_{T,\alpha} = \sum_{k,m,\sigma} V_{k\alpha,m}(t) c^{\dagger}_{k\sigma,\alpha}(t) d_{m\sigma}(t) + V^*_{k\alpha,m}(t) d^{\dagger}_{m\sigma}(t) c_{k\sigma,\alpha}(t). \tag{4.82}$$

The model described by equation 4.79 represents a molecular complex ($\mathcal{H}_{mol}$), coupled via tunneling interactions ($\mathcal{H}_{T,\alpha}$) to a set of reservoirs ($\mathcal{H}_{\alpha}$), each of them labeled by the index α. The molecular Hamiltonian $\mathcal{H}_{mol}$ describes a molecule, with an arbitrary number of orbital levels with energies $\epsilon_m(t)$. The leads or metallic contacts, or if you wish, electrodes, are described by the Hamiltonian $\mathcal{H}_{\alpha}$, where $\epsilon_{k\alpha}(t)$ represents the band structure of the specific metal. The interaction between the molecule and the reservoirs is modeled through the Hamiltonian $\mathcal{H}_{T,\alpha}$, with interaction strength $V_{k\alpha,m}(t)$. The operators appearing in expressions 4.80, 4.81 and 4.82, create or annihilate electrons in the molecule ($d^{\dagger}_{m\sigma}(t)$, $d_{m\sigma}(t)$), and create and annihilate electrons in the metallic leads ($c^{\dagger}_{k\sigma,\alpha}(t)$, $c_{k\sigma,\alpha}(t)$).

Moreover, in [89], the authors were pursuing a general expression for the particle current flowing through the central region whether a molecule, vacuum or a quantum dot. It is the defined the general expression for the current given by:

$$J_{\alpha}(t) = -e \left\langle \dot{\mathcal{N}}_{\alpha}(t) \right\rangle = -e \frac{d \langle \mathcal{N}_{\alpha}(t) \rangle}{dt} = -\frac{ie}{\hbar} \left\langle [\mathcal{H}, \mathcal{N}_{\alpha}(t)] \right\rangle, \tag{4.83}$$

where $N_\alpha(t) = \sum_{k,\sigma} c^\dagger_{k\sigma,\alpha}(t)c_{k\sigma,\alpha}(t)$ is the particle number operator. After some straightforward algebra, the current $J_\alpha(t)$ can be written as:

$$J_L(t) = \frac{ie}{\hbar} \sum_{k,\alpha,m} \left(V_{k,\alpha,m}(t)\left\langle c^\dagger_{k\alpha}(t)d_m(t) \right\rangle - V^*_{k,\alpha,m}(t)\left\langle d^\dagger_m(t)c_{k\alpha}(t) \right\rangle \right), \quad (4.84)$$

or in terms of contour order Green's functions it reads:

$$J_L(t) = 2e \sum_{k,\alpha,m} \Re e\left[V_{k,\alpha,m}(t)G^<_{m,k\alpha}(t,t) \right]. \quad (4.85)$$

To evaluate the expression above, $G^<_{m,k\alpha}(t,t)$ should be specified, and since is a contour kernel, depending on two times, Langreth rules have to be used. From the equation of motion method, as used in appendix B, $G^<_{m,k\alpha}(t,t)$ can be obtained first by writing the contour order Green's function $G_{m,k\alpha}(t,t)$ as follows:

$$G_{m,k\alpha}(t,t') = \sum_n \int V^*_{k\alpha,n}(t_1)G_{mn}(t,t_1)g_{k\alpha}(t_1,t')dt_1, \quad (4.86)$$

and then by applying Langreth rules [89], [88], [68] to write contour kernels, giving:

$$G^<_{m,k\alpha}(t,t) = \frac{i}{\hbar} \sum_n \int_{-\infty}^{t} V^*_{k\alpha,n}(\tau)e^{-\frac{i}{\hbar}\epsilon_{k\alpha}(t)(\tau-t)}\left[G^R_{mn}(t,\tau)f(\epsilon^0_{k\alpha}) + G^<_{mn}(t,\tau) \right]d\tau$$

$$(4.87)$$

This constitutes the very first result I want to convey from the MJW formalism.

4.3.2 Meir-Jauho-Wingreen Particle Current

Replacing expression 4.87 into Eq. 4.85, yields the particle current as express below (I set now $\alpha = L$, refering to the left electrode):

$$J_L(t) = -\frac{2e}{\hbar}\Im m \sum_{k\alpha,m,n} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}\epsilon^0_{k\alpha}(\tau-t)}V_{k\alpha,m}(t)V^*_{k\alpha,n}(\tau)$$

$$\times e^{-\frac{i}{\hbar}\int_t^\tau \Delta_{k\alpha}(\tau')d\tau'}\left[G^R_{mn}(t,\tau)f_L(\epsilon^0_{k\alpha}) + G^<_{mn}(t,\tau) \right]d\tau. \quad (4.88)$$

To further re-organize expression 4.88, it is convenient according to (A. P. Jauho, 1998), to redefine the tunneling rate $V_{k\alpha,m}(t)$ as:

$$V_{k\alpha,m}(t) \rightarrow V_{\alpha,m}(\epsilon,t),$$

which suggests that the band structure of the leads denoted as $\epsilon_{k\alpha}^0$ becomes ϵ in the continuum limit, hence, transforming expression 4.88 into:

$$J_L(t) = -\frac{2e}{\hbar} \Im \sum_{k\alpha,m,n} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}\epsilon(\tau-t)} V_{\alpha,m}(\epsilon,t) V_{\alpha,n}^*(\epsilon,\tau) e^{\frac{i}{\hbar}\int_{\tau}^{t}\Delta_\alpha(\epsilon,\tau')d\tau'} \quad (4.89)$$

$$\times \left[G_{mn}^R(t,\tau) f_L(\epsilon) + G_{mn}^<(t,\tau) \right] d\tau. \quad (4.90)$$

By replacing the sum over k in the above expression by an integral over the density of states $D_\alpha(\epsilon)$, Eq. 4.90 re-reads as follows:

$$J_L(t) = -\frac{2e}{\hbar} \Im \sum_{\alpha} \int \frac{d\epsilon D_\alpha(\epsilon)}{2\pi} \sum_{m,n} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}\epsilon(\tau-t)} (2\pi) V_{\alpha,m}(\epsilon,t) V_{\alpha,n}^*(\epsilon,\tau)$$

$$\times e^{\frac{i}{\hbar}\int_{\tau}^{t}\Delta_\alpha(\epsilon,\tau')d\tau'} \left[G_{mn}^R(t,\tau) f_L(\epsilon) + G_{mn}^<(t,\tau) \right] d\tau. \quad (4.91)$$

The message I attempt to convey is almost ready. To do so, I here define [89] the parameter $\Gamma_{mn}^L(\epsilon,\tau,t)$ as follows:

$$\Gamma_{nm}^L(\epsilon,\tau,t) = (2\pi) \sum_{\alpha} D_\alpha(\epsilon) V_{\alpha,m}(\epsilon,t) V_{\alpha,n}^*(\epsilon,\tau) e^{\frac{i}{\hbar}\int_{\tau}^{t}\Delta_\alpha(\epsilon,\tau')d\tau'}, \quad (4.92)$$

from where Eq. 4.91 becomes:

$$J_L(t) = -\frac{2e}{\hbar} \Im \int \frac{d\epsilon}{2\pi} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}\epsilon(\tau-t)} \sum_{m,n} \Gamma_{nm}^L(\epsilon,\tau,t)$$

$$\times \left[G_{mn}^R(t,\tau) f_L(\epsilon) + G_{mn}^<(t,\tau) \right] d\tau, \quad (4.93)$$

which is usually expressed in terms of the trace as follows:

$$J_L(t) = -\frac{2e}{\hbar} \int_{-\infty}^{t} d\tau \int \frac{d\epsilon}{2\pi}$$

$$\text{Tr}\left(\Im \left[e^{-\frac{i}{\hbar}\epsilon(\tau-t)} \Gamma^L(\epsilon,\tau,t) \left(G^R(t,\tau) f_L(\epsilon) + G^<(t,\tau) \right) \right] \right), \quad (4.94)$$

The above expression is known as the Meir-Jauho-Wingreen formula for the particle current.

It can be useful for the reader to discuss the time invariance of expression 4.94. For the time invariant case, in [89] it is assumed that $\Gamma^L(\epsilon,\tau,t) \to \Gamma^L(\epsilon)$ and $\Gamma^R(\epsilon,\tau,t) \to \Gamma^R(\epsilon)$, and then, the dependence with respect to time of the Green's functions $G^R(t,\tau)$ and $G^<(t,\tau)$ is absorbed as follows:

$$G^R(t,\tau) \Rightarrow G^R(t-\tau); \quad G^<(t,\tau) \Rightarrow G^<(t-\tau). \quad (4.95)$$

Therefore, by replacing expression 4.95 into expression 4.94, the steady state charge current J_L is given by:

$$J_L = -\frac{2e}{\hbar} \int_{-\infty}^{t} d\tau \int \frac{d\epsilon}{2\pi} \mathrm{Tr}\left(\Im m\left[e^{-\frac{i}{\hbar}\epsilon(\tau-t)} \boldsymbol{\Gamma}^L(\epsilon)\left(\boldsymbol{G}^R(t-\tau)f_L(\epsilon) + \boldsymbol{G}^<(t-\tau)\right)\right]\right).$$
(4.96)

Furthermore, by Fourier transforming the retarded and lesser Green's functions, and using the fact that:

$$\Im m\left[\boldsymbol{G}^R(\epsilon)\right] = -\frac{1}{2}\left[\boldsymbol{G}^R(\epsilon) - \boldsymbol{G}^A(\epsilon)\right]$$

the charge current J_L reads:

$$J_L = \frac{ie}{\hbar} \int \frac{d\epsilon}{2\pi} \mathrm{Tr}\left(\boldsymbol{\Gamma}^L(\epsilon)\boldsymbol{G}^<(\epsilon) + \boldsymbol{\Gamma}^L(\epsilon)f_L(\epsilon)\left(\boldsymbol{G}^R(\epsilon) - \boldsymbol{G}^A(\epsilon)\right)\right).$$
(4.97)

Moreover, when the observable of interest is expressed as a proportionate coupling between the two leads as:

$$J(t) = xJ_L(t) - (1-x)J_R(t),$$
(4.98)

with the condition of:

$$\boldsymbol{\Gamma}^L(\epsilon) = \lambda\boldsymbol{\Gamma}^R(\epsilon),$$
(4.99)

with x and λ related through:

$$x = \frac{1}{1+\lambda}, \qquad 1-x = \frac{\lambda}{1+\lambda},$$
(4.100)

the total current J can be constructed as follows:

$$J(t) = \frac{ie}{\hbar} \int \frac{d\epsilon}{2\pi} \mathrm{Tr}\left(x\boldsymbol{\Gamma}^L(\epsilon)\boldsymbol{G}^<(\epsilon) + x\boldsymbol{\Gamma}^L(\epsilon)f_L(\epsilon)\left(\boldsymbol{G}^R(\epsilon) - \boldsymbol{G}^A(\epsilon)\right)\right)$$
$$- \frac{ie}{\hbar} \int \frac{d\epsilon}{2\pi} \mathrm{Tr}\left((1-x)\boldsymbol{\Gamma}^R(\epsilon)\boldsymbol{G}^<(\epsilon) + (1-x)\boldsymbol{\Gamma}^R(\epsilon)f_R(\epsilon)\left(\boldsymbol{G}^R(\epsilon) - \boldsymbol{G}^A(\epsilon)\right)\right),$$

and by using expressions 4.99 and 4.100 to elaborate furthermore, J finally reads:

$$J(t) = \frac{ie}{\hbar} \int \frac{d\epsilon}{2\pi} (f_L(\epsilon) - f_R(\epsilon))\mathrm{Tr}\left[\frac{\boldsymbol{\Gamma}^L(\epsilon)\boldsymbol{\Gamma}^R(\epsilon)}{\boldsymbol{\Gamma}^L(\epsilon) + \boldsymbol{\Gamma}^R(\epsilon)}\left(\boldsymbol{G}^R(\epsilon) - \boldsymbol{G}^A(\epsilon)\right)\right].$$
(4.101)

This is the Landauer formalism to calculate charge current through a tunneling junction, from where the Landauer conductance reads:

$$G(\epsilon) = \frac{ie^2}{\hbar} \mathrm{Tr}\left[\frac{\boldsymbol{\Gamma}^L(\epsilon)\boldsymbol{\Gamma}^R(\epsilon)}{\boldsymbol{\Gamma}^L(\epsilon) + \boldsymbol{\Gamma}^R(\epsilon)}\left(\boldsymbol{G}^R(\epsilon) - \boldsymbol{G}^A(\epsilon)\right)\right] = \frac{ie^2}{\hbar}T(\epsilon),$$
(4.102)

namely, the Landauer conductance, where $T(\epsilon) = \mathrm{Tr}\,\boldsymbol{\Gamma}^L(\epsilon)\boldsymbol{G}^R(\epsilon)\boldsymbol{\Gamma}^R(\epsilon)\boldsymbol{G}^A(\epsilon)$ is known as the Landauer transmission.

4.3.3 Self-Energy and Contour Green's Functions

By deriving the equation of motion for the contour order kernel $G_{nm}(t,t')$, one writes:

$$\left(i\hbar\frac{\partial}{\partial t} - \epsilon_n(t)\right)G_{nm}(t,t') = \delta(t-t')\delta_{nm} + \sum_{k\alpha} V^*_{k\alpha n}(t)G_{k\alpha n}(t,t'). \qquad (4.103)$$

which can be further simplify to give:

$$\left(i\hbar\frac{\partial}{\partial t} - \epsilon_n(t)\right)G_{nm}(t,t') = \delta(t-t')\delta_{nm}$$
$$+ \sum_{k\alpha n'} V^*_{k\alpha n}(t)\int g_{k\alpha}(t,\tau)V_{k\alpha n'}(\tau)G_{n'm}(\tau,t')d\tau.$$
$$(4.104)$$

By solving Eq. 4.104, the contour order Green's function $G_{nm}(t,t')$ reads in closed form as follows:

$$G_{nm}(t,t') = g_n(t,t')\delta_{nm}$$
$$+ \sum_{k\alpha n'} \int\int g_n(t,\tau')V^*_{k\alpha n}(\tau')g_{k\alpha}(\tau',\tau)V_{k\alpha n'}(\tau)G_{n'm}(\tau,t')d\tau d\tau',$$

which after further simplification gives:

$$G_{nm}(t,t') = g_n(t,t')\delta_{nm} + \sum_{n'} \int\int g_n(t,\tau')\Sigma_{nn'}(\tau',\tau)G_{n'n}(\tau,t')d\tau d\tau'. \quad (4.105)$$

or in Matrix form $(g(t,t') = Ig(t,t'))$, expression 4.105 can be as well stated as shown below:

$$\boldsymbol{G}(t,t') = \boldsymbol{g}(t,t') + \int\int \boldsymbol{g}(t,\tau')\boldsymbol{\Sigma}(\tau',\tau)\boldsymbol{G}(\tau,t')d\tau d\tau'. \qquad (4.106)$$

where the matrix element of the self energy $\Sigma_{mn}(t,t')$ is given by:

$$\Sigma_{mn}(t,t') = \sum_{k\alpha} V^*_{k\alpha m}(t)g_{k\alpha}(t,t')V_{k\alpha n}(t') \qquad (4.107)$$

For further reference about the procedures described above, see chapter 7.

From the Langreth rules, $\boldsymbol{G}^<(t,t')$ can be obtained from Eq. 4.106. First Writing:

$$\boldsymbol{G}^<(t,t') = \boldsymbol{I}\boldsymbol{g}^<(t,t') + \int \left(\boldsymbol{B}^R(t,\tau)\boldsymbol{G}^<(\tau,t') + \boldsymbol{B}^<(t,\tau)\boldsymbol{G}^a(\tau,t')\right)d\tau \quad (4.108)$$

where $B(t,\tau)$, $B^R(t,\tau)$ and $B^<(t,\tau)$ are defined, according to the same rules

$$B(t,t') = \int g(t,\tau)\Sigma(\tau,t')d\tau,$$

$$B^R(t,t') = \int g^R(t,\tau)\Sigma^R(\tau,t')d\tau,$$

$$B^<(t,t') = \int \left(g^R(t,\tau)\Sigma^<(\tau,t') + g^<(t,\tau)\Sigma^a(\tau,t')\right)d\tau.$$

By recalling that integrals of the form:

$$\int \left[g^R(t,\tau)\right]^{-1} g^<(\tau,t')d\tau,$$

vanish, after some tedious algebra, though straight forward, expression 4.108 re-organizes like below:

$$G^<(t,t') = \int\int G^R(t,\tau')\Sigma^<(\tau',\tau)G^a(\tau,t')d\tau d\tau'. \qquad (4.109)$$

Similar procedure follows for obtaining $G^>(t,t')$, which gives:

$$G^>(t,t') = \int\int G^R(t,\tau')\Sigma^>(\tau',\tau)G^a(\tau,t')d\tau d\tau'. \qquad (4.110)$$

4.4 Alternative Derivation of Transport Formulas as a Function of Contour Green's Functions

Here, I provide an alternative derivation for a generalized expression for the energy current (as compare to the work reported in [89]), mostly used in the available literature such as in the work resonant tunneling junction by Galperin [93], [94], in the work by T. Saygun in paramagnetic dimers [67] and in the work presented in the appended papers to this thesis, mainly for papers I and III.

The energy current can be defined in terms of the energy gained or lost by an arbitrary reservoir in the non equilibrium paradigm, that is, a physical system coupled to an environment. From the above conception, I define the energy current $J_\alpha^{(\epsilon)}(t)$ as follows:

$$J_\alpha^{(\epsilon)}(t) = -\left\langle \frac{d\mathcal{H}_\alpha}{dt} \right\rangle, \qquad (4.111)$$

and elaborating write:

$$
\begin{aligned}
J_\alpha^{(\epsilon)}(t) &= -\left\langle \frac{d\mathcal{H}_\alpha}{dt} \right\rangle = -\left\langle -\frac{i}{\hbar}[\mathcal{H}_\alpha, \mathcal{H}] \right\rangle \\
&= \frac{i}{\hbar}\left\langle \left[\sum_{k\sigma} \epsilon_{k\sigma}(t) c_{k\sigma}^\dagger(t) c_{k\sigma}(t), \mathcal{H} \right] \right\rangle = \frac{i}{\hbar}\sum_{k\sigma} \epsilon_{k\sigma}(t)\left\langle \left[c_{k\sigma}^\dagger(t) c_{k\sigma}(t), \mathcal{H} \right] \right\rangle, \\
&= \frac{i}{\hbar}\sum_{k\sigma} \epsilon_{k\sigma}(t)\left\langle c_{k\sigma}^\dagger(t)\left[c_{k\sigma}(t), \mathcal{H} \right] + \left[c_{k\sigma}^\dagger(t), \mathcal{H} \right] c_{k\sigma}(t) \right\rangle \\
&= \frac{i}{\hbar}\sum_{k\sigma} \epsilon_{k\sigma}(t)\left\langle c_{k\sigma}^\dagger(t)\left[c_{k\sigma}(t), \mathcal{H} \right] - \left(c_{k\sigma}^\dagger(t)\left[c_{k\sigma}(t), \mathcal{H} \right] \right)^\dagger \right\rangle, \\
&= -\frac{2}{\hbar}\sum_{k\sigma m} \epsilon_{k\sigma}(t)\,\mathfrak{Im}\,V_{mk\sigma}(t)\left\langle c_{k\sigma}^\dagger(t) d_{m\sigma}(t) \right\rangle \qquad\qquad (4.112)
\end{aligned}
$$

and using first order perturbation theory, the expectation value in the above expression may be written as below:

$$
\left\langle c_{k\sigma}^\dagger(t) d_{m\sigma}(t) \right\rangle = -\frac{i}{\hbar}\int_{-\infty}^{t} \left\langle \left[c_{k\sigma}^\dagger(t) d_{m\sigma}(t), \mathcal{H}(\tau) \right] \right\rangle d\tau, \qquad (4.113)
$$

and replacing the above expression back in the result given by equation 4.112, the following elaboration can be made:

$$
\begin{aligned}
J_\alpha^{(\epsilon)}(t) &= -\frac{2}{\hbar}\sum_{k\sigma m} \epsilon_{k\sigma}(t)\,\mathfrak{Im}\,V_{mk\sigma}(t)\left[-\frac{i}{\hbar}\int_{-\infty}^{t} \left\langle \left[c_{k\sigma}^\dagger(t) d_{m\sigma}(t), \mathcal{H}(\tau) \right] \right\rangle d\tau \right], \\
&= -\frac{2}{\hbar^2}\sum_{k\sigma m} \epsilon_{k\sigma}(t)\,\mathbb{IM}\,V_{mk\sigma}(t) \\
&\qquad \times (-i)\int_{-\infty}^{t} \left\langle \left[c_{k\sigma}^\dagger(t) d_{m\sigma}(t), \sum_{k'\sigma'm'} V_{m'k'\sigma'}^*(\tau) d_{m'\sigma'}^\dagger(\tau) c_{k'\sigma'}(\tau) \right] \right\rangle d\tau, \\
&= -\frac{2}{\hbar^2}\sum_{k\sigma m}\sum_{k'\sigma'm'} \epsilon_{k\sigma}(t)\,\mathfrak{Im}(-i)\int_{-\infty}^{t} V_{mk\sigma}(t) V_{m'k'\sigma'}^*(\tau) \\
&\qquad\qquad \times \left\langle \left[c_{k\sigma}^\dagger(t) d_{m\sigma}(t), d_{m'\sigma'}^\dagger(\tau) c_{k'\sigma'}(\tau) \right] \right\rangle d\tau.
\end{aligned}
$$

$$(4.114)$$

The term $\left\langle\left[c_{k\sigma}^{\dagger}(t)d_{m\sigma}(t), d_{m'\sigma'}^{\dagger}(\tau)c_{k'\sigma'}(\tau)\right]\right\rangle$ can be written in terms of Green's functions from the following procedure:

$$
\left\langle\left[c_{k\sigma}^{\dagger}(t)d_{m\sigma}(t), d_{m'\sigma'}^{\dagger}(\tau)c_{k'\sigma'}(\tau)\right]\right\rangle
$$

$$
= \left\langle c_{k\sigma}^{\dagger}(t)c_{k'\sigma'}(\tau)d_{m\sigma}(t)d_{m'\sigma'}^{\dagger}(\tau)\right\rangle - \left\langle d_{m'\sigma'}^{\dagger}(\tau)d_{m\sigma}(t)c_{k'\sigma'}(\tau)c_{k\sigma}^{\dagger}(t)\right\rangle,
$$

$$
\approx \left\langle c_{k\sigma}^{\dagger}(t)c_{k'\sigma'}(\tau)\right\rangle\left\langle d_{m\sigma}(t)d_{m'\sigma'}^{\dagger}(\tau)\right\rangle - \left\langle d_{m'\sigma'}^{\dagger}(\tau)d_{m\sigma}(t)\right\rangle\left\langle c_{k'\sigma'}(\tau)c_{k\sigma}^{\dagger}(t)\right\rangle,
$$

$$
= \left(\frac{\hbar}{i}\right)\mathcal{G}_{k\sigma}^{<}(\tau,t)\delta_{kk'}\delta_{\sigma\sigma'}\left(-\frac{\hbar}{i}\right)\mathcal{G}_{mm'\sigma\sigma'}^{>}(t,\tau)
$$

$$
- \left(-\frac{\hbar}{i}\right)\mathbf{G}_{mm'\sigma\sigma'}^{<}(t,\tau)\left(\frac{\hbar}{i}\right)\mathcal{G}_{k\sigma}^{>}(\tau,t)\delta_{kk'}\delta_{\sigma\sigma'},
$$

$$
= \hbar^2\left(\mathbf{G}_{mm'\sigma\sigma'}^{>}(t,\tau)\mathcal{G}_{k\sigma}^{<}(\tau,t) - \mathbf{G}_{mm'\sigma\sigma'}^{<}(t,\tau)\mathcal{G}_{k\sigma}^{>}(\tau,t)\right)\delta_{kk'}\delta_{\sigma\sigma'},
$$

and when replacing the above result back in expression 4.114, the energy current reads in convolution form as it shows:

$$
J_{\alpha}^{(\epsilon)}(t) = -2\sum_{k\sigma mm'}\epsilon_{k\sigma}(t)\Im m(-i)\int_{-\infty}^{t}V_{mk\sigma}(t)V_{m'k\sigma}^{*}(\tau)
$$

$$
\times\left(\mathbf{G}_{mm'\sigma\sigma}^{>}(t,\tau)\mathcal{G}_{k\sigma}^{<}(\tau,t) - \mathbf{G}_{mm'\sigma\sigma}^{<}(t,\tau)\mathcal{G}_{k\sigma}^{>}(\tau,t)\right)d\tau.
$$

$$(4.115)$$

I now define the lesser and greater self-energy through the expression:

$$
\Sigma_{mn\sigma}^{</>}(t,t') = 2\pi\rho(\epsilon)V_{m\sigma}^{*}(\epsilon,t)\mathcal{G}_{\sigma}^{</>}(\epsilon,t,t')V_{n\sigma}(\epsilon,t'),
$$

$$(4.116)$$

according to the convention adopted by Y. Meir $et.al$ in [95], [89], and in accordance with expression 4.92. Replacing expression 4.116 back in Eq. 4.115, yields the energy current:

$$
J_{\alpha}^{(\epsilon)}(t) = -2\sum_{\sigma mn}\int\frac{d\epsilon}{2\pi}\epsilon(t)\Im m(-i)
$$

$$
\times\int_{-\infty}^{t}\left(G_{mn\sigma\sigma}^{>}(\epsilon,t,\tau)\Sigma_{nm\sigma}^{<}(\epsilon,\tau,t) - G_{mn\sigma\sigma}^{<}(\epsilon,t,\tau)\Sigma_{mn\sigma}^{>}(\epsilon,\tau,t)\right)d\tau.
$$

$$(4.117)$$

Do note that I have used the transformation $\frac{1}{2\pi}\sum_{k}(\cdot) \rightarrow \int d\epsilon\rho(\epsilon)(\cdot)$ in order to include an integral over energy in expression 4.117, and also note that the dependence of the lesser and greater Green's function on the energy ϵ is due to their explicit dependence on the occupation function of the reservoirs (see Eq. 4.109 and Eq. 4.110).

5. Non-Equilibrium Molecular Magnetism

"In the history of science, ever since the famous trial of Galileo, it has repeatedly been claimed that scientific truth cannot be reconciled with the religious interpretation of the world. Although I am now convinced that scientific truth is unassailable in its own field, I have never found it possible to dismiss the content of religious thinking as simply part of an outmoded phase in the consciousness of mankind, a part we shall have to give up from now on. Thus in the course of my life I have repeatedly been compelled to ponder on the relationship of these two regions of thought, for I have never been able to doubt the reality of that to which they point"

and,

"Where no guiding ideals are left to point the way, the scale of values disappears and with it the meaning of our deeds and sufferings, and at the end can lie only negation and despair. Religion is therefore the foundation of ethics, and ethics the presupposition of life"

Werner Heisenberg in 1970,1974,

in his speech on the Romano Guardini Prize: Scientific and Religious Truth (1974)

5.1 Molecular Magnetism in the Scope of This Thesis

Once some light was shed on the incognitos about the quantum theory of magnetism, new questions starting to emerge when the resistance of Gold, Copper and Lead showed an anomaly in the low temperature resistivity, and it was only until the late 1950's, when this issues settled to be approached by physicists, once the purity control of a metal was more developed [22]. Following the work done by C. Zener on transition metals [24], first M. Ruderman and C. Kittel [96], followed by Kei Yosida [32] and Tadao Kasuya [31], studied the nature of the exchange interactions among impurity spins in doped metals, arriving at an expression for the effective

exchange coupling among these spins interacting only through the conduction electrons, interaction that receives the name RKKY due to its main contributors (Ruderman-Kittel-Kasuda-Yosida). In the coming years the resistance anomaly will be fully explained by J. Kondo [26] and by K. Wilson [72], settling down years of mystery about the effect of magnetic impurities on metallic compounds. This great progress in the field, that was screened for some years by the progress in other areas of condensed matter [97], such as high-temperature superconductivity, topological insulators and ultra cold atoms, will re-capture the interest of the scientific community at the stake of the development of methods to manipulate and control matter at the atomic scale, which is what the emergent field of nanotechnology aims for [40]. Herein, local probing techniques such as Scanning Tunneling Microscopy STM and Atomic Force Microscopy AFM has increased the interest in impurity physics and in recent years, great efforts in engineering this spin-spin interactions at the atomic level has capture much of the interest in the experimental teams working in doped thin films and in magnetic semiconductors [5], [98], [3], [99], [100], [6], [45], [4].

Several experimental attempts to engineer the atom-by-atom magnetic exchange interactions have been made [3], [2], and some of them quite successful such as the engineered dimer of Cobalt atoms [10] and the design of nanomagnets with different architectures tuning the exchange interaction via RKKY [2]. Theoretically, the study of the spin-spin interactions has been study from the perspective of the Kadanoff-Baym formalism [101], from the side of the *Keldysh Green's functions* what is known as Non-equilibrium magnetic exchange interactions, and in systems that resemble the dimerization of, for instance, Cobalt atoms adsorbed on Copper surfaces [10], trimmers of spin exhibiting richer ordering phenomena such as spin frustration , among many other interesting systems of relevance at the stake of tailoring new nanomagnets with novel magnetic and thermal properties.

Within the current chapter, I will give a brief overview of the emergence of the spin-spin interactions at the atomic level, focusing on the isotropic Heisenberg exchange interaction, moving forward towards the RKKY interaction, deriving a useful expression for the effective exchange to then, formulate a theory in the grounds of effective spin action and spin Hamiltonians that will lead to the Non-equilibrium expressions for the isotropic Heisenberg exchange interaction, symmetric like Ising interaction and anti-symmetric like Dzyaloshinskii-Moriya interaction. To conclude, I will provide a short, but substantial overview of the application of the Non-equilibrium magnetic interaction formalism in single molecule magnet spin dynamics, which will be later discussed in the chapter about contributions.

5.2 Coulomb and Exchange Interaction.

To understand the logic behind the model proposed at the end of the chapter, besides getting a clear picture of how to treat vibrational effects, it is of fundamental importance to understand the effects of the Coulomb interaction in magnetism in general, hence, derive that part of this interactions that deals with the exchange of single particle states among the electrons interacting. This part of the Coulomb interaction playing a vital role in magnetism is known as the exchange interaction, and it has many different flavors depending on the degrees of freedom involved, as well as the nature of the kinematics of the electrons, that is, whether they are stationary or itinerant [17].

In quantum mechanics the exchange interaction between two electrons reads:

$$\mathcal{H}_{Coul} = \int d^3r_1 d^3r_2 \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|} |\psi(r_1)|^2 |\psi(r_2)|^2. \qquad (5.1)$$

When considering a many-body system, one rather expresses the above expression in terms of the electron densities $n(r_1)$ and $n(r_2)$ (classically):

$$\mathcal{H}_{Coul}^{(cl)} = \frac{1}{2} \int d^3r_1 d^3r_2 \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|} n(r_1)n(r_2). \qquad (5.2)$$

When extending the above expression to the quantum mechanical case, one uses the numer density operator $n(r_r, s_z)$, which can be constructed using the electron field operators $\psi(r, s_z)$, where s_z is the spin coordinate. Therefore, the number density operator reads $n(r_r, s_z) = \psi^\dagger(r, s_z)\psi(r, s_z)$, and hence, the quantum mechanical Coulomb interaction reads:

$$\mathcal{H}_{Coul}^{(qm)} = \frac{1}{2} \sum_{s_{z_1}, s_{z_2}} \int d^3r_1 d^3r_2 \frac{e^2\psi^\dagger(r_1, s_{z_1})\psi(r_1, s_{z_1})\psi^\dagger(r_2, s_{z_2})\psi(r_2, s_{z_2})}{4\pi\epsilon_0|r_1 - r_2|}.$$

$$(5.3)$$

For the case of localized electrons, the quantum field operators are replaced with superpositions of Wannier localized states, where the expansion coefficients are the corresponding annihilation/creation operators of the Wannier state, to look like:

$$\psi^\dagger(r, s_z) = \sum_{j\sigma} \Phi(r - R_j)\chi_\sigma(s_z)c_{j\sigma},$$

where $\Phi(r - R_j)$ is the localized Wannier orbital around R_j, $\chi_\sigma(s_z)$ is the spin wave function and $c_{j\sigma}$. By using the above defined field operator in expression 5.3, the quantum mechanical Coulomb interaction reads:

$$\mathcal{H}_{Coul}^{(qm)} = \frac{1}{2} \sum_{\sigma\sigma'} \sum_{ij} U_{ij} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{j\sigma'} c_{i\sigma} - \frac{1}{2} \sum_{\sigma\sigma'} \sum_{ij} J_{ij} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{j\sigma} c_{i\sigma'}, \qquad (5.4)$$

where the first term is known as the direct Coulomb interaction and the second term is known as the direct exchange interaction, and the latter one is a consequence of the quantum mechanical version of the Coulomb interaction, and the main responsible for the phenomenon of magnetism in materials, hence from the classical point of view, magnetism in matter can not be predicted (Bohr-Van Leeuwen theorem). In equation 5.4, the terms U_{ij} and J_{ij} are known as the Direct Coulomb parameter and the exchange parameter respectively, and they are given by:

$$U_{ij} = \int d^3r_1 d^3r_2 \frac{e^2 \Phi^*(r_1 - R_i)\Phi(r_1 - R_i)\Phi^*(r_2 - R_j)\Phi(r - R_j)}{4\pi\epsilon_0 |r_1 - r_2|}, \quad (5.5)$$

$$J_{ij} = \int d^3r_1 d^3r_2 \frac{e^2 \Phi^*(r_1 - R_i)\Phi(r_1 - R_j)\Phi^*(r_2 - R_i)\Phi(r - R_j)}{4\pi\epsilon_0 |r_1 - r_2|}. \quad (5.6)$$

Often, it is useful to express the Coulomb-exchange interaction in terms of spin operators to make clear the effect of this interaction on the magnetism of the system being studied. Consider the spin operators s_j^+, s_j^- and $s_j^{\tilde{z}}$ such that:

$$s_j^+ = \hbar c_{j\uparrow}^\dagger c_{j\downarrow}, \quad s_j^- = \hbar c_{j\downarrow}^\dagger c_{j\uparrow}, \quad s_j^{\tilde{z}} = \frac{\hbar}{2}\left(c_{j\uparrow}^\dagger c_{j\uparrow} - c_{j\downarrow}^\dagger c_{j\downarrow}\right), \quad (5.7)$$

the quantum mechanical Coulomb interaction finally reads:

$$\mathcal{H}_{Coul}^{(qm)} = \frac{1}{2}\sum_{\sigma\sigma'}\sum_{ij}\left(U_{ij} - \frac{1}{2}J_{ij}\right)c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{j\sigma'} c_{i\sigma}$$

$$- \frac{1}{2\hbar^2}\sum_{ij,i\neq j} J_{ij}\left(s_i^+ s_j^- + s_i^- s_+^- + 2s_i^{\tilde{z}} s_j^{\tilde{z}}\right), \quad (5.8)$$

and by acknowledging that $s_i^+ s_j^- + s_i^- s_-^- = 2\left(s_i^x s_j^x + s_i^y s_j^y\right)$, then the second term of expression 5.8 becomes the Heisenberg Hamiltonian for exchange interaction and is given by:

$$\mathcal{H}_H = -\frac{1}{2\hbar^2}\sum_{ij,i\neq j} J_{ij}\left(s_i^+ s_j^- + s_i^- s_+^- + 2s_i^{\tilde{z}} s_j^{\tilde{z}}\right) = -\frac{1}{\hbar^2}\sum_{ij,i\neq j} J_{ij} s_i \cdot s_j. \quad (5.9)$$

For the case in which only nearest neighbors are considered ($J_{ij} = \frac{J}{2}$), the Heisenberg Hamiltonian reads:

$$\mathcal{H}_H = -\frac{J}{2\hbar^2}\sum_{ij,i\neq j} s_i \cdot s_j. \quad (5.10)$$

The above interaction requires direct influence between spins s_i and s_j, though in this document I am more interested in motivate how indirect interaction between spins, that is, localized spins interacting through conduction electrons, can as well give rise to an effective spin-spin interaction like

the Heisenberg interaction depending on the band structure of the background electrons that serve as intermediary between the spins. Following, I will motivate how can this be done in a free electron gas and then extend this philosophy for the case of non-thermal systems with the aid of the coherent state path integral.

5.3 What is and How to use the Lindhard Function?

The Lindhard function $\mathcal{L}(q)$ appears in diverse problems in condensed matter physics ranging from the random phase approximation (RPA) to effective exchange interactions as exposed by Kasuda, Kittel and Ruderman, and Yosida. The Lindhard function $\mathcal{L}(q)$ is defined as [74], [17]:

$$\mathcal{L}(q) = \frac{1}{g(\epsilon_F)} \int \frac{d\mathbf{k}}{4\pi^3} \frac{f(\epsilon_k) - f(\epsilon_{k+q})}{\epsilon_{k+q} - \epsilon_k}, \tag{5.11}$$

where $g(\epsilon_F)$ is the density of states, and $f(\epsilon_k)$ is the Fermi function. Expression 5.11 can be re-express as follows:

$$\mathcal{L}(q) = \frac{1}{g(\epsilon_F)} \int \frac{d\mathbf{k}}{4\pi^3} f(\epsilon_k) \left[\frac{1}{\epsilon_{k+q} - \epsilon_k} - \frac{1}{\epsilon_k - \epsilon_{k-q}} \right].$$

$$= \frac{1}{g(\epsilon_F)} \int \frac{d\mathbf{k}}{4\pi^3} f(\epsilon_k) \left[\frac{1}{\frac{\hbar^2 kq}{m}\left(\cos\theta + \frac{q}{2k}\right)} - \frac{1}{\frac{\hbar^2 kq}{m}\left(\cos\theta - \frac{q}{2k}\right)} \right].$$

The above expression needs further elaboration, in order to achieve a suitable form to analyze the low temperature behavior, that can be done in few lines with obvious steps in between:

$$\mathcal{L}(q) = \frac{1}{g(\epsilon_F)} \int \frac{d\mathbf{k}}{4\pi^3} f(\epsilon_k) \left[\frac{1}{\frac{\hbar^2 kq}{m}\left(\cos\theta + \frac{q}{2k}\right)} - \frac{1}{\frac{\hbar^2 kq}{m}\left(\cos\theta - \frac{q}{2k}\right)} \right]$$

$$= \frac{m}{g(\epsilon_F)\hbar^2 q} \int_0^{+\infty} \frac{kdk}{2\pi^2} \int_0^{\pi} \sin\theta d\theta f(\epsilon_k) \left[\frac{1}{\cos\theta + \frac{q}{2k}} - \frac{1}{\cos\theta - \frac{q}{2k}} \right]. \tag{5.12}$$

Expression 5.12 when analized Around $T = 0$, $f(\epsilon_k) \approx 1$ for $\epsilon_k < \epsilon_F$; for $\epsilon_k = \epsilon_F$, $f(\epsilon_k) \approx \frac{1}{2}$; and for $\epsilon_k > \epsilon_F$, $f(\epsilon_k) \approx 0$. Now, for $\epsilon_k < \epsilon_F$, $\mathcal{L}(q)$ given by expression 5.12 can be written in the following way:

$$\mathcal{L}(q) = \frac{m}{g(\epsilon_F)\hbar^2 q} \int_0^{k_F} \frac{kdk}{2\pi^2} \int_0^{\pi} \sin\theta d\theta \left[\frac{1}{\cos\theta + \frac{q}{2k}} - \frac{1}{\cos\theta - \frac{q}{2k}} \right]. \tag{5.13}$$

Moreover, I can make the following substitution in expression 5.13: $\lambda = \cos\theta$, giving $d\lambda = -\sin\theta d\theta$, being $\lambda = -1$ when $\theta = \pi$, and being $\lambda = 1$ when

$\theta = 0$. By replacing the latter substitution back in expression 5.13, $\mathcal{L}(q)$ can be further evaluated as follows:

$$\mathcal{L}(q) = -\frac{m}{g(\epsilon_F)\hbar^2 q} \int_0^{k_F} \frac{kdk}{2\pi^2} \int_1^{-1} d\lambda \left[\frac{1}{\lambda + \frac{q}{2k}} - \frac{1}{\lambda - \frac{q}{2k}} \right],$$

$$= \frac{m}{2\pi^2 g(\epsilon_F)\hbar^2 q} \int_0^{k_F} kdk \left[\int_{-1}^1 \frac{d\lambda}{\lambda + \frac{q}{2k}} - \int_{-1}^1 \frac{d\lambda}{\lambda - \frac{q}{2k}} \right],$$

$$= \frac{m}{2\pi^2 g(\epsilon_F)\hbar^2 q} \int_0^{k_F} kdk \left[Ln \left| \frac{\frac{q}{2k}+1}{\frac{q}{2k}-1} \right| + Ln \left| \frac{-\left(1+\frac{q}{2k}\right)}{1-\frac{q}{2k}} \right| \right],$$

$$= \frac{m}{\pi^2 g(\epsilon_F)\hbar^2 q} \int_0^{k_F} kdk Ln \left| \frac{\frac{q}{2k}+1}{\frac{q}{2k}-1} \right|,$$

and using the density of states for the free electron gas $g(\epsilon_F)$ given in references [kittel,ashcroft], I finally write $\mathcal{L}(q)$ compactly as follows:

$$\mathcal{L}(q) = \frac{2m\epsilon_F}{3n\pi^2\hbar^2 q} \int_0^{k_F} kLn \left| \frac{k + \frac{q}{2}}{k - \frac{q}{2}} \right| dk. \tag{5.14}$$

The integral in the above expression can be solved using integration by parts, to give [fuxiang, fuxiang, mahan]: finally reads:

$$\mathcal{L}(q) = \frac{2m\epsilon_F}{3n\pi^2\hbar^2 q} \left[\frac{k_F^2 - \frac{q^2}{4}}{2} Ln \left| \frac{k_F + \frac{q}{2}}{k_F - \frac{q}{2}} \right| + \frac{qk_F}{2} \right]. \tag{5.15}$$

To further simplify the above expression, one can replace $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$ and $k_F = \left(3\pi^2 n\right)^{\frac{1}{3}}$, into expression 5.15 to give the following after few algebraic steps:

$$\mathcal{L}(q) = \frac{1}{2} + \frac{1 - \frac{q^2}{4k_F^2}}{4\left(q/2k_F\right)} Ln \left| \frac{1 + \frac{q}{2k_F}}{1 - \frac{q}{2k_F}} \right| = \frac{1}{2} + \frac{4k_F^2 - q^2}{8qk_F} Ln \left| \frac{2k_F + q}{2k_F - q} \right|. \tag{5.16}$$

Often, in references such as [17], [74] use the following variable in expression 5.16, $x = \frac{q}{2k_F}$, which gives the following general expression for the Lindhard function at zero temperature:

$$\mathcal{L}(x) = \frac{1}{2} + \frac{1 - x^2}{4x} Ln \left| \frac{1 + x}{1 - x} \right|, \tag{5.17}$$

contrary to what is seen in refs. by Kei Yosida [32] and Tadao Kasuya [31].

The Lindhard function appears often in the final expression for the effective

exchange interaction as in the RKKY formulation as seen in expression 5.36, result that becomes crucial when fitting experimental data to RKKY exchange couplings, when tailoring nanomagnets by engineering atom-by-atom interactions [1], [2].

5.4 RKKY: Context and Summary

Now, I will give a brief, but detailed summary on the RKKY (Ruderman-Kittel-Kasuda-Yosida) interaction, its basic assumptions, how the effective SD Hamiltonian is derived [32], [76], [31], [25], [26], and from this, how the concept of effective exchange interaction arises (For a detailed discussion see ref. [17], and from a discussion on its consequences and broad range of applicability see ref. [74].). The RKKY theory, has some basic ingredients summarized as follows [96]:

1. Some basic facts considered in the process of deriving an effective exchange interaction include:
   a) Magnetic Impurities in metals change significantly its properties [24], [22].
   b) The density of magnetic impurities is low such that there is no direct interaction among them [2].
   c) However, there is an effective interaction among the magnetic impurities mediated by the conduction electrons [26], [2], [72], [17].
2. Magnetic impurities whose moments are due to nuclear spins or inner d or f electron spins are considered [72].
3. The interaction between conduction electrons represented by the field operator $\psi(r, s_z)$ with spin operator s and a magnetic impurity with spin operator $S(r)$, can be described by the s-d exchange Hamiltonian given by [25], [26], [32], [76]:

$$\mathcal{H}_{SD} = \frac{J}{\hbar^2} \sum_{s_z} \int dr\, S(r) \cdot \psi^\dagger(r, s_z) s \psi^\dagger(r, s_z) \tag{5.18}$$

To derive a Heisenberg-like exchange interaction from Hamiltonian in expression 5.18, some work through spin wave functions must be done, which will be illustrated in the following section.

5.4.1 Working with Spin Wave Functions

5.4.1.1 *Orthogonality of Spin Wave Functions*

Keeping always in mid that a spin in an arbitrary direction (ϕ, θ) is given by:

$$| \uparrow_{\theta,\phi} \rangle = \cos\left(\frac{\theta}{2}\right) | \uparrow \rangle + \sin\left(\frac{\theta}{2}\right) e^{i\phi} | \downarrow \rangle \tag{5.19}$$

From now on, the goal will be to calculate terms of the form:

$$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s\chi_\beta(s_z),$$

with $s = \left(s_x, s_y, s_z\right)$. Therefore the above sumation decomposes as follows:

$$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s\chi_\beta(s_z) =$$

$$\sum_{\alpha\beta}\sum_{s_z}\left[\chi_\alpha^*(s_z)s_x\chi_\beta(s_z),\chi_\alpha^*(s_z)s_y\chi_\beta(s_z),\chi_\alpha^*(s_z)s_z\chi_\beta(s_z)\right],$$

(5.20)

which leaves 3 terms to evaluate:
$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_x\chi_\beta(s_z)$, $\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_y\chi_\beta(s_z)$,
and $\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_z\chi_\beta(s_z)$, resulting in the following expressions:

$$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_z\chi_\beta(s_z) = \sum_{\alpha\beta}\frac{\hbar}{2}\sigma_{\alpha\beta}^{(z)}. \tag{5.21}$$

$$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_x\chi_\beta(s_z) = \sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)\left(\frac{s_+ + s_-}{2}\right)\chi_\beta(s_z)$$

$$= \frac{1}{2}\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_+\chi_\beta(s_z) + \frac{1}{2}\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_-\chi_\beta(s_z)$$

$$= \frac{\hbar}{2}\sum_{\alpha\beta}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\sum_{s_z}\chi_\alpha^*(s_z)\chi_\beta(s_z)$$

$$+ \frac{\hbar}{2}\sum_{\alpha\beta}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\sum_{s_z}\chi_\alpha^*(s_z)\chi_\beta(s_z) = \frac{\hbar}{2}\sum_{\alpha\beta}\sigma_{\alpha\beta}^{(x)}.$$

(5.22)

$$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s_y\chi_\beta(s_z) = \sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)\left(\frac{s_+ - s_-}{2i}\right)\chi_\beta(s_z)$$

$$= \frac{\hbar}{2}\sum_{\alpha\beta}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\sum_{s_z}\chi_\alpha^*(s_z)\chi_\beta(s_z) = \frac{\hbar}{2}\sum_{\alpha\beta}\sigma_{\alpha\beta}^{(y)}.$$

(5.23)

Now, I proceed by combining expressions 5.20, 5.21, 5.22 and 5.23, to produce the following result:

$$\sum_{\alpha\beta}\sum_{s_z}\chi_\alpha^*(s_z)s\chi_\beta(s_z) = \frac{\hbar}{2}\sum_{\alpha\beta}\sigma_{\alpha\beta} = \frac{\hbar}{2}\sum_{\alpha\beta}\left(\sigma_{\alpha\beta}^{(x)},\sigma_{\alpha\beta}^{(y)},\sigma_{\alpha\beta}^{(z)}\right). \tag{5.24}$$

5.4.1.2 *Scalar Product with sigma Matrices.*

Consider a spin operator of an impurity $S = \left(S_x, S_y, S_z \right)$, and the term $\sum_{\alpha\beta} S(r) \cdot \sigma_{\alpha\beta} c^\dagger_{k\alpha} c_{k'\beta}$. The latter, acquires a structure after the following elaboration:

$$
\sum_{\alpha\beta} S(r) \cdot \sigma_{\alpha\beta} c^\dagger_{k\alpha} c_{k'\beta} = \sum_{\alpha\beta} \left(S_x(r), S_y(r), S_z(r) \right) \cdot \left(\sigma_{\alpha\beta,x}, \sigma_{\alpha\beta,y}, \sigma_{\alpha\beta,z} \right) c^\dagger_{k\alpha} c_{k'\beta}
$$

$$
= \sum_{\alpha\beta} \left(S_x(r)\sigma_{\alpha\beta,x} + S_y(r)\sigma_{\alpha\beta,y} + S_z(r)\sigma_{\alpha\beta,z} \right) c^\dagger_{k\alpha} c_{k'\beta}
$$

$$
= \sum_{\alpha\beta} \left(\left(\frac{S_+(r) + S_-(r)}{2} \right) \sigma_{\alpha\beta,x} + \left(\frac{S_+(r) - S_-(r)}{2i} \right) \sigma_{\alpha\beta,y} + S_z(r)\sigma_{\alpha\beta,z} \right) c^\dagger_{k\alpha} c_{k'\beta},
$$

$$
= \sum_{\alpha\beta} \left[\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} S_+(r) + \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} S_-(r) + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} S_z(r) \right] c^\dagger_{k\alpha} c_{k'\beta}.
$$

The last line of the elaboration made above, can be simplified by noting that:

$$
\sum_{\alpha\beta} \begin{pmatrix} \uparrow\uparrow & \uparrow\downarrow \\ \downarrow\uparrow & \downarrow\downarrow \end{pmatrix}_{\alpha\beta} c^\dagger_{k\alpha} c_{k'\beta} =
$$

$$
(\uparrow\uparrow) c^\dagger_{k\uparrow} c_{k'\uparrow} + (\uparrow\downarrow) c^\dagger_{k\uparrow} c_{k'\downarrow} + (\downarrow\uparrow) c^\dagger_{k\downarrow} c_{k'\uparrow} + (\downarrow\downarrow) c^\dagger_{k\downarrow} c_{k'\downarrow}. \quad (5.25)
$$

which leads to the following result:

$$
\sum_{\alpha\beta} S(r) \cdot \sigma_{\alpha\beta} c^\dagger_{k\alpha} c_{k'\beta}
$$

$$
= S^+(r) c^\dagger_{k\downarrow} c_{k'\uparrow} + S^-(r) c^\dagger_{k\uparrow} c_{k'\downarrow} + S_z(r) \left(c^\dagger_{k\uparrow} c_{k'\uparrow} - c^\dagger_{k\downarrow} c_{k'\downarrow} \right).
$$

$$
(5.26)
$$

5.4.2 Deriving the Effective Interaction

5.4.2.1 *Kondo-Like Hamiltonian*

The Hamiltonian in expression 5.18, requires the field operator $\psi(r, s_z)$, which can be expanded in plane wave basis as follows:

$$
\psi(r, s_z) = \sum_{k\alpha} \frac{e^{ik\cdot r}}{\sqrt{V}} \chi_\alpha(s_z) c_{k\alpha}, \quad\quad (5.27)
$$

therefore, the term $\psi^\dagger(r, s_z) s \psi^\dagger(r, s_z)$ in expression 5.18 can be expanded like this:

$$\psi^\dagger(r, s_z) s \psi^\dagger(r, s_z) = \left(\sum_{k\alpha} \frac{e^{ik\cdot r}}{\sqrt{V}} \chi_\alpha^*(s_z) c_{k\alpha}^\dagger \right) s \left(\sum_{k\beta} \frac{e^{-ik'\cdot r}}{\sqrt{V}} \chi_\beta(s_z) c_{k\beta} \right),$$

$$= \sum_{kk'} \sum_{\alpha\beta} \frac{1}{V} e^{-i(k-k')\cdot r} \chi_\alpha^*(s_z) s \chi_\beta(s_z) c_{k\alpha}^\dagger c_{k\beta}. \qquad (5.28)$$

Expression 5.28 can be used to derive then, the Hamiltonian H_{sd} from expression 5.18:

$$\mathcal{H}_{SD} = \frac{J}{\hbar^2} \sum_{kk'} \sum_{\alpha\beta} \sum_{s_z} \int dr\, S(r) \cdot \frac{1}{V} e^{-i(k-k')\cdot r} \chi_\alpha^*(s_z) s \chi_\beta(s_z) c_{k\alpha}^\dagger c_{k\beta},$$

$$= \frac{J}{2V\hbar} \sum_{kk'} \sum_{\alpha\beta} \int dr\, e^{-i(k-k')\cdot r} S(r) \cdot \sigma_{\alpha\beta} c_{k\alpha}^\dagger c_{k\beta},$$

to finally arrive at:

$$\mathcal{H}_{SD} = \frac{J}{2V\hbar} \sum_{kk'} \int dr\, e^{-i(k-k')\cdot r}$$

$$\times \left[S^+(r) c_{k\downarrow}^\dagger c_{k'\uparrow} + S^-(r) c_{k\uparrow}^\dagger c_{k'\downarrow} + S_z(r) \left(c_{k\uparrow}^\dagger c_{k'\uparrow} - c_{k\downarrow}^\dagger c_{k'\downarrow} \right) \right].$$
$$(5.29)$$

Note that to derive the above expression I have used equation 5.26.

5.4.2.2 The Effective Interaction
To derive an effective Hamiltonian, denoted by $\mathcal{H}_{eff}$, the following expression is used:

$$\mathcal{H}_{eff} = \sum_{k\alpha} \langle k\alpha | \mathcal{H}_{SD} | k\alpha \rangle n_f(\epsilon_k). \qquad (5.30)$$

Time-independent perturbation theory becomes essential at the moment to express the perturbed wave function ψ_n in the following way:

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} = \psi_n^{(0)} + \sum_{m\neq n} \frac{\langle \psi_m^{(0)} | \mathcal{H}_{SD} | \psi_n^{(0)} \rangle}{\epsilon_n - \epsilon_m} \psi_m^{(0)}.$$

From the above equality, it is straight-forward to see that the perturbed state $|k\alpha\rangle$, to first order can be written as follows:

$$|k\alpha\rangle = |k\alpha, 0\rangle + \sum_{k'\neq k, \beta} \frac{\langle k'\beta, 0 | \mathcal{H}_{SD} | k\alpha, 0 \rangle}{\epsilon_k - \epsilon_{k'}} \left(1 - n_f(\epsilon_{k'}) \right) |k'\beta, 0\rangle, \qquad (5.31)$$

where the factor $\left(1 - n_f(\epsilon_{k'})\right)$ guarantees that the state $|k'\beta,0\rangle$ is unoccupied. From expression 5.31, the term $\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle$ can be computed as follows:

$$\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle = \left(\langle k\alpha,0| + \sum_{k'\neq k,\beta} \langle k\beta,0| \frac{\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} \left(1 - n_f(\epsilon_{k'})\right)\right)$$

$$\times \mathcal{H}_{SD} \left(|k\alpha,0\rangle + \sum_{k''\neq k,\beta} \frac{\langle k''\beta',0|\mathcal{H}_{SD}|k\alpha,0\rangle}{\epsilon_k - \epsilon_{k''}} \left(1 - n_f(\epsilon_{k''})\right)|k''\beta',0\rangle\right).$$

By performing the tedious multiplications shown above, the expectation value $\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle$ looks now like:

$$\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle = \sum_{k'\neq k,\beta} \langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle \frac{\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} \left(1 - n_f(\epsilon_{k'})\right)$$

$$+ \sum_{k''\neq k,\beta'} \frac{\langle k''\beta',0|\mathcal{H}_{SD}|k\alpha,0\rangle}{\epsilon_k - \epsilon_{k''}} \left(1 - n_f(\epsilon_{k''})\right) \langle k\alpha,0|\mathcal{H}_{SD}|k''\beta',0\rangle$$

$$\sum_{k'\neq k,\beta} \sum_{k''\neq k,\beta'} \langle k'\beta,0|\mathcal{H}_{SD}|k''\beta',0\rangle$$

$$\times \frac{\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} \frac{\langle k''\beta',0|\mathcal{H}_{SD}|k\alpha,0\rangle}{\epsilon_k - \epsilon_{k''}}$$

$$\times \left(1 - n_f(\epsilon_{k'})\right)\left(1 - n_f(\epsilon_{k''})\right),$$

and by switching summation indexes ($k'' \to k'$) in the second term of the above expression, and noting that I have used the fact that: $\langle k\alpha,0|\mathcal{H}_{SD}|k\alpha,0\rangle \propto \langle k\alpha,0||k\beta,0\rangle = 0$ for $\alpha \neq \beta$, the above expression reduces to:

$$\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle = 2 \sum_{k'\neq k,\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} \left(1 - n_f(\epsilon_{k'})\right)$$

$$+ \sum_{k'\neq k,\beta} \sum_{k''\neq k,\beta'} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k''\beta',0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle\langle k''\beta',0|\mathcal{H}_{SD}|k\alpha,0\rangle}{(\epsilon_k - \epsilon_{k'})(\epsilon_k - \epsilon_{k''})}$$

$$\times \left(1 - n_f(\epsilon_{k'})\right)\left(1 - n_f(\epsilon_{k''})\right).$$

Do acknowledge that the second term vanishes in the above calculation, therefore, the expectation value $\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle$ gives:

$$\langle k\alpha|\mathcal{H}_{SD}|k\alpha\rangle = 2 \sum_{k'\neq k,\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} \left(1 - n_f(\epsilon_{k'})\right).$$

$$(5.32)$$

From the replacement of expression 5.32 into eq. 5.30, the effective Hamiltonian $\mathcal{H}_{eff}$ defined earlier in the latter is found to give:

$$\mathcal{H}_{eff} = 2k, \sum_{k'\neq k,\alpha\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} n_f(\epsilon_k)\left(1 - n_f(\epsilon_{k'})\right).$$

(5.33)

Moreover, it is just intuitive that, the effective interaction should depend somehow in the difference between the occupations of the state $|k\alpha\rangle$ and the state $|k'\beta\rangle$, therefore one could perform the following trick on expression 5.33: Separate the sum (the factor of 2 indicates two summations) in two, the exchange the indexes k and k', and α and β in the second sum, and gather the terms, as is shown next:

$$\mathcal{H}_{eff} = 2 \sum_{kk'\neq k,\alpha\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} n_f(\epsilon_k)\left(1 - n_f(\epsilon_{k'})\right)$$

$$= \sum_{kk'\neq k,\alpha\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} n_f(\epsilon_k)\left(1 - n_f(\epsilon_{k'})\right)$$

$$+ \sum_{kk'\neq k,\alpha\beta} \frac{\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle}{\epsilon_{k'} - \epsilon_k} n_f(\epsilon_{k'})\left(1 - n_f(\epsilon_k)\right)$$

$$= \sum_{kk'\neq k,\alpha\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}}$$

$$\times \left(n_f(\epsilon_k)\left(1 - n_f(\epsilon_{k'})\right) - n_f(\epsilon_{k'})\left(1 - n_f(\epsilon_k)\right)\right),$$

which finally gives:

$$\mathcal{H}_{eff} = \sum_{kk'\neq k,\alpha\beta} \frac{\langle k'\beta,0|\mathcal{H}_{SD}|k\alpha,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle}{\epsilon_k - \epsilon_{k'}} \left(n_f(\epsilon_k) - n_f(\epsilon_{k'})\right)$$

$$= \sum_{kk'\neq k,\alpha\beta} \frac{\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle\langle k\alpha,0|\mathcal{H}_{SD}|k'\beta,0\rangle^*}{\epsilon_k - \epsilon_{k'}} \left(n_f(\epsilon_k) - n_f(\epsilon_{k'})\right).$$

(5.34)

By replacing expression 5.30 in expression 5.34 (do note that $\mathcal{H}_{SD}$ appears twice in expression 5.34, hence one is evaluated at r and the other at r'), $\mathcal{H}_{eff}$ gives:

$$\mathcal{H}_{eff} = -\frac{1}{2\hbar^2} \int \int dr dr' \mathcal{J}_{eff}(r,r')S(r)\cdot S(r'),$$

(5.35)

where the effective indirect exchange interaction $\mathcal{J}_{eff}(r,r')$, can be obtained by comparing the above expression with the one defining the Heisen-

berg exchange interaction (expression 5.10) 'which is given by:

$$\mathcal{J}_{eff}(\boldsymbol{r},\boldsymbol{r}') = -\frac{J^2}{V^2} \sum_{\boldsymbol{k}\boldsymbol{k}'\neq\boldsymbol{k}} \frac{\left(n_f(\epsilon_{\boldsymbol{k}})-n_f(\epsilon_{\boldsymbol{k}'})\right)e^{-i(\boldsymbol{k}-\boldsymbol{k}')\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{\epsilon_{\boldsymbol{k}}-\epsilon'_{\boldsymbol{k}}}. \qquad (5.36)$$

The above expression demonstrates the possibility to obtained an effective indirect exchange interaction between impurities at $\boldsymbol{r}$ and at $\boldsymbol{r}'$, interacting through conduction electrons. As noted from [17], expression 5.36 can be re-express in terms of the Lindhard function defined through expression 5.11, this, as it is shown below:

$$\begin{aligned}
\mathcal{J}_{eff}(\boldsymbol{r}) &= -\frac{J^2}{V^2} \sum_{\boldsymbol{k}\boldsymbol{k}'\neq\boldsymbol{k}} \frac{\left(n_f(\epsilon_{\boldsymbol{k}})-n_f(\epsilon_{\boldsymbol{k}'})\right)e^{-i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}}{\epsilon_{\boldsymbol{k}}-\epsilon'_{\boldsymbol{k}}}, \\
&= -\frac{V^2 m k_F J^2}{8\pi^2\hbar^2} \sum_{\boldsymbol{q}} \mathcal{L}\left(\frac{q}{2k_F}\right)e^{i\boldsymbol{q}\cdot\boldsymbol{r}}, \\
&= -\frac{V^2 m k_F J^2}{2i(2\pi)^4\hbar^2 r} \int_0^{+\infty} q\mathcal{L}\left(\frac{q}{2k_F}\right)\left(e^{iqr}-e^{iqr}\right)dq, \\
&= -\frac{V^2 m k_F^3 J^2}{8i\pi^4\hbar^2 r} \int_{-\infty}^{+\infty} x\mathcal{L}(x)e^{2ik_Frx}dx, \qquad (5.37)
\end{aligned}$$

and by performing the last integral in the above expression as done in ref. [17], $\mathcal{J}_{eff}(\boldsymbol{r})$ finally reads:

$$\mathcal{J}_{eff}(\boldsymbol{r}) = -\frac{9^2 J^2}{8E_F} \frac{[\sin(2k_Fr)-(2k_Fr)\cos(2k_Fr)]}{(2k_Fr)^4}. \qquad (5.38)$$

For an illustration of the solution given by Eq. 5.38 see figure 5.1. Here, it is shown that the RKKY interaction decays as the distance between impurities increases, observed for ad-atoms in [2].
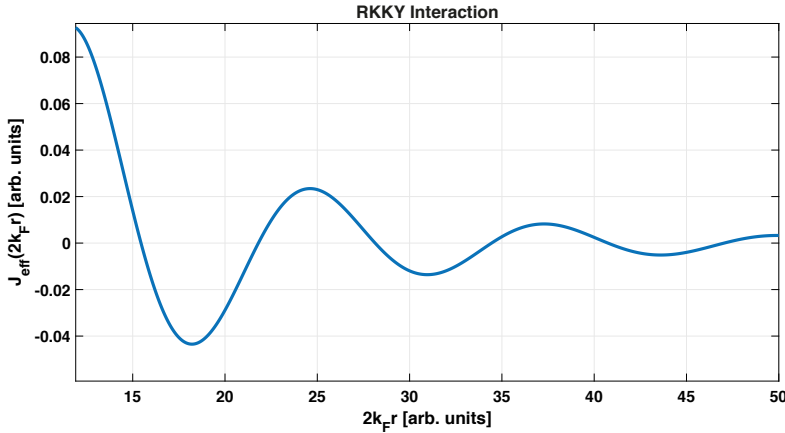
Figure 5.1. Zero-Temperature Solution for the RKKY Interaction.

5.4.3 Final Comments on the RKKY: Relevance for this Thesis

The RKKY interaction derives from the assumption of magnetic impurities in metals interacting through conduction electrons. These impurities posses an eminent localized magnetic moment, and as a consequence of their low concentration in the metal, this interaction is set to be purely mediated by the electronic bath. In this section, I attempted to derive with the greatest level of detail the RKKY exchange formula as described in texts such as [74] and [17], built on the work by Yosida [32], [76] and Kasuya [31]. This to show that from a phenomenological Hamiltonian, by imposing a basis representation on the electron wave-functions, and averaging over the electronic degrees of freedom, and effective Hamiltonian for the spin-spin interaction can be obtained. In the following section, I will lead you through a similar procedure to an equivalent formalism for the effective exchange among magnetic impurities in metals, with the differentiating factor, that, in such a case the electron bath is driven by an external field, be it electric fields or temperatures. Through the formalism that is yet to be explained, presented by Prof. Jonas Fransson in ref. [102], [68], with extensive application in single molecule spin dynamics and in voltage-induced magnetic switching [67], [103], I will attempt to convince the audience that the former is an extension to the RKKY interaction for the non-equilibrium case, by setting the following comparisons:

1. In the present section an effective Hamiltonian was derived from a phenomenological interaction, by averaging over the electronic degrees of freedom, and by comparison with the phenomenological Heisenberg Hamiltonian [21], the effective RKKY exchange was written in closed form.

2. In the next section, departing from the partition function of an electronic system in the presence of magnetic impurities, the electronic degrees of freedom are averaged out by integrating the electronic Grassman variables from a coherent state path integral, leaving an effective partition function with an associated effective classical action, only in terms of spin degrees of freedom emerging from the magnetic impurities. From this effective spin action, an effective Hamiltonian for the spin-spin interaction is derived, and by comparison with the phenomenological Heisenberg [21], Dzyaloshinskii-Moriya and Ising interactions [20], effective exchange interactions of these types are derived under the assumption of a non-equilibrium drive, as in the context of chapter 4. These expressions play a central role in the work presented in this thesis.

5.5 Non-Equilibrium Effective Magnetic Exchange Interactions From Coherent State Path Integrals

5.5.1 Path Integral Formulation

The quantum partition function describing a set of Fermionic and Bosonic degrees of freedom, can be written as a coherent state path integral in the Keldysh contour [68], [88], similarly to the one within the Matsubara formalism given by expression 4.48. For the case of relevance in this chapter, I will use the Keldysh Coherent State Path Integral to write the partition function as follows [104], [105], [106]:

$$\mathcal{Z} = \mathcal{Z}_0^{-1} \int \mathcal{D}\left(\psi,\overline{\psi}\right) e^{iS\left[\psi,\overline{\psi}\right]}, \tag{5.39}$$

where $\mathcal{Z}_0$ is the partition function of the system at the point where, whatever interactions are present in the partition function $\mathcal{Z}$, are absent. The Keldysh action here is given by:

$$S\left[\psi,\overline{\psi}\right] = \int_\gamma \int_\gamma dt dt' \overline{\psi}(t)\left(i\hbar\frac{\partial}{\partial t} - \mathcal{H}_0 - \mathcal{H}_I\right)\psi(t'). \tag{5.40}$$

The Fermionic field $\psi(t)$ is a spinor specified by the upper and lower Keldysh components $\psi(t) = (\psi_+(t), \psi_-(t))^T$, $\mathcal{H}_0$ is the non-interacting Hamiltonian and $\mathcal{H}_I$ is the Hamiltonian containing the effective boson-boson interaction.

The case of interest for the work presented here, the Hamiltonian $\mathcal{H}_I$, contains Bosonic degrees of freedom such as spins and possibly vibrational quanta. The Bosonic field operator $\eta(t)$ is constructed such that $\eta(t) = (\eta_1(t), \eta_2(t), \eta_3(t)) \in \mathcal{S}^2$. Therefore, the partition function considering the Bosonic degree of freedom can be written as [81], [86], [107]:

$$\mathcal{Z} = \mathcal{Z}_0^{-1} \int \int \mathcal{D}\eta \mathcal{D}\left(\psi,\overline{\psi}\right) e^{iS\left[\psi,\overline{\psi}\right]}. \tag{5.41}$$

Here, the integral over the Fermionic degrees of freedom can be performed from expression 5.41 in the following way:

$$
\begin{aligned}
\mathcal{Z} &= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \, Det \left|(-i)\left(i\hbar\frac{\partial}{\partial t} - \mathcal{H}_0 - \mathcal{H}_I\right)\right|, \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \, Det \left|(-i)\left(G^{-1} - \mathcal{H}_I\right)\right|, \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \, exp\left[Ln \, Det\left|(-i)\left(G^{-1} - \mathcal{H}_I\right)\right|\right], \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \, exp\left[Ln \int \mathcal{D}\left(\psi,\overline{\psi}\right) e^{-S_E\left[\overline{\psi},\psi,\eta\right]}\right], \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \, e^{-S_{eff}\left[\eta\right]}, \tag{5.42}
\end{aligned}
$$

from where the inverse of the non-interacting Green's function is given by $G^{-1} = i\hbar \frac{\partial}{\partial t} - \mathcal{H}_0$ (representing the electronic bath) and, the effective classical action $S_E[\bar{\psi}, \psi, \eta]$ and the resulting effective action $S_{eff}[\eta]$, are given by:

$$S_E[\bar{\psi}, \psi, \eta] = (-i)\left(G^{-1} - \mathcal{H}_I\right), \quad (5.43)$$

$$S_{eff}[\eta] = -Ln \int \mathcal{D}(\psi, \bar{\psi}) e^{-S_E[\bar{\psi}, \psi, \eta]} = -Ln \, Det \left|(-i)\left(G^{-1} - \mathcal{H}_I\right)\right|. \quad (5.44)$$

The effective action, can be further elaborated through the following important steps:

$$S_{eff}[\eta] = -Ln \, Det \left|(-i)\left(G^{-1} - \mathcal{H}_I\right)\right| = -Tr \, Ln \left|(-i)G^{-1}(1 - G\mathcal{H}_I)\right|,$$

$$= -Tr \, Ln \left|(-i)G^{-1}\right| - Tr \, Ln \left|(1 - G\mathcal{H}_I)\right|,$$

$$= -Tr \, Ln \left|(-i)G^{-1}\right| + Tr \sum_{n=1}^{+\infty} \frac{(G\mathcal{H}_I)^n}{n},$$

finally, $S_{eff}[\eta]$ reads:

$$S_{eff}[\eta] = -Tr \, Ln \left|(-i)G^{-1}\right| + Tr(G\mathcal{H}_I) + \frac{1}{2} Tr(G\mathcal{H}_I)(G\mathcal{H}_I) + \frac{1}{3} \dots . \quad (5.45)$$

For graphical details of expression 5.45, see figure 5.2.
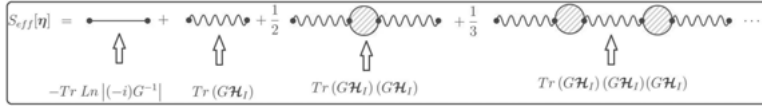
Figure 5.2. Feynman Diagram Representation of the Effective Action

For the present work, I am interested in investigating the product of interactions to lowest order, that is, $\frac{1}{2} Tr(G\mathcal{H}_I)(G\mathcal{H}_I)$, term that is labeled as $\delta S_{eff}[\eta]$:

$$\delta S_{eff}[\eta] = \frac{1}{2} Tr(G(t, \tau)\mathcal{H}_I(\tau))(G(\tau, t')\mathcal{H}_I(t')). \quad (5.46)$$

and it will be elaborated in the following section once $\mathcal{H}_I$ is specified.

5.5.2 Bare Spin Hamiltonian

$\mathcal{H}_I(\tau)$, namely the bare spin Hamiltonian, is given by:

$$\mathcal{H}_I(\tau) = \sum_m J_m \sigma \cdot s_m(t), \quad (5.47)$$

where J_m is the Coulomb integral as defined for the case of the Heisenberg exchange interaction, given by expression 5.6, and $s_m(t)$ is the spin operator at site m evaluated at time t. From expression 5.46 and definition given in expression 5.47, the following procedure is put forward:

$$
\begin{aligned}
\delta S_{eff}[\eta] &= \frac{1}{2} Tr\left(G(t,\tau)\mathcal{H}_I(\tau)\right)\left(G(\tau,t')\mathcal{H}_I(t')\right), \\
&= \frac{1}{2} Tr\left(G(t,\tau)\sum_m J_m \boldsymbol{\sigma}\cdot s_m(t)\right)\left(G(\tau,t')\sum_n J_n \boldsymbol{\sigma}\cdot s_n(t')\right), \\
&= \frac{1}{2}\sum_{m,n} J_m J_n Tr\left(s_m(t)\cdot G(t,\tau)\boldsymbol{\sigma} G(\tau,t')\boldsymbol{\sigma}\cdot s_n(t')\right),
\end{aligned}
$$

then by pre-multiplying with i and $(-i)$ and with e and $\frac{1}{e}$, $\delta S_{eff}[\eta]$ gives:

$$
\delta S_{eff}[\eta] = \frac{ie}{2}\int\int dt dt' \sum_{m,n} \frac{J_m J_n}{e}(-i)\boldsymbol{sp}\left(s_m(t)\cdot G(t,\tau)\boldsymbol{\sigma} G(\tau,t')\boldsymbol{\sigma}\cdot s_n(t')\right).
$$

(5.48)

The above expression coincides with the one reported by Fransson *et. al* in [102]. Henceforth the expression for the effective interaction Hamiltonian can be directly cast from expression 5.48:

$$
\mathcal{H}_{eff} = \frac{ie}{2} J_m J_n(-i)\boldsymbol{sp}\left(s_m(t)\cdot G(t,\tau)\boldsymbol{\sigma} G(\tau,t')\boldsymbol{\sigma}\cdot s_n(t')\right).
$$

(5.49)

Herein, I will invoke formulas from vector analysis [16] and the charge and spin decomposition for the Green's function given by $G = G_0 + G_1 \cdot \boldsymbol{\sigma}$, to simplify furthermore, the effective spin Hamiltonian, by introducing the comfort variable $\mathcal{K}_{eff} = (G_0 + G_1 \cdot \boldsymbol{\sigma})(\boldsymbol{\sigma}\cdot s_m)(G_0 + G_1 \cdot \boldsymbol{\sigma})(\boldsymbol{\sigma}\cdot s_n)$ and following the next steps through:

$$
\begin{aligned}
\mathcal{K}_{eff} &= (G_0 + G_1 \cdot \boldsymbol{\sigma})(\boldsymbol{\sigma}\cdot s_m)(G_0 + G_1 \cdot \boldsymbol{\sigma})(\boldsymbol{\sigma}\cdot s_n), \\
&= [G_0(\boldsymbol{\sigma}\cdot s_m)+(G_1 \cdot \boldsymbol{\sigma})(s_m \cdot \boldsymbol{\sigma})][G_0(\boldsymbol{\sigma}\cdot s_n)+(G_1 \cdot \boldsymbol{\sigma})(s_n \cdot \boldsymbol{\sigma})], \\
&= [G_0(\boldsymbol{\sigma}\cdot s_m)+G_1 \cdot s_m + i(G_1 \times s_m)\cdot \boldsymbol{\sigma}] \\
&\qquad \times [G_0(\boldsymbol{\sigma}\cdot s_n)+G_1 \cdot s_n + i(G_1 \times s_n)\cdot \boldsymbol{\sigma}], \\
&= \textcolor{red}{G_0(\boldsymbol{\sigma}\cdot s_m)G_0(\boldsymbol{\sigma}\cdot s_n)}+\textcolor{red}{(G_1 \cdot s_m)(G_1 \cdot s_n)} \\
&\qquad\qquad \textcolor{red}{-[(G_1 \times s_m)\cdot \boldsymbol{\sigma}][(G_1 \times s_n)\cdot \boldsymbol{\sigma}]} \\
&\quad +\textcolor{magenta}{(G_1 \cdot s_m)G_0(\boldsymbol{\sigma}\cdot s_n)}+\textcolor{magenta}{G_0(\boldsymbol{\sigma}\cdot s_m)(G_1 \cdot s_n)} \\
&\quad +\textcolor{red}{i(G_1 \times s_m)\cdot \boldsymbol{\sigma} G_0(\boldsymbol{\sigma}\cdot s_n)}+\textcolor{red}{iG_0(\boldsymbol{\sigma}\cdot s_m)(G_1 \times s_n)\cdot \boldsymbol{\sigma}} \\
&\quad +\textcolor{red}{i(G_1 \times s_m)\cdot \boldsymbol{\sigma}(G_1 \cdot s_n)}+\textcolor{red}{i(G_1 \cdot s_m)(G_1 \times s_n)\cdot \boldsymbol{\sigma}}.
\end{aligned}
$$

(5.50)

In the above procedure, the colors are used to track the calculation shown below, and specifically, the terms in magenta add up to give zero. More-

over, I proceed as follows:

$$\mathcal{K}_{eff} = G_0(\boldsymbol{\sigma} \cdot s_m)G_0(\boldsymbol{\sigma} \cdot s_n) + (\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n)$$
$$- [(\boldsymbol{G}_1 \times s_m) \cdot \boldsymbol{\sigma}][(\boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma}]$$
$$+ (\boldsymbol{G}_1 \cdot s_m)G_0(\boldsymbol{\sigma} \cdot s_n) + G_0(\boldsymbol{\sigma} \cdot s_m)(\boldsymbol{G}_1 \cdot s_n)$$
$$+ i(\boldsymbol{G}_1 \times s_m) \cdot \boldsymbol{\sigma}(\boldsymbol{\sigma} \cdot s_n)G_0 + iG_0(\boldsymbol{\sigma} \cdot s_m)(\boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma},$$
$$= G_0 G_0 s_m \cdot s_n + iG_0 G_0 s_m \times s_n \cdot \boldsymbol{\sigma}$$
$$+ (\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n) - (\boldsymbol{G}_1 \times s_m) \cdot (\boldsymbol{G}_1 \times s_n)$$
$$- i(\boldsymbol{G}_1 \times s_m) \times (\boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma}$$
$$+ (\boldsymbol{G}_1 G_0 \cdot s_m)(\boldsymbol{\sigma} \cdot s_n) + (\boldsymbol{\sigma} \cdot s_m)(G_0 \boldsymbol{G}_1 \cdot s_n) + i(\boldsymbol{G}_1 G_0 \times s_m) \cdot s_n$$
$$+ i s_m \cdot (G_0 \boldsymbol{G}_1 \times s_n) - (\boldsymbol{G}_1 G_0 \times s_m) \times s_n \cdot \boldsymbol{\sigma} - s_m \times (G_0 \boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma},$$

and using the vector Identity [16]:

$$(\boldsymbol{A} \cdot \boldsymbol{B})(\boldsymbol{C} \cdot \boldsymbol{D}) = (\boldsymbol{A} \times \boldsymbol{C}) \cdot (\boldsymbol{B} \times \boldsymbol{D}) + (\boldsymbol{B} \cdot \boldsymbol{C})(\boldsymbol{A} \cdot \boldsymbol{D}),$$

I proceed furthermore as below:

$$\mathcal{K}_{eff} = G_0 G_0 s_m \cdot s_n + iG_0 G_0 s_m \times s_n \cdot \boldsymbol{\sigma} + (\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n)$$
$$- (\boldsymbol{G}_1 \times s_m) \cdot (\boldsymbol{G}_1 \times s_n) + i\boldsymbol{G}_1 \times \boldsymbol{G}_1 \times s_m \times s_n \cdot \boldsymbol{\sigma}$$
$$+ (\boldsymbol{G}_1 G_0 \cdot s_m)(\boldsymbol{\sigma} \cdot s_n) + (\boldsymbol{\sigma} \cdot s_m)(G_0 \boldsymbol{G}_1 \cdot s_n) + i\boldsymbol{G}_1 G_0 \cdot s_m \times s_n$$
$$+ iG_0 \boldsymbol{G}_1 \cdot s_n \times s_m - (\boldsymbol{G}_1 G_0 \times s_m) \times s_n \cdot \boldsymbol{\sigma} - s_m \times (G_0 \boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma},$$
$$= G_0 G_0 s_m \cdot s_n + iG_0 G_0 s_m \times s_n \cdot \boldsymbol{\sigma} + (\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n)$$
$$- (\boldsymbol{G}_1 \cdot \boldsymbol{G}_1)s_m \cdot s_n + (\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n)$$
$$+ (\boldsymbol{G}_1 G_0 \cdot s_m)(\boldsymbol{\sigma} \cdot s_n) + (\boldsymbol{\sigma} \cdot s_m)(G_0 \boldsymbol{G}_1 \cdot s_n) + i\boldsymbol{G}_1 G_0 \cdot s_m \times s_n$$
$$- iG_0 \boldsymbol{G}_1 \cdot s_m \times s_n - (\boldsymbol{G}_1 G_0 \times s_m) \times s_n \cdot \boldsymbol{\sigma} - s_m \times (G_0 \boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma},$$
$$= (G_0 G_0 - \boldsymbol{G}_1 \cdot \boldsymbol{G}_1)s_m \cdot s_n$$
$$- i(G_0 \boldsymbol{G}_1 - \boldsymbol{G}_1 G_0) \cdot s_m \times s_n + 2(\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n)$$
$$+ (\boldsymbol{G}_1 G_0 \cdot s_m)(\boldsymbol{\sigma} \cdot s_n) + (\boldsymbol{\sigma} \cdot s_m)(G_0 \boldsymbol{G}_1 \cdot s_n) - (\boldsymbol{G}_1 G_0 \times s_m) \times s_n \cdot \boldsymbol{\sigma}$$
$$- s_m \times (G_0 \boldsymbol{G}_1 \times s_n) \cdot \boldsymbol{\sigma} + iG_0 G_0 s_m \times s_n \cdot \boldsymbol{\sigma}, \tag{5.51}$$

and hence, the term $sp\left[\mathcal{K}_{eff}\right]$ in expression 5.49 reads:

$$sp\left[\mathcal{K}_{eff}\right] = 2(G_0 G_0 - \boldsymbol{G}_1 \cdot \boldsymbol{G}_1)s_m \cdot s_n$$
$$- 2i(G_0 \boldsymbol{G}_1 - \boldsymbol{G}_1 G_0) \cdot s_m \times s_n + 4(\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n). \tag{5.52}$$

I the above result, I have used the fact that the terms (in blue) linear in $\boldsymbol{\sigma}$ appearing on expression 5.51 are traceless (their trace in the spin space is zero). Using this result back in expression 5.49, $\mathcal{H}_{eff}$ now reads:

$$\mathcal{H}_{eff} = ieJ_m J_n(G_0 G_0 - \boldsymbol{G}_1 \cdot \boldsymbol{G}_1)s_m \cdot s_n$$
$$+ eJ_m J_n(G_0 \boldsymbol{G}_1 - \boldsymbol{G}_1 G_0) \cdot s_m \times s_n + 2ieJ_m J_n(\boldsymbol{G}_1 \cdot s_m)(\boldsymbol{G}_1 \cdot s_n), \tag{5.53}$$

and by comparing it with the typical spin Hamiltonian with Heisenberg, Dzyaloshinskii-Moriya and Ising contributions given by:

$$\mathcal{H}_{spin} = \sum_{mn} \mathcal{J}_{mn} s_m \cdot s_n + D_{mn} \cdot s_m \times s_n + s_m \cdot \mathbb{I}_{mn} \cdot s_n, \qquad (5.54)$$

the Heisenberg like effective exchange $\mathcal{J}_{mn}$, in the spectral domain reads:

$$\mathcal{J}_{mn}(\omega) = \frac{J_m J_n}{2} \int \int \frac{G_{mn}^{(0)<}(\epsilon) G_{nm}^{(0)>}(\epsilon') - G_{mn}^{(0)>}(\epsilon) G_{nm}^{(0)<}(\epsilon')}{\hbar\omega - \epsilon + \epsilon'} \frac{d\epsilon}{2\pi} \frac{d\epsilon'}{2\pi},$$

$$- \frac{J_m J_n}{2} \int \int \frac{G_{mn}^{(1)<}(\epsilon) \cdot G_{nm}^{(1)>}(\epsilon') - G_{mn}^{(1)>}(\epsilon) \cdot G_{nm}^{(1)<}(\epsilon')}{\hbar\omega - \epsilon + \epsilon'} \frac{d\epsilon}{2\pi} \frac{d\epsilon'}{2\pi},$$

$$(5.55)$$

and seemingly, the Dzyaloshinskii-Moriya like [108], [109] and Ising like interactions read:

$$D_{mn}(\omega) = \frac{J_m J_n}{4} \int \left[G_{mn}^{(0)<}(\epsilon + \omega) G_{nm}^{(1)>}(\epsilon) - G_{mn}^{(0)>}(\epsilon + \omega) G_{nm}^{(1)<}(\epsilon) \right] \frac{d\epsilon}{2\pi}$$

$$- \frac{J_m J_n}{4} \int \left[G_{mn}^{(1)<}(\epsilon + \omega) G_{nm}^{(0)>}(\epsilon) - G_{mn}^{(1)>}(\epsilon + \omega) G_{nm}^{(0)<}(\epsilon) \right] \frac{d\epsilon}{2\pi}$$

$$(5.56)$$

$$\mathbb{I}_{mn}(\omega) = \frac{J_m J_n}{2} \int \int \frac{G_{mn}^{(1)<}(\epsilon) G_{nm}^{(1)>}(\epsilon') - G_{mn}^{(1)>}(\epsilon) G_{nm}^{(1)<}(\epsilon')}{\hbar\omega - \epsilon + \epsilon'} \frac{d\epsilon}{2\pi} \frac{d\epsilon'}{2\pi}$$

$$- \frac{J_m J_n}{2} \int \int \frac{G_{mn}^{(1)<}(\epsilon') G_{nm}^{(1)>}(\epsilon) - G_{mn}^{(1)>}(\epsilon') G_{nm}^{(1)<}(\epsilon)}{\hbar\omega - \epsilon + \epsilon'} \frac{d\epsilon}{2\pi} \frac{d\epsilon'}{2\pi}.$$

$$(5.57)$$

The formulas for exchange under a non-equilibrium drive, namely expressions 5.55, 5.56 and 5.57, are extensively used in the papers reported in this thesis, along with the transport formulas derived in the previous chapter.

5.6 Experimental Implications of the Non-Equilibrium RKKY Theory for Magnetic Exchange in the Context of This Thesis

Expressions 5.55, 5.56 and 5.57 have been extensively and successfully used from a theoretical standpoint, to predict the formation of ground states in dimers of Cobalt atoms and their detection through transport measurements [102], [67], [103], to calculate the renormalized magnetic exchange by the action of an effective phonon-phonon interactions and in cutting edge theoretical models for single molecule magnet spin dynamics and

how energy is driven by the change in magnetic entropy in such systems [110], [68] and as reported in paper IV. In paper I included in this dissertation, I extended the scope of this analysis to energy currents and to thermoelectric response coefficients, where the possibility to determine the entropy production rate driven by the spin state formation was examined, result that might trigger the interest in the scientific community based on the expected impact in spin qubit architectures. In paper II, I considered single ion magnetic anisotropy of a driven single molecule magnet, and as observed experimentally [6], [10] and predicted theoretically from simpler models [48], [111], the method developed through out the chapter allows for capturing the change in the behavior of the uniaxial magnetic anisotropy of SMM as is driven electrically. This is made possible by the facility of encoding the electronic structure of the molecular magnet in the charge Green's function $G^{(0)}$ and in the spin Green's function $G^{(1)}$, which determines the transport characteristics through the junctions, but more importantly, plays a fundamental role in the strength and sign of the effective interactions among spins in the magnet, which is in accordance with the experiments reported by A. A. Khajetoorians [2].

When the latter is understood, it is necesary to keep in mind that, once the effective magnetic interactions are induced through the action of the electronic structure that couples the spins in the system by means of the Kondo like correlation [102], [67], the current state of the spin will be then affected, and as a backaction effect, this will lead to a zeeman like splitting in the electronic structure hosting the localized spin moments, which requires the computation of a renormalized version of the charge and the spin Green's functions to properly capture in the transport calculations, the effect of the spin backaction, and then a clear correlation between the spin excitations and the charge, spin or heat current will emerge [103]. This very line of thought followed by the theoretical work reported in [67], [103], which is in accordance with experiments by Heiko Weber [10] *et.al* and A. A. Khajetoorians [1], [2], is adopted in the work presented in this thesis, with strong reference to paper I and Paper III.

As experimental efforts to engineer spin-spin interactions advance rapidly as discussed through this thesis, the application of the theory of Non-Equilibrium RKKY exchange interactions as presented in [102] and explained in this chapter becomes fundamental to unveil the microscopic mechanisms giving rise to definite spin ordering in the molecular magnet of interest. Nonetheless, new explorations and extensions to this theory with regards to its applicability in the experimental context of nanomagnet tailoring is required, and as a future line of action, I think the work presented by Nordström *et.al* in [112] combined with the advances in superconducting STM experiments [113] will provide the necessary flavor to contribute

to the design of new experimental paradigms and with unveiling unknown mechanisms in the scope of molecular magnet design.

6. Electrons, Phonons and Spins

"From the Macroscopic to the Microscopic Scale, we Met Solitons at all Scales"

Thierry Dauxois and Michel Peyrard.
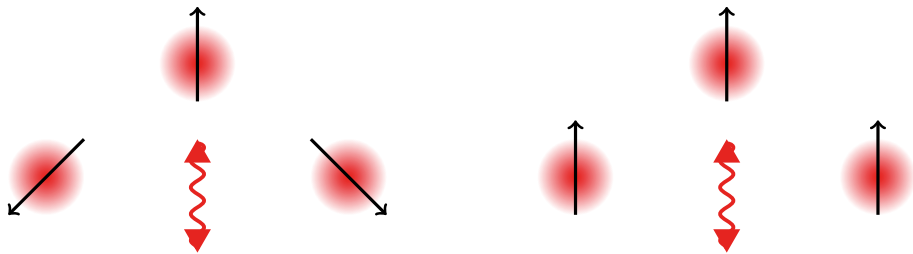
Electrons and Phonons interact in quantum matter to give rise to a broad range of phenomena, and perhaps, the most discussed among them, being the polarons and bipolaron effects [17], and the origin of attractive interaction in conventional superconductivity [74]. The attractive interaction in conventional superconductors, which in the context of the BCS theory is explained by the interaction of two electrons by means of their individual coupling to a phonon mode, is a nice example of how two fermions coupled effectively through a boson bath. From a theoretical perspective, when spins enter into the picture, one could think to extrapolate the philosophy of the effective interaction in the BCS theory (recall the effective interaction among spins through conduction electrons or RKKY like phenomena discussed in Chapter 5), to argue that, if spins and phonons do not interact directly, they can rather interact through conduction electrons, this, mediated by the Kondo coupled spins to electrons and the vibrations coupled to electrons in the spirit of the polaron model [68], [74], and furthermore, as spins interact effectively with each other through the electron cloud, effective interactions among phonons may also arise through the mediation of electrons [112]. Experimentally, the problem of direct spin-phonon coupling has been addressed in [53] and in the specific context of molecular junctions, Svetlana *et.al* has reported on the strong spin-phonon coupling between a single mode in a carbon nanotube based NEMS (nano electromechanical system) [6], [4], with a Turbium ion embedded within it. Important theoretical support to the findings presented in the latter work have been in the scientific literature, which include the study of the magnetic nature of quantum nano objects determined by the modulation of its resonance frequency by a magnetic field [57], electrical detection of quantum

coherent phenomena using ESR (Electron Spin Resonance) [114], the interplay between high anisotropy single molecule magnets (SMM) and local molecular vibrations in the process of quantum spin tunneling [56] and the effect on molecular vibrations in tunneling magnetoresistance [55] which as well supports findings reported in [4].

This line of argumentation, suggests that the phenomenon of spin-phonon coupling or rather the effect of vibrational modes in magnetic interactions and quantities, remains a relevant challenge to target. Some aspects of great interest for the community include magnetic stability of single molecule magnets [43], effect of molecular vibrations in single ion anisotropy [49], [47], [59], modulation of discrete phonon density of states by magnetic interactions [53], magnetic ordering of molecular magnets [115], [2], among others, and the interplay between magnetism, quantum coherence and electron-phonon interaction emerges as an interesting fundamental problem to approach, using electrical, thermal and magnetic probing available experimentally, which motivates the discussion of the present chapter.

Here, I consider the basics of the emergence of the electron-phonon interaction in quantum matter, and put it in the context of molecular junctions [74], [17]. Furthermore, I consider the renormalization of the electronic Hamiltonian by the electron-phonon interaction after the implementation of the Lang-Firsov transformation [116], which is detailed below. The exemplification of this transformation in the context of magnetic molecules was investigated in [55] and is considered in paper II where the uniaxial magnetic anisotropy modulated by non-equilibrium driving is evaluated for interacting single molecule magnet (SMM) embeeded in a metallic ferromagnetic junction in the presence of a single vibration mode. I deeply discuss the renormalization of the electron-electron correlation by the electron-phonon interaction in [117].

6.1 Electron-Phonon Interaction

I will now comment on the emergence of the electron-phonon interaction in quantum matter systems, and how it reflects the properties of the system under study. Later, I will comment on how relevant this interaction is in molecular junctions and the commonly used models to approach the physical insights of such systems. This discussion is based on the refs. [17], [74].

6.1.1 Potential Created by Ionic Vibrations

In [17], the emergence of the electron phonon interaction is discussed for the Jellium model, ionic crystals and metals, departing from a harmonic vibrational potential of the form:

$$h(r) = \sum_{jk} \left[\mathcal{U}(r - r_{jk}) - \mathcal{U}(r - R_{jk}) \right] = \sum_{jk} \left[\mathcal{U}(r - R_{jk} - u_k) - \mathcal{U}(r - R_{jk}) \right].$$

(6.1)

Note that the term $\mathcal{U}(r - R_{jk} - u_k) - \mathcal{U}(r - R_{jk})$ can be simplified as follows:

$$\frac{\mathcal{U}(r - R_{jk} - u_k) - \mathcal{U}(r - R_{jk})}{r - R_{jk} - u_k - \left(r - R_{jk} \right)} = \frac{\mathcal{U}(r - R_{jk} - u_k) - \mathcal{U}(r - R_{jk})}{-u_k}$$

$$\approx \nabla \mathcal{U}(r - R_{jk}), \qquad (6.2)$$

giving:

$$\mathcal{U}(r - R_{jk} - u_k) - \mathcal{U}(r - R_{jk}) = -u_k \nabla \mathcal{U}(r - R_{jk}), \qquad (6.3)$$

where $\mathcal{U}$ stands for the lattice potential, which is being deformed. r is the coordinate of the electrons in the periodic potential $\mathcal{U}$, u_k is the displacement of the electrons relative to their equilibrium position, R_{jk} is the equilibrium position for electron j in the unit cell k. By replacing expression 6.3 back in equation 6.1, the potential $h(r)$ reads:

$$h(r) = - \sum_{jk} u_k \nabla \mathcal{U}(r - R_{jk}). \qquad (6.4)$$

To fully account for quantum mechanical effects such as heating at low temperatures, quantum interference and modification of the exchange integrals induced by the effect of vibrations, the potential given by expression 6.4 is to be quantized. The quantum mechanical version of $h(r)$, namely $h_{QM}(r)$, can be obtained by replacing u_k by its quantum mechanical version [17], giving:

$$h_{QM}(r) = - \sum_{jk} \sum_{qs} \left(\frac{\hbar}{2NM_k \omega_{qs}} \right)^{1/2} e^{q \cdot R_j} \nabla \mathcal{U}(r - R_{jk}) \cdot \epsilon_k^s(q) \left(a_{qs} + a_{-qs}^\dagger \right).$$

(6.5)

The above expression contains the basic ingredients to examine the emergence of the electron-phonon interaction as a function of the system physical properties and the deformation of the lattice potential.

6.1.2 Electron-Phonon Interaction in Metals

Electron-Phonon interaction in metals is considered here as an example to illustrate the emergence of this phenomena in quantum matter, and as

such, I consider that the interaction Hamiltonian $\mathcal{H}_{ep}$, of the single electron evaluated @ r, including all other phonons (vibrations) in the metal, can be obtained from the quantum mechanical potential $h_{QM}(r)$ by multiplying it by the electron number density operator $\psi^\dagger(r, s_z)\psi(r, s_z)$, then integrating it over all positions and summed over all the spin configurations. This argument gives rise to the following form of the electron-phonon Hamiltonian $\mathcal{H}_{ep}$:

$$\mathcal{H}_{ep} = \sum_{s_z} \int dr \psi^\dagger(r, s_z) h_{QM}(r) \psi(r, s_z), \qquad (6.6)$$

where the field operator $\psi(r, s_z)$ is expanded as:

$$\psi(r, s_z) = \sum_{nk\sigma} \Phi_{nk\sigma}(r, s_z) c_{nk\sigma}. \qquad (6.7)$$

By replacing expression 6.7 into expression 6.6, the electron-phonon Hamiltonian $\mathcal{H}_{ep}$ can be further elaborated as follows:

$$\mathcal{H}_{ep} = \sum_{s_z} \int dr \sum_{n'k'\sigma'} \Phi^*_{n'k'\sigma'}(r, s_z) c^\dagger_{n'k'\sigma} h_{QM}(r) \sum_{nk\sigma} \Phi_{nk\sigma}(r, s_z) c_{nk\sigma},$$

$$= \sum_{s_z} \sum_{n'k'\sigma'} \sum_{nk\sigma} \int dr \Phi^*_{n'k'\sigma'}(r, s_z) c^\dagger_{n'k'\sigma} h_{QM}(r) \Phi_{nk\sigma}(r, s_z) c_{nk\sigma},$$

to finally give the following of the electron-phonon Hamiltonian:

$$\mathcal{H}_{ep} = \sum_{qs} \sum_{nn'kk'} \sum_{\sigma\sigma'} g_{qs}(n'k'\sigma', nk\sigma) \left(a_{qs} + a^\dagger_{-qs} \right) c^\dagger_{n'k'\sigma} c_{nk\sigma}, \qquad (6.8)$$

where $g_{qs} = g_{qs}(n'k'\sigma', nk\sigma)$ is known as the electron-phonon coupling constant and is given by:

$$g_{qs} = -\sum_{jks_z} \left(\frac{\hbar}{2NM_k\omega_{qs}} \right)^{1/2} e^{q\cdot R_j} \int dr \Phi^*_{n'k'\sigma'}(r, s_z) \Phi_{nk\sigma}(r, s_z)$$

$$\times \nabla \mathcal{U}(r - R_{jk}) \cdot \epsilon^s_k(q). \qquad (6.9)$$

From the above expression, one understands that the electrons and phonons coupled in metals through the spatial variations of the lattice potential in the direction of propagation of the phonons given by the polarization vector $\epsilon^s_k(q)$.

6.1.3 The Jellium Model

In the Jellium model, the positively charged ions are smoothed out and form a featureless elastic continuum that serves as a medium for the electrons to move. In this context, lattice vibrations possess normal modes all

with the same frequency $\omega_p^{(Ion)} = \left(\frac{Z^2 n e^2}{m \epsilon_0}\right)$, where Z is the valence of the ion, n is the ion number density and M is the ion mass. $\omega_p^{(Ion)}$ is called the ion plasma frequency, which represents the oscillation frequency of positive ions, with a restoring force provided by the electric field produced by the polarization of the electron gas in the metal.

a dipole of magnitude $p = Zex$ is produced due to the relative motion of positive ions in the electronic background, which produces a polarization $P = pn = Zexn$. To obtain the frequency $\omega_p^{(Ion)}$, one applies Newton's second law in the following way:

$$F = ma \Rightarrow m \frac{d^2 x}{dt^2} = F = Ze|\boldsymbol{E}| = -Ze \frac{P}{\epsilon_0} = -\frac{Z^2 e^2 n x}{\epsilon_0},$$

where the electric field $\boldsymbol{E}$ is related to the polarization through: $\boldsymbol{E} = \frac{P}{\epsilon_0}$. As such, the frequency $\omega_p^{(Ion)}$ can be directly calculated to be:

$$\omega_p^{(Ion)} = \sqrt{\frac{Z^2 e^2 n}{M \epsilon_0}}. \tag{6.10}$$

Moreover, the ionic displacement at $\boldsymbol{R}$ associated with the motion of this positive ions can be represented by $\boldsymbol{u}(\boldsymbol{R})$, which yields an electric dipole moment p given by:

$$p = Ze\boldsymbol{u}(\boldsymbol{R}), \tag{6.11}$$

and a polarization $\boldsymbol{P}$ of:

$$\boldsymbol{P} = np = Zen\boldsymbol{u}(\boldsymbol{R}). \tag{6.12}$$

The above expressed polarization corresponds to an induced charge density of $-\nabla \cdot \boldsymbol{P} = -Zen\nabla \cdot \boldsymbol{u}(\boldsymbol{R})$, which interacts with the electronic charge density of $-e \sum_{s_z} \psi^\dagger(\boldsymbol{r}, s_z)\psi(\boldsymbol{r}, s_z)$ through the Coulomb interaction, which can be quantitatively stated in through the following procedure:

$$\mathcal{H}_{Coul} = \frac{1}{4\pi\epsilon_0} \int \int \frac{n_Q(\boldsymbol{R}) n_e(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{R}|} d\boldsymbol{r} d\boldsymbol{R},$$

$$= \frac{Ze^2 n}{4\pi\epsilon_0} \sum_{s_z} \int \int \frac{\nabla \cdot \boldsymbol{u}(\boldsymbol{R})\psi^\dagger(\boldsymbol{r}, s_z)\psi(\boldsymbol{r}, s_z)}{|\boldsymbol{r} - \boldsymbol{R}|} d\boldsymbol{r} d\boldsymbol{R},$$

The above Hamiltonian that represents an effective Coulomb interaction, is representative for the electron-phonon problem, as it contains the potential created by the background ions as well as the electronic charge density through the field operators $\psi^\dagger(\boldsymbol{r}, s_z)$ and $\psi(\boldsymbol{r}, s_z)$. Therefore, is accurate to assign the above Hamiltonian to the electron-phonon interaction, which is

given by:

$$\mathcal{H}_{ep} = \frac{Ze^2 n}{4\pi\epsilon_0} \sum_{s_z} \int \int \frac{\boldsymbol{\nabla} \cdot \boldsymbol{u}(\boldsymbol{R})\psi^\dagger(\boldsymbol{r},s_z)\psi(\boldsymbol{r},s_z)}{|\boldsymbol{r}-\boldsymbol{R}|} d\boldsymbol{r} d\boldsymbol{R}. \qquad (6.13)$$

To obtained a final expression in terms of second quantized electron operators, the field operators $\psi(\boldsymbol{r},s_z)$ are expanded as a linear combination of plane waves $\psi(\boldsymbol{r},s_z) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}\sigma} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\chi_\sigma(s_z)c_{\boldsymbol{k}\sigma}$, yielding the following form of the electron-phonon Hamiltonian:

$$\mathcal{H}_{ep} = \frac{Ze^2 n}{4\pi\epsilon_0} \sum_{\boldsymbol{k}\boldsymbol{k}'} \sum_{\sigma} \int \int \frac{d\boldsymbol{r} d\boldsymbol{R}}{V} \frac{\boldsymbol{\nabla} \cdot \boldsymbol{u}(\boldsymbol{R})e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}}{|\boldsymbol{r}-\boldsymbol{R}|} c_{\boldsymbol{k}'\sigma}^\dagger c_{\boldsymbol{k}\sigma}, \qquad (6.14)$$

To proceed further with the derivation of a suitable form for the electron-phonon Hamiltonian, I now use the quantum mechanical version of the displacement operator $\boldsymbol{u}(\boldsymbol{r})$ as given in refs. [74], [17]:

$$\boldsymbol{u}(\boldsymbol{r}) = \sum_{\boldsymbol{q}s} \left(\frac{\hbar}{2NM\omega_{\boldsymbol{q}s}}\right)^{1/2} \boldsymbol{\epsilon}^{(s)}(\boldsymbol{q})e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\left(a_{\boldsymbol{q}s} + a_{-\boldsymbol{q}s}^\dagger\right), \qquad (6.15)$$

yielding the following expression for $\boldsymbol{\nabla} \cdot \boldsymbol{u}(\boldsymbol{R})$:

$$\boldsymbol{\nabla} \cdot \boldsymbol{u}(\boldsymbol{R}) = i\sum_{\boldsymbol{q}s} \left(\frac{\hbar}{2NM\omega_{\boldsymbol{q}s}}\right)^{1/2} \boldsymbol{q}\cdot\boldsymbol{\epsilon}^{(s)}(\boldsymbol{q})\left(a_{\boldsymbol{q}s} + a_{-\boldsymbol{q}s}^\dagger\right)e^{i\boldsymbol{q}\cdot\boldsymbol{R}}. \qquad (6.16)$$

A final step is needed to arrive at a suitable and convenient form for the electron-phonon Hamiltonian, with regards to the electron-phonon coupling constant. Moving forward, expression 6.16 is replaced in equation 6.14, which gives:

$$\mathcal{H}_{ep} = \sum_{\boldsymbol{k}\boldsymbol{q}} \sum_{s\sigma} g_{\boldsymbol{q}s}\left(a_{\boldsymbol{q}s} + a_{-\boldsymbol{q}s}^\dagger\right)c_{\boldsymbol{k}+\boldsymbol{q},\sigma}^\dagger c_{\boldsymbol{k}\sigma}, \qquad (6.17)$$

where the electron-phonon coupling constant is given by:

$$g_{\boldsymbol{q}s} = i\left[\frac{Z^2 e^6 n\hbar^2}{4M\epsilon_0^3}\left(\frac{n}{N}\right)^2\right]^{1/4} \frac{\boldsymbol{q}\cdot\boldsymbol{\epsilon}^{(s)}(\boldsymbol{q})}{|\boldsymbol{q}|^2} = i\left[\frac{Z^2 e^6 n\hbar^2}{4MV^2\epsilon_0^3}\right]^{1/4} \frac{\boldsymbol{q}\cdot\boldsymbol{\epsilon}^{(s)}(\boldsymbol{q})}{|\boldsymbol{q}|^2}. \qquad (6.18)$$

6.1.4 Electron-Phonon Interaction in Molecular Crystals

In an ionic crystal, the cations and anions in the same unit cell oscillate in opposite directions, inducing an oscillating dipole which will polarize the crystal, and thus will create an electric field that will be felt by the electrons. This longitudinal optical mode in which the cations and anions oscillate, will create an electric field thus creating a potential with which the electrons interact.

From the above statement, the electron-phonon Hamiltonian $\mathcal{H}_{ep}$ written as:

$$\mathcal{H}_{ep} = \sum_{s_z} \int d\boldsymbol{r}\, \Psi^{\dagger}(r, s_z) h(r) \Psi(r, s_z), \qquad (6.19)$$

can be completely determined by specifying $h(r)$ as $h(r) = -e\phi(r)$, where $\phi(r)$ is related to the electric field through $\boldsymbol{E}(r) = -\boldsymbol{\nabla}\phi(r)$, and once the electric field has been specified the operator $h(r)$ can be determined and hence the Hamiltonian $\mathcal{H}_{ep}$.

To proceed with this task, let's consider the cationic and anionic displacements in the j-th cell $\boldsymbol{u}_{j+}$ and $\boldsymbol{u}_{j-}$ respectively to be given by:

$$\boldsymbol{u}_{j+} = \sum_{\boldsymbol{q}} \left(\frac{\hbar}{2N\omega_{\boldsymbol{q}}}\right)^{1/2} \frac{\boldsymbol{\epsilon}_{+}(\boldsymbol{q})}{\sqrt{M_{+}}} \left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}, \qquad (6.20)$$

$$\boldsymbol{u}_{j-} = \sum_{\boldsymbol{q}} \left(\frac{\hbar}{2N\omega_{\boldsymbol{q}}}\right)^{1/2} \frac{\boldsymbol{\epsilon}_{-}(\boldsymbol{q})}{\sqrt{M_{-}}} \left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}, \qquad (6.21)$$

where M_{+} and M_{-} are respectively the masses of the cations and anions, and I have suppressed the polarization index s as I am considering the longitudinal optical branch, hence all polarization vectors and phonon operators are associated to this branch. To start the calculation of interest at the moment, recall that the polarization vector $\boldsymbol{P}$, the electric dipole moment p and the electric field $\boldsymbol{E}$ relate through:

$$\boldsymbol{E} = -\frac{\boldsymbol{P}}{\epsilon_0} = -\frac{N}{\epsilon_0 V} p, \qquad (6.22)$$

where the oscillating electric dipole moment is given by:

$$p = Ze\left(\boldsymbol{u}_{+}(\boldsymbol{R}_j) - \boldsymbol{u}_{-}(\boldsymbol{R}_j)\right). \qquad (6.23)$$

The above expression gives a clear message: the displacement between positively and negatively charged clouds will induce an electric dipole and as a result, an electric field given by (For important discussion about this matter see ref. [118]):

$$\boldsymbol{E} = -\frac{ZeN}{\epsilon_0 V} \sum_{\boldsymbol{q}} \left(\frac{\hbar}{2N\omega_{\boldsymbol{q}}}\right)^{1/2} \left(\frac{\boldsymbol{\epsilon}_{+}(\boldsymbol{q})}{\sqrt{M_{+}}} - \frac{\boldsymbol{\epsilon}_{-}(\boldsymbol{q})}{\sqrt{M_{-}}}\right) \left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}, \qquad (6.24)$$

and since I have assumed a longitudinal mode, it is correct to state $\left(\frac{\boldsymbol{\epsilon}_{+}(\boldsymbol{q})}{\sqrt{M_{+}}} - \frac{\boldsymbol{\epsilon}_{-}(\boldsymbol{q})}{\sqrt{M_{-}}}\right) = c(q)\boldsymbol{q}$, hence transforming expression 6.24 into:

$$\boldsymbol{E} = -\frac{ZeN}{\epsilon_0 V} \sum_{\boldsymbol{q}} \left(\frac{\hbar}{2N\omega_{\boldsymbol{q}}}\right)^{1/2} c(q)\boldsymbol{q} \left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}. \qquad (6.25)$$

After some algebra (not so straight forward, for details see [17]), from expression 6.25, the electric scalar potential $\phi(\boldsymbol{R}_j)$ responsible for the induction of the electric dipole can be obtain from the know relation $\boldsymbol{E}(\boldsymbol{R}_j) = -e\nabla\phi(\boldsymbol{R}_j)$ [16], giving:

$$\phi(\boldsymbol{R}_j) = -i\frac{ZeN}{\epsilon_0 V}\sum_{\boldsymbol{q}}\left(\frac{\hbar}{2N\omega_{\boldsymbol{q}}}\right)^{1/2}\frac{\boldsymbol{q}}{|\boldsymbol{q}|^2}\cdot\left(\frac{\epsilon_+(\boldsymbol{q})}{\sqrt{M_+}} - \frac{\epsilon_-(\boldsymbol{q})}{\sqrt{M_-}}\right)\left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right)e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j}.$$

(6.26)

Up to this point, let's don't forget what is the goal of this calculation: to determine the electron-phonon Hamiltonian $\mathcal{H}_{ep}$. To do so, I will need to determine as well the operator $h(\boldsymbol{r})$, defined through $h(\boldsymbol{r}) = -e\phi(\boldsymbol{r})$. Therefore, using expression 6.26, $h(\boldsymbol{r})$ reads:

$$h(\boldsymbol{r}) = i\frac{Ze^2N}{\epsilon_0 V}\sum_{\boldsymbol{q}}\left(\frac{\hbar}{2N\omega_{\boldsymbol{q}}}\right)^{1/2}\frac{\boldsymbol{q}}{|\boldsymbol{q}|^2}\cdot\left(\frac{\epsilon_+(\boldsymbol{q})}{\sqrt{M_+}} - \frac{\epsilon_-(\boldsymbol{q})}{\sqrt{M_-}}\right)\left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right)e^{i\boldsymbol{q}\cdot\boldsymbol{r}}. \quad (6.27)$$

Now we focus on expression 6.19, which defines the electron-phonon Hamiltonian in terms of the field operator $\Psi(\boldsymbol{r}, s_z)$. To elaborate on the latter, we use the expansion $\Psi(\boldsymbol{r}, s_z) = \sum_{\boldsymbol{k}\sigma}\phi_{\boldsymbol{k}}(\boldsymbol{r})c_{\boldsymbol{k}\sigma}\chi_{\sigma}(s_z)$ and replace it on expression 6.19, which is shown below:

$$\mathcal{H}_{ep} = \sum_{s_z}\int d\boldsymbol{r}\left(\sum_{\boldsymbol{k}'\sigma'}\phi_{\boldsymbol{k}'}^{*}(\boldsymbol{r})c_{\boldsymbol{k}'\sigma'}^{\dagger}\chi_{\sigma'}^{*}(s_z)\right)h(\boldsymbol{r})\left(\sum_{\boldsymbol{k}\sigma}\phi_{\boldsymbol{k}}(\boldsymbol{r})c_{\boldsymbol{k}\sigma}\chi_{\sigma}(s_z)\right),$$

$$= \sum_{s_z}\sum_{\boldsymbol{k}\sigma}\sum_{\boldsymbol{k}'\sigma'}\int d\boldsymbol{r}\phi_{\boldsymbol{k}'}^{*}(\boldsymbol{r})h(\boldsymbol{r})\phi_{\boldsymbol{k}}(\boldsymbol{r})\chi_{\sigma'}^{*}(s_z)\chi_{\sigma}(s_z)c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}\sigma},$$

$$= \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'}\int d\boldsymbol{r}\phi_{\boldsymbol{k}'}^{*}(\boldsymbol{r})h(\boldsymbol{r})\phi_{\boldsymbol{k}}(\boldsymbol{r})\sum_{s_z}\chi_{\sigma'}^{*}(s_z)\chi_{\sigma}(s_z)c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}\sigma},$$

$$= \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'}\int d\boldsymbol{r}\phi_{\boldsymbol{k}'}^{*}(\boldsymbol{r})h(\boldsymbol{r})\phi_{\boldsymbol{k}}(\boldsymbol{r})\delta_{\sigma\sigma'}c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}\sigma},$$

and implementing the delta with the summation over σ', the following close form for the electron-phonon Hamiltonian emerges as below:

$$\mathcal{H}_{ep} = \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma}\int d\boldsymbol{r}\phi_{\boldsymbol{k}'}^{*}(\boldsymbol{r})h(\boldsymbol{r})\phi_{\boldsymbol{k}}(\boldsymbol{r})c_{\boldsymbol{k}'\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}. \quad (6.28)$$

To wrap up the discussion for this section, the result from expression 6.27 for the operator $h(\boldsymbol{r})$, is now replaced in expression 6.28, which gives the following closed form for the Electron-Phonon Hamiltonian:

$$\mathcal{H}_{ep} = \sum_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\sigma}g_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}}\left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger}\right)c_{\boldsymbol{k}'\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}, \quad (6.29)$$

where the electron-phonon coupling constant has been defined as:

$$g_{kk'q} = i\frac{Ze^2N}{\epsilon_0 V}\left(\frac{\hbar}{2N\omega_q}\right)^{1/2}\frac{q}{|q|^2}\cdot\left(\frac{\epsilon_+(q)}{\sqrt{M_+}} - \frac{\epsilon_-(q)}{\sqrt{M_-}}\right)\int dr\phi_{k'}^*(r)\phi_k(r)e^{iq\cdot r}.$$
(6.30)

Note that $g_{kk'q}$ diverges as $q \to 0$, that is, in the long-wavelength limit. This indicates the strong-polaron effect in an ionic crystal.

As a last remark, my notes with full detail of the derivations presented in [17] are available[1].

6.1.5 Final Comments on the Emergence of the Electron-Phonon Interaction

In this section of the present chapter I have discussed the mechanisms by which electrons and phonons coupled in condensed matter systems. I believe, that is of capital importance, to understand under which physical conditions this coupling emerges, and how the intrinsic properties of a given condensed matter system might modulate this interaction, for instance through a crystal or ligand field, in order to make sense of experimental observations such as the ones reported in [53]. When simplifying the nature of the electron-phonon interaction, what is the case for the work presented in this thesis, it is relevant, to determine whether the differences in the predictions made with the simplified model are attributed to the over simplified assumption on the electron-phonon interactions or to other simplifications assumed of different nature (Not related to the electron-phonon coupling).

In the work presented here, I assume that the phonons lie on the acoustic branch independent of any type of wave vector. For the molecules consider herein, the nature of the electron-phonon interaction derives from the ionic vibrations (displacements) of the nuclear degrees of freedom in the molecule, hence resembling much more the nature of this interactions from the molecular crystals discussion than from the Jellium model one. Additionally I assumed that the electron-phonon coupling is spin independent. In the following sections, I will discuss the molecular systems in which the electronic, vibrational and spin degrees of freedom converge and discuss what the implications of the vibrations will be on the electron and spin related quantities.

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[1]See electron-phonon interaction at the nanoscale in:
https://sites.google.com/site/yohannandawid/

6.2 Molecular Systems of Interest

The molecular systems of interest are magnetic molecules where the single magnetic units do not interact among each other, though they couple through the Kondo interaction with an electronic level. The coupling among electronic levels creates an effective interaction among the magnetic units as in experiments reported in [119], through the so mentioned in this thesis, the RKKY interaction. In figure 6.1, these type of molecules are schematized, showing all the relevant interactions. The Generalized model Hamil-
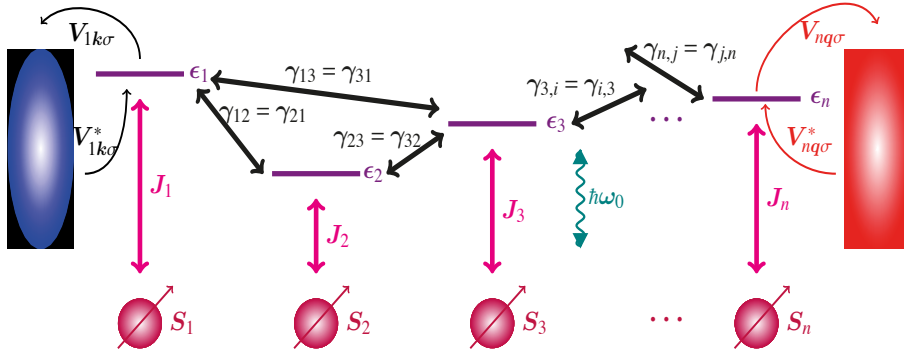
Figure 6.1. Molecules of Interest: System made of n energy levels labeled as ϵ_i, coupled to n single magnetic units with spin moment S_i through the Kondo interaction J_i, and coupled among each other with amplitude γ_{ij}. The label i denotes units from 1 to n. Additionally, I am interested in molecules vibrating coherently with single frequency mode ω_0, with associated energy $\hbar\omega_0$. Here in this set up, phonons and electrons are coupled via the constant λ, that was discussed phenomenologically in the previous section. In the context of this thesis, these type of molecules are studied in the context of Scanning Tunneling Microscopy experiments, where the molecule is coupled to two metallic leads representing the STM tip (blue) through the amplitudes $V_{1k\sigma}$, and the substrate (red) through the amplitude $V_{nq\sigma}$.

tonian representing the type of physics shown in figure 6.1 is given by:

$$\mathcal{H} = \mathcal{H}_{Leads} + \mathcal{H}_T + \mathcal{H}_{mol}^{(e)} + \mathcal{H}_{mol}^{(vib)} + \mathcal{H}_{mol}^{(e-vib)} + \mathcal{H}_{mol}^{(spin)}, \tag{6.31}$$

$$\mathcal{H}_{Leads} = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{q\sigma} \epsilon_{q\sigma} c_{q\sigma}^{\dagger} c_{q\sigma}, \tag{6.32}$$

$$\mathcal{H}_T = \sum_{mk\sigma} V_{mk\sigma} c_{k\sigma}^{\dagger} d_{m\sigma} + V_{mk\sigma}^{*} d_{m\sigma}^{\dagger} c_{k\sigma}$$

$$+ \sum_{mq\sigma} V_{mq\sigma} c_{q\sigma}^{\dagger} d_{m\sigma} + V_{mq\sigma}^{*} d_{m\sigma}^{\dagger} c_{q\sigma}, \tag{6.33}$$

$$\mathcal{H}_{mol}^{(e)} = \sum_{m\sigma} \epsilon_{m\sigma} d_{m\sigma}^{\dagger} d_{m\sigma} + \sum_{m_1 m_2 \sigma} \gamma_{m_1 m_2} d_{m_1 \sigma}^{\dagger} d_{m_2 \sigma}$$

$$+ \sum_{m} U_m n_{m\uparrow} n_{m\downarrow}, \tag{6.34}$$

$$\mathcal{H}_{mol}^{(vib)} = \sum_{m} \hbar \omega_m a_m^{\dagger} a_m, \tag{6.35}$$

$$\mathcal{H}_{mol}^{(e-vib)} = \sum_{m\sigma} \lambda_m \left(a_m^{\dagger} + a_m \right) d_{m\sigma}^{\dagger} d_{m\sigma}, \tag{6.36}$$

$$\mathcal{H}_{mol}^{(spin)} = \sum_{m\sigma_1 \sigma_2} J_m d_{m\sigma_1}^{\dagger} \boldsymbol{\sigma}_{\sigma_1 \sigma_2} d_{m\sigma_2} \cdot \mathbf{S}_m(t). \tag{6.37}$$

The descriptions of the individual models presented in the above lines are as follows: $\mathcal{H}_{Leads}$ represents the Hamiltonian describing the physics of metallic reservoirs with band structure specified by $\epsilon_{k\sigma}$ and $\epsilon_{q\sigma}$ for the left and right reservoir respectively, that is, the metallic STM tip and the metallic substrate. This Hamiltonian, considers metallic reservoirs (Magnetic or Non-Magnetic) as free electron gases at different temperatures T_L and T_R, and at different chemical potentials μ_L and μ_R, and with electron occupation density given by the corresponding Fermi-Dirac distribution $f_L(\epsilon_{k\sigma}; \mu_L, T_L)$ and $f_R(\epsilon_{q\sigma}; \mu_R, T_R)$. The multilevel molecular Hamiltonian is a sum of contributions from the electronic part $\mathcal{H}_{mol}^{(e)}$, vibrational part $\mathcal{H}_{mol}^{(vib)}$, electron-vibration coupling contribution $\mathcal{H}_{mol}^{(e-vib)}$, and the electron-spin coupling contribution $\mathcal{H}_{mol}^{(e-spin)}$. The electronic part of the multilevel molecular Hamiltonian $\mathcal{H}_{mol}^{(e)}$ consists in a summation over all spins and energy levels (labeled as m) of the on site energy represented by parameter $\epsilon_{m\sigma}$, hopping between levels represented by parameter $\gamma_{m_1 m_2}$ and on site electron-electron interaction represented by the parameter U_m. The vibrational part of the molecular Hamiltonian $\mathcal{H}_{mol}^{(vib)}$, sums over each single vibrational mode $\hbar \omega_m$ coupled to each of the several m energy levels of the molecule. In the case in which all energy levels coupled to the same single vibrational mode, the Hamiltonian $\mathcal{H}_{mol}^{(vib)}$ consists in just one term $\hbar \omega_0 a^{\dagger} a$. Each of these vibrational modes couples to electrons from each of the energy levels, in-

teraction which is represented by the model Hamiltonian $\mathcal{H}_{mol}^{(e-vib)}$ where the interaction strength is represented by λ_m (For meaninful phenomenological interpretation of this parameter, see discussion presented in the previous section). Lastly, the coupling between the level electrons and a single localized spin moment $S_m(t)$ is given by the model Hamiltonian $\mathcal{H}_{mol}^{(e-spin)}$, and the parameter J_m represents the Kondo interaction. The latter Hamiltonian, is known as the spin-spin Hamiltonian in the Kondo limit, where the localized spin moment is a mean field formed by the contribution of individual localized electrons in rare earth or transition metal molecular magnets (magnetic units). The operators $d_{m\sigma}^{\dagger}$ and $d_{m\sigma}$ create and annihilate a single electron in the level ϵ_m with spin σ, respectively. The operators $c_{k,q\sigma}^{\dagger}$ and $c_{k,q\sigma}$ create and annihilate a single electron in the left (right) lead with wave-vector k (q) and spin σ respectively. The hybridization or tunneling amplitude and its conjugate amplitude between the left (right) lead and the $m-th$ molecular electronic level are denoted as $V_{mk\sigma}$ and $V_{mk\sigma}^{*}$ ($V_{mq\sigma}$ and $V_{mq\sigma}^{*}$) respectively. The operator $n_{m\sigma} = d_{m\sigma}^{\dagger}d_{m\sigma}$ is known as the particle number operator, which has the number of particles in level ϵ_m as an associated eigenvalue. Lastly, the Bosonic operators $a_m^{\dagger}$ and a_m respectively create and annihilate a phonon mode with frequency ω_m. In the context of the work presented here, and for algebraic simplicity, I only consider a single phonon mode equally coupled to all electronic levels, which will simplify the factorization of the total Green's function in electronic and vibrational components (correction). This assumption is rather supported up to some reasonable doubt by the experiment reported by Svetlana Klyatskaya and collaborators in [50] where discrete phonon density of states was engineered, as well supported by previous theoretical work reported by B. Lassagne [57].

6.3 Factorization of the Electronic and Vibronic Contributions of the Molecular Green's Function: Lang-Firsov

The Green's function for the system described by the model Hamiltonian given expression 6.31, is a challenging problem, mainly due to the representation of the Fermionic and Bosonic degrees of freedom, which will yield no possible Diagonalization with conventional methods. The Lang-Firsov transformation, is a useful map that, by canonically[2] transforming the model Hamiltonian of interest, decouples Fermionic and Bosonic degrees of freedom present in the model, at the stake of renormalizing

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[2]Canonical Transformations transform the structure of a given model, leaving its consequences unchanged.

some of its parameters, for instance the energy levels ϵ and an the on-site electron-electron interaction U_m. This transformation that was initially proposed in [116], has been extensively used in exactly solvable models in condensed matter [74], in studying inelastic effects in electron transport [120], [64], set-ups resembling electron-paramagnetic spectroscopy, direct spin-phonon decoupling [55], among others. Particularly, I will use the Lang-Firsov transformation in paper II to decoupled Bosonic and Fermionic degrees of freedom, to express the total Green's function as as the product of the electronic Green's function and the Phonon correlation function, which will later be derived in detailed. Once this approximation has been made, the effect of the phonon mode on the uniaxial magnetic anisotropy can be evaluated using the non-equilibrium effective exchange formulas given by [102].

To illustrate the use of this canonical transformation, I will considered to single spin examples and discussed the effective renormalization of the energy level of the molecule and the electron-electron correlation.

6.3.1 Spin Independent Models

A single spin coupled to a vibrating electronic level (Quantum Dot) is described by the following Hamiltonian:

$$\mathcal{H}_{QD} = \sum_{\sigma} \epsilon_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + U n_{\uparrow} n_{\downarrow} + \hbar \omega_0 a^{\dagger} a + \sum_{\sigma} \lambda d_{\sigma}^{\dagger} d_{\sigma} \left(a^{\dagger} + a \right), \qquad (6.38)$$

and for simplicity, for the mean time, I will ignore the on-site interactions, which then simplifies the above Hamiltonian to:

$$\mathcal{H}_{QD} = \sum_{\sigma} \epsilon_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + \hbar \omega_0 a^{\dagger} a + \sum_{\sigma} \lambda d_{\sigma}^{\dagger} d_{\sigma} \left(a^{\dagger} + a \right), \qquad (6.39)$$

where the parameters in the model Hamiltonias given by expressions 6.38 and 6.39 are defined according to the logic described in the previous section. Moreover, A transformed Hamiltonian $\overline{\mathcal{H}}_{QD}$ can be defined with the aid of the transformation $\overline{\mathcal{H}}_{QD} = e^{S} \mathcal{H}_{QD} e^{-S}$ (A canonical Transformation), by the following expression:

$$\overline{\mathcal{H}}_{QD} = e^{S} \mathcal{H}_{QD} e^{-S},$$
$$= \mathcal{H}_{QD} + [S, \mathcal{H}_{QD}] + \frac{1}{2!} [S, [S, \mathcal{H}_{QD}]] + \frac{1}{3!} [S, [S, [S, [S, \mathcal{H}_{QD}]]]] + \cdots,$$

$$(6.40)$$

where the generator of the transformation denoted by S is given by:

$$S = \sum_{\sigma} \frac{\lambda}{\hbar \omega_0} d_{\sigma}^{\dagger} d_{\sigma} \left(a^{\dagger} - a \right). \qquad (6.41)$$

To illustrate the transformation given by expression 6.40 in a rather simple and straightforward way, let's consider a spin independent generator,and the evaluate the first three terms in expression 6.40 as the other vanish. This evaluation yields:

$$[S, \mathcal{H}_{QD}] = -\frac{2\lambda^2}{\hbar\omega_0} d^\dagger d - \lambda d^\dagger d \left(a^\dagger + a\right), \qquad (6.42)$$

$$[S, [S, \mathcal{H}_{QD}]] = \frac{2\lambda^2}{\hbar\omega_0} d^\dagger d, \qquad (6.43)$$

$$[S, [S, [S, \mathcal{H}_{QD}]]] = 0. \qquad (6.44)$$

Replacing expressions 6.42, 6.43 and 6.44 into expression 6.39, the renormalized and decoupled Hamiltonian reads now:

$$\overline{\mathcal{H}}_{QD} = \left(\epsilon - \frac{\lambda^2}{\hbar\omega_0}\right) d^\dagger d + \hbar\omega_0 a^\dagger a = \bar{\epsilon} d^\dagger d + \hbar\omega_0 a^\dagger a, \qquad (6.45)$$

where the energy of the dot is re-normalized to give: $\bar{\epsilon} = \epsilon - \frac{\lambda^2}{\hbar\omega_0}$. This renormalization will later be shown to induced an effective multilevel dot effect in the system as described in [74], [68].

6.3.2 Spin Dependent Models

Now, consider the generator S given by:

$$S = \frac{\lambda}{\hbar\omega_0} \sum_\sigma d_\sigma^\dagger d_\sigma \left(a^\dagger - a\right). \qquad (6.46)$$

Now, consider the quantum dot Hamiltonian $\mathcal{H}_{Q.D}$ given by:

$$\mathcal{H}_{Q.D} = \sum_\sigma \epsilon_\sigma d_\sigma^\dagger d_\sigma + U n_\uparrow n_\downarrow + \hbar\omega_0 a^\dagger a + \lambda \sum_\sigma d_\sigma^\dagger d_\sigma \left(a^\dagger + a\right) + J s_e \cdot S. \qquad (6.47)$$

where $s_e = \sum_{\sigma\sigma'} d_\sigma^\dagger \sigma_{\sigma\sigma'} d_{\sigma'}$ is the electron spin operator. The latter is used, to re-write the Hamiltonian from expression 6.47 as follows:

$$\mathcal{H}_{Q.D} = \sum_\sigma \epsilon_\sigma d_\sigma^\dagger d_\sigma + U n_\uparrow n_\downarrow + \hbar\omega_0 a^\dagger a$$
$$+ \lambda \sum_\sigma d_\sigma^\dagger d_\sigma \left(a^\dagger + a\right) + J \sum_{\sigma\sigma'} \sigma_{\sigma\sigma'} \cdot S d_\sigma^\dagger d_{\sigma'}. \qquad (6.48)$$

As before, I want to show how the Bosonic-Fermionic decoupling takes, from the transformation specified by:

$$\overline{\mathcal{H}}_{Q.D} = e^S \mathcal{H}_{Q.D} e^{-S}$$
$$= \mathcal{H}_{Q.D} + [S, \mathcal{H}_{Q.D}] + \frac{1}{2!} [S, [S, \mathcal{H}_{Q.D}]] + \frac{1}{3!} [S, [S, [S, \mathcal{H}_{Q.D}]]] + \cdots. \qquad (6.49)$$

To do so, the following commutators were evaluated:

$$[S, \mathcal{H}_{Q.D}] = -\lambda \sum_\sigma d_\sigma^\dagger d_\sigma \left(a^\dagger + a \right) - \frac{2\lambda^2}{\hbar\omega_0} \sum_\sigma n_\sigma - \frac{4\lambda^2}{\hbar\omega_0} n_\uparrow n_\downarrow,$$

(6.50)

$$[S, [S, \mathcal{H}_{Q.D}]] = \frac{2\lambda^2}{\hbar\omega_0} \sum_\sigma n_\sigma + \frac{4\lambda^2}{\hbar\omega_0} n_\uparrow n_\downarrow,$$

(6.51)

$$[S, [S, [S, \mathcal{H}_{Q.D}]]] = 0,$$

(6.52)

and after replacing all three of these expressions, namely equations 6.50, 6.51 and 6.52 in equation 6.49, the decoupled Hamiltonian reads:

$$\overline{\mathcal{H}}_{Q.D} = \sum_\sigma \left(\epsilon_\sigma - \frac{\lambda^2}{\hbar\omega_0} \right) d_\sigma^\dagger d_\sigma + \left(U - \frac{2\lambda^2}{\hbar\omega_0} \right) n_\uparrow n_\downarrow + \hbar\omega_0 a^\dagger a + J s_e \cdot S,$$

$$= \sum_\sigma \overline{\epsilon}_\sigma d_\sigma^\dagger d_\sigma + \overline{U} n_\uparrow n_\downarrow + \hbar\omega_0 a^\dagger a + J s_e \cdot S.$$

(6.53)

In the above expression I have introduced the renormalized parameters for the dot energy $\overline{\epsilon}_\sigma$ and for the interaction strength $\overline{U}$ given by:

$$\overline{\epsilon}_\sigma = \epsilon_\sigma - \frac{\lambda^2}{\hbar\omega_0} \qquad \overline{U} = U - \frac{2\lambda^2}{\hbar\omega_0}.$$

(6.54)

The consequences of the on-site interaction renormalization are discussed latter in the chapter, which are of great physical relevance and will provide insightful intuition with respect to the effect of electron-phonon coupling in the nature of electron-electron interaction in the system.

6.3.3 Electron-Phonon Decoupling in Multilevel Molecules

For more complex molecular realization than just a spin moment and an electronic level, it becomes impractical to implement the Lang-Firsov transformation as done for the spin-independent and the spin-dependent cases illustrated in the previous two sections. A way out, is to transform individual electron operators just, and then replace the new version of the transformed single particle electron operators into the Hamiltonian of interest. For the case that occupies this section, I make the following change of notation $d_{m\sigma}(t) \to \overline{d}_{m\sigma}(t)$ and $d_{n\sigma'}^\dagger(t) \to \overline{d}^\dagger_{n\sigma'}(t)$, and then, After Applying the Lang-Firsov transformation to individual operators $\overline{d}_{m\sigma}(t)$ and $\overline{d}^\dagger_{n\sigma'}(t)$ gives:

$$\overline{d}_{m\sigma}(t) \to d_{m\sigma}(t)\chi_m(t); \quad \overline{d}^\dagger_{n\sigma'}(t) \to d^\dagger_{n\sigma'}(t)\chi_n^\dagger(t),$$

where now the operators $d_{m\sigma}(t)$ and $d_{n\sigma'}^\dagger(t)$ are the single electron operator whose dynamical evolution is then independent of the vibrational

degrees degrees of freedom. Moreover, operators $\chi_m(t)$ and $\chi_n^{\dagger}(t)$, are known as momentum shift operators and emerge as a consequence of applying the Lang-Firsov transformation to individual electron operators. From ref. [fransson book], this operators are given by $\chi_m(t) = e^{-\frac{\lambda_m}{\hbar\omega_m}\left(a_m^{\dagger} - a_m\right)}$ and $\chi_n^{\dagger}(t) = e^{\frac{\lambda_n}{\hbar\omega_n}\left(a_n^{\dagger} - a_n\right)}$ [mahan, fransson book]. Following this line of reasoning, the full Green's function can be transformed and factorized as follows:

$$\overline{G}_{mn\sigma\sigma'}(t,t') = -\frac{i}{\hbar}\left\langle T_K \overline{d}_{m\sigma}(t)\overline{d^{\dagger}}_{n\sigma'}(t')\right\rangle \rightarrow$$

$$\overline{G}_{mn\sigma\sigma'}(t,t') = -\frac{i}{\hbar}\left\langle T_K d_{m\sigma}(t)\chi_m(t)d^{\dagger}_{n\sigma'}(t')\chi_n^{\dagger}(t')\right\rangle$$

$$\approx -\frac{i}{\hbar}\left\langle T_K d_{m\sigma}(t)d^{\dagger}_{n\sigma'}(t')\right\rangle\left\langle \chi_m(t)\chi_n^{\dagger}(t')\right\rangle, \quad (6.55)$$

and by defining:

$$G_{mn\sigma\sigma'}(t,t') = -\frac{i}{\hbar}\left\langle T_K d_{m\sigma}(t)d^{\dagger}_{n\sigma'}(t')\right\rangle;$$

$$A_{mn}(t,t') = \left\langle \chi_m(t)\chi_n^{\dagger}(t')\right\rangle, \quad (6.56)$$

The following factorization applies:

$$\overline{G}_{mn\sigma\sigma'}(t,t') \approx G_{mn\sigma\sigma'}(t,t')A_{mn}(t,t'), \quad (6.57)$$

where $G_{mn\sigma\sigma'}(t,t')$ is the renormalized electronic Green's function and $A_{mn}(t,t')$ is the vibrational correlation function, which accounts for the corrections of the electronic propagator due to electron-phonon coupling.

The renormalized model Hamiltonian now reads:

$$\overline{\mathcal{H}} = \overline{\mathcal{H}}_{Leads} + \overline{\mathcal{H}}_T + \overline{\mathcal{H}}_{mol}^{(e)} + \overline{\mathcal{H}}_{mol}^{(vib)} + \overline{\mathcal{H}}_{mol}^{(e-vib)} + \overline{\mathcal{H}}_{mol}^{(spin)},$$

(6.58)

$$\overline{\mathcal{H}}_{Leads} = \mathcal{H}_{Leads} = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \sum_{q\sigma} \epsilon_{q\sigma} c_{q\sigma}^\dagger c_{q\sigma}, \qquad (6.59)$$

$$\overline{\mathcal{H}}_T = \sum_{mk\sigma} V_{mk\sigma} c_{k\sigma}^\dagger d_{m\sigma} \chi_m + V_{mk\sigma}^* d_{m\sigma}^\dagger \chi_m^\dagger c_{k\sigma}$$
$$+ \sum_{mq\sigma} V_{mq\sigma} c_{q\sigma}^\dagger d_{m\sigma} \chi_m + V_{mq\sigma}^* d_{m\sigma}^\dagger \chi_m^\dagger c_{q\sigma}, \qquad (6.60)$$

$$\overline{\mathcal{H}}_{mol}^{(e)} = \sum_{m\sigma} \bar{\epsilon}_{m\sigma} d_{m\sigma}^\dagger d_{m\sigma} + \sum_{m_1 m_2 \sigma} \gamma_{m_1 m_2} d_{m_1 \sigma}^\dagger d_{m_2 \sigma}$$
$$+ \sum_m \overline{U}_m n_{m\uparrow} n_{m\downarrow}, \qquad (6.61)$$

$$\overline{\mathcal{H}}_{mol}^{(vib)} = \sum_m \hbar \omega_m a_m^\dagger a_m, \qquad (6.62)$$

$$\overline{\mathcal{H}}_{mol}^{(spin)} = \sum_{m\sigma_1 \sigma_2} J_m d_{m\sigma_1}^\dagger \boldsymbol{\sigma}_{\sigma_1 \sigma_2} d_{m\sigma_2} \cdot \boldsymbol{S}_m(t). \qquad (6.63)$$

From expression 6.60, do note that the price paid for decoupling the electronic and vibrational degrees of freedom is, the inclusion of an inelastic component in the tunneling Hamiltonian. The work that concerns this thesis, makes the single phonon mode assumption as well as the weak electron-phonon coupling one ($\chi \approx 1$ and $\chi^\dagger \approx 1$), which leads to the following renormalized tunneling Hamiltonian:

$$\overline{\mathcal{H}}_T = \sum_{mk\sigma} V_{mk\sigma} c_{k\sigma}^\dagger d_{m\sigma} + V_{mk\sigma}^* d_{m\sigma}^\dagger c_{k\sigma}$$
$$+ \sum_{mq\sigma} V_{mq\sigma} c_{q\sigma}^\dagger d_{m\sigma} + V_{mq\sigma}^* d_{m\sigma}^\dagger c_{q\sigma}, \qquad (6.64)$$

and the free phonon Hamiltonian now reads:

$$\overline{\mathcal{H}}_{mol}^{(vib)} = \hbar \omega_0 a^\dagger a, \qquad (6.65)$$

and as a consequence, the phonon correlation function is now an scalar function given by $A(t,t') = \left\langle \chi(t) \chi^\dagger(t') \right\rangle$, which will be calculated in the next section. A final comment is needed and is, that when the weak-coupling limit approximation is assumed, and the molecule is then connected to a bath as in the case for scanning tunneling microscopy experiments, restrictions proposed by Hewson and Newns are imposed on the parameters λ and ω_0, with respect to the coupling strength to the reservoir [121].

6.4 Derivation of the Phonon Correlation Function

In this section, the task is to evaluate the expectation value on the vibration space denoted as: $A(t, t') = \langle \chi(t) \chi^\dagger(t') \rangle$. The present exposition is quite specific and detailed, with the aim of leading to the results derived in chapter 4 of ref. [?], where several enlightening steps are missing.

I will start by recalling that the vibrational operators $\chi(t)$ and $\chi^\dagger(t')$ are given by [fransson book, mahan]:

$$\chi(t) = e^{i\omega_0 a^\dagger a t} \chi e^{-i\omega_0 a^\dagger a t} = e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}(a^\dagger - a)} e^{-i\omega_0 a^\dagger a t} \qquad (6.66)$$

$$\chi^\dagger(t') = e^{i\omega_0 a^\dagger a t'} \chi^\dagger e^{-i\omega_0 a^\dagger a t'} = e^{i\omega_0 a^\dagger a t'} e^{\frac{\lambda}{\hbar\omega_0}(a^\dagger - a)} e^{-i\omega_0 a^\dagger a t'} \qquad (6.67)$$

where $\chi = e^{-\frac{\lambda}{\hbar\omega_0}(a^\dagger - a)}$ and
$\chi^\dagger = e^{\frac{\lambda}{\hbar\omega_0}(a^\dagger - a)}$, and the expectation value $\langle \chi(t) \chi^\dagger(t') \rangle$ in the weak coupling regime (for small λ) can be calculated as a thermal average through:

$$A(t, t') = \langle \chi(t) \chi^\dagger(t') \rangle = \frac{1}{\sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} | n \rangle} \sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} \chi(t) \chi^\dagger(t') | n \rangle.$$

$$(6.68)$$

From expression 6.68, there are two important calculations to perform, one is $\sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} | n \rangle$ and the other one is $\sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} \chi(t) \chi^\dagger(t') | n \rangle$. The first calculation reads:

$$\sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} | n \rangle = \sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 n} | n \rangle = \sum_{n=0}^{+\infty} e^{-n\beta\hbar\omega_0},$$

$$= \sum_{n=0}^{+\infty} \left(1 + e^{-\beta\hbar\omega_0} + e^{-2\beta\hbar\omega_0} + e^{-3\beta\hbar\omega_0} + \cdots \right),$$

$$= \frac{1}{1 - e^{-\beta\hbar\omega_0}} = \frac{e^{\beta\hbar\omega_0}}{e^{\beta\hbar\omega_0} - 1},$$

hence giving:

$$\sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} | n \rangle = e^{\beta\hbar\omega_0} n_B(\omega_0), \qquad (6.69)$$

where $n_B(\omega_0) = \frac{1}{e^{\beta\hbar\omega_0} - 1}$ is the Bose-Einstein distribution. The second important calculation to evaluate, is the expectation value given by equation 6.68, which requires the calculation of $\sum_{n=0}^{+\infty} \langle n | e^{-\beta\hbar\omega_0 a^\dagger a} \chi(t) \chi^\dagger(t') | n \rangle$. To

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proceed, let's first evaluate the term $\chi(t)$ in the following form:

$$\chi(t) = e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}\left(a^\dagger - a\right)} e^{-i\omega_0 a^\dagger a t},$$

$$= e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}a^\dagger} e^{\frac{\lambda}{\hbar\omega_0}a} e^{-\frac{1}{2}\left[-\frac{\lambda}{\hbar\omega_0}a^\dagger, \frac{\lambda}{\hbar\omega_0}a\right]} e^{-i\omega_0 a^\dagger a t},$$

$$= e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}a^\dagger} e^{\frac{\lambda}{\hbar\omega_0}a} e^{-\frac{1}{2}\left(-\frac{\lambda}{\hbar\omega_0}\right)\left(\frac{\lambda}{\hbar\omega_0}\right)\left[a^\dagger, a\right]} e^{-i\omega_0 a^\dagger a t},$$

finally writing $\chi(t)$ as:

$$\chi(t) = e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2} e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}a^\dagger} e^{\frac{\lambda}{\hbar\omega_0}a} e^{-i\omega_0 a^\dagger a t}. \qquad (6.70)$$

The above expression can be further simplified by introducing an identity operator (red):

$$\chi(t) = e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2} e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}a^\dagger} \textcolor{red}{e^{-i\omega_0 a^\dagger a t} e^{i\omega_0 a^\dagger a t}} e^{\frac{\lambda}{\hbar\omega_0}a} e^{-i\omega_0 a^\dagger a t}. \qquad (6.71)$$

The above expression has some complexity associated with it, with regards to the evaluation of the product $\chi(t)\chi^\dagger(t')$. In order to re-write the above equation in a more orthodox way, the former is split into three parts; the constant amplitude $e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2}$ (in black below), the operator $e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}a^\dagger} e^{-i\omega_0 a^\dagger a t}$ (in red below) and the operator $e^{i\omega_0 a^\dagger a t} e^{\frac{\lambda}{\hbar\omega_0}a} e^{-i\omega_0 a^\dagger a t}$ (in blue below), and proceed in the simplification as follows:

$$\chi(t) = e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2} \textcolor{red}{e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0}a^\dagger} e^{-i\omega_0 a^\dagger a t}} \textcolor{blue}{e^{i\omega_0 a^\dagger a t} e^{\frac{\lambda}{\hbar\omega_0}a} e^{-i\omega_0 a^\dagger a t}}$$

$$= e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2} \textcolor{red}{h(t)}\textcolor{blue}{k(t)}. \qquad (6.72)$$

To completely specify $\chi(t)$, functions $h(t)$ and $k(t)$ must be calculated. Let's proceed with the evaluation of $h(t)$:

$$h(t) = e^{i\omega_0 a^\dagger a t} e^{-\frac{\lambda}{\hbar\omega_0} a^\dagger} e^{-i\omega_0 a^\dagger a t} = e^{i\omega_0 a^\dagger a t} \left(\sum_{k=0}^{+\infty} \frac{1}{k!} \left[-\frac{\lambda}{\hbar\omega_0} a^\dagger \right]^k \right) e^{-i\omega_0 a^\dagger a t},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[-\frac{\lambda}{\hbar\omega_0} \right]^k e^{i\omega_0 a^\dagger a t} \left[a^\dagger \right]^k e^{-i\omega_0 a^\dagger a t},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[-\frac{\lambda}{\hbar\omega_0} \right]^k \left(\left[a^\dagger \right]^k + i k \omega_0 t \left[a^\dagger \right]^k + \frac{1}{2!} (i\omega_0 t)^2 (k)^2 \left[a^\dagger \right]^k + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[-\frac{\lambda}{\hbar\omega_0} \right]^k \left(\left[a^\dagger \right]^k + i k \omega_0 t \left[a^\dagger \right]^k + \frac{1}{2!} (i k \omega_0 t)^2 \left[a^\dagger \right]^k + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[-\frac{\lambda}{\hbar\omega_0} \right]^k \left[a^\dagger \right]^k \left(1 + i k \omega_0 t + \frac{1}{2!} (i k \omega_0 t)^2 + \frac{1}{3!} (i k \omega_0 t)^3 + \cdots \right),$$

arriving finally at the following expression:

$$h(t) = \sum_{k=0}^{+\infty} \frac{1}{k!} \left[-\frac{\lambda a^\dagger}{\hbar\omega_0} e^{i\omega_0 t} \right]^k = exp\left(-\frac{\lambda a^\dagger}{\hbar\omega_0} e^{i\omega_0 t} \right). \qquad (6.73)$$

Now let's calculate $k(t)$:

$$k(t) = e^{i\omega_0 a^\dagger a t} e^{\frac{\lambda}{\hbar\omega_0} a} e^{-i\omega_0 a^\dagger a t} = e^{i\omega_0 a^\dagger a t} \left(\sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda}{\hbar\omega_0} a \right]^k \right) e^{-i\omega_0 a^\dagger a t},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda}{\hbar\omega_0} \right]^k e^{i\omega_0 a^\dagger a t} a^k e^{-i\omega_0 a^\dagger a t},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda}{\hbar\omega_0} \right]^k \left(a^k + i\omega_0 t \left[a^\dagger a, a^k \right] + \frac{1}{2!} (i\omega_0 t)^2 \left[a^\dagger a, \left[a^\dagger a, a^k \right] \right] + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda}{\hbar\omega_0} \right]^k \left(a^k + i\omega_0 t (-k) a^k + \frac{1}{2!} (i\omega_0 t)^2 \left[a^\dagger a, (-k) a^k \right] + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda}{\hbar\omega_0} \right]^k \left(a^k + (-i k \omega_0 t) a^k + \frac{1}{2!} (i\omega_0 t)^2 (-k)^2 a^k + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda}{\hbar\omega_0} \right]^k a^k \left(1 + (-i k \omega_0 t) + \frac{1}{2!} (-i k \omega_0 t)^2 + \frac{1}{3!} (-i k \omega_0 t)^3 + \cdots \right),$$

then, I finally write the function $k(t)$ as shown below:

$$k(t) = \sum_{k=0}^{+\infty} \frac{1}{k!} \left[\frac{\lambda a}{\hbar\omega_0} e^{-i\omega_0 t} \right]^k = exp\left(\frac{\lambda a}{\hbar\omega_0} e^{-i\omega_0 t} \right). \qquad (6.74)$$

Now, replacing expressions 6.73 and 6.74 into expression 6.72

$$\chi(t) = e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2} exp\left(-\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t}\right) exp\left(\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t}\right), \qquad (6.75)$$

and from the above result, $\chi^\dagger(t')$ reads:

$$\chi^\dagger(t') = e^{-\frac{1}{2}\left(\frac{\lambda}{\hbar\omega_0}\right)^2} exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right) exp\left(-\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t'}\right). \qquad (6.76)$$

From expressions 6.75 and 6.76, the product $\chi(t)\chi^\dagger(t')$ reads:

$$\chi(t)\chi^\dagger(t') = e^{-\left(\frac{\lambda}{\hbar\omega_0}\right)^2} exp\left(-\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t}\right)$$

$$\times exp\left(\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t}\right) exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right) exp\left(-\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t'}\right).$$
$$(6.77)$$

In the above expression, the term in red labeled as $f(t,t')$ can be further-more elaborated as follows:

$$f(t,t') = exp\left(\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t}\right) exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right),$$

$$= exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right)\left[exp\left(-\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right) exp\left(\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t}\right) exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right)\right],$$

$$= exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right)\left[e^{\Lambda \boldsymbol{a}^\dagger}e^{\Lambda' \boldsymbol{a}}e^{-\Lambda \boldsymbol{a}^\dagger}\right] = exp\left(\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}\right)\left[e^{\Lambda \Lambda'}e^{\Lambda' \boldsymbol{a}}\right],$$

$$= e^{\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}}\left[e^{-\left(-\frac{\lambda}{\hbar\omega_0}e^{i\omega_0 t'}\right)\left(\frac{\lambda}{\hbar\omega_0}e^{-i\omega_0 t}\right)}e^{\frac{\lambda}{\hbar\omega_0}e^{-i\omega_0 t}\boldsymbol{a}}\right]$$

$$= e^{\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}}e^{\left(\frac{\lambda}{\hbar\omega_0}\right)^2 e^{i\omega_0 t'}e^{-i\omega_0 t}}e^{\frac{\lambda}{\hbar\omega_0}e^{-i\omega_0 t}\boldsymbol{a}},$$

therefore arriving at the following result:

$$f(t,t') = e^{\left(\frac{\lambda}{\hbar\omega_0}\right)^2 e^{-i\omega_0(t-t')}}e^{\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}}e^{\frac{\lambda}{\hbar\omega_0}e^{-i\omega_0 t}\boldsymbol{a}}, \qquad (6.78)$$

where in the above elaboration we have use expression 11.1.
By replacing the above expression back in expression 6.77,
the term $\chi(t)\chi^\dagger(t')$ reads:

$$\chi(t)\chi^\dagger(t') = e^{-\left(\frac{\lambda}{\hbar\omega_0}\right)^2}e^{-\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t}}e^{\left(\frac{\lambda}{\hbar\omega_0}\right)^2 e^{-i\omega_0(t-t')}}e^{\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}}e^{\frac{\lambda}{\hbar\omega_0}e^{-i\omega_0 t}\boldsymbol{a}}e^{-\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t'}},$$

$$= e^{-\left(\frac{\lambda}{\hbar\omega_0}\right)^2}e^{\left(\frac{\lambda}{\hbar\omega_0}\right)^2 e^{-i\omega_0(t-t')}}e^{\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t'}}e^{-\frac{\lambda \boldsymbol{a}^\dagger}{\hbar\omega_0}e^{i\omega_0 t}}e^{-\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t'}}e^{\frac{\lambda \boldsymbol{a}}{\hbar\omega_0}e^{-i\omega_0 t}},$$

$$= e^{-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left(1-e^{-i\omega_0(t-t')}\right)}e^{\frac{\lambda}{\hbar\omega_0}\left(e^{i\omega_0 t'}-e^{i\omega_0 t}\right)\boldsymbol{a}^\dagger}e^{-\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\boldsymbol{a}},$$

the above result can then be replaced into expression 6.68, to give the following phonon correlation function:

$$A(t,t') = \frac{e^{-\beta\hbar\omega_0}}{n_B(\omega_0)} e^{-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left(1-e^{-i\omega_0(t-t')}\right)}$$

$$\times \sum_{n=0}^{+\infty} e^{-\beta\hbar\omega_0 n} \langle n| e^{\frac{\lambda}{\hbar\omega_0}\left(e^{i\omega_0 t'}-e^{i\omega_0 t}\right)a^\dagger} e^{-\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)a} |n\rangle.$$

(6.79)

The expectation value in the above expression can be calculated using the result derived in expression 11.8, which yields the following simplification for the Kernel function $A(t,t')$:

$$A(t,t') = \frac{e^{-\beta\hbar\omega_0}}{n_B(\omega_0)} e^{-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left(1-e^{-i\omega_0(t-t')}\right)} \sum_{n=0}^{+\infty} e^{-\beta\hbar\omega_0 n} \mathcal{L}_n\left(\left|\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\right|^2\right),$$

(6.80)

where $\mathcal{L}_n(x)$ is the Laguerre polynomial of n-th order. One of the properties of the Laguerre polynomials reads:

$$\sum_{n=0}^{+\infty} t^n \mathcal{L}_n(x) = \frac{1}{1-t} e^{-\frac{tx}{1-t}}.$$

From such unique characteristic, I can pursue a further simplification for the term:

$$\sum_{n=0}^{+\infty} e^{-\beta\hbar\omega_0 n} \mathcal{L}_n\left(\left|\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\right|^2\right),$$

Which is performed from the procedure shown below (where $t = e^{-\beta\hbar\omega_0}$ and $x = \left|\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\right|^2$):

$$\sum_{n=0}^{+\infty} e^{-\beta\hbar\omega_0 n} \mathcal{L}_n\left(\left|\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\right|^2\right)$$

$$= \sum_{n=0}^{+\infty} \left[e^{-\beta\hbar\omega_0}\right]^n \mathcal{L}_n\left(\left|\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\right|^2\right),$$

$$= \frac{1}{1-e^{-\beta\hbar\omega_0}} exp\left[-\frac{e^{-\beta\hbar\omega_0}\left|\frac{\lambda}{\hbar\omega_0}\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\right|^2}{1-e^{-\beta\hbar\omega_0}}\right],$$

$$= \frac{e^{\beta\hbar\omega_0}}{e^{\beta\hbar\omega_0}-1} exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \frac{\left(e^{-i\omega_0 t'}-e^{-i\omega_0 t}\right)\left(e^{i\omega_0 t'}-e^{i\omega_0 t}\right)}{e^{\beta\hbar\omega_0}-1}\right],$$

$$= e^{\beta\hbar\omega_0} n_B(\omega_0) exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2 n_B(\omega_0)\left(2-e^{-i\omega_0(t-t')}-e^{i\omega_0(t-t')}\right)\right],$$

then $A(t,t')$ furthermore shrinks as follows:

$$A(t,t') = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left(1-e^{-i\omega_0}(t-t')\right)\right]\frac{e^{-\beta\hbar\omega_0}}{n_B(\omega_0)}e^{\beta\hbar\omega_0}n_B(\omega_0)$$

$$\times exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2 n_B(\omega_0)\left(2-e^{-i\omega_0(t-t')}-e^{i\omega_0(t-t')}\right)\right],$$

$$= exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left(1-e^{-i\omega_0}(t-t')\right)\right]$$

$$\times exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left(2-e^{-i\omega_0(t-t')}-e^{i\omega_0(t-t')}\right)n_B(\omega_0)\right],$$

$$(6.81)$$

then, the phonon kernel finally reads:

$$A(t,t') = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left((1+n_B(\omega_0))\left(1-e^{-i\omega_0(t-t')}\right)+n_B(\omega_0)\left(1-e^{i\omega_0(t-t')}\right)\right)\right].$$

$$(6.82)$$

6.5 Relevant Comments About the Phonon Correlation Function

The kernel derived in the previous section, namely $A(t,t')$ plays the role of a correlation function that renormalizes effectively the electronic Green's function as it will be shown in the next section, though is not a phonon Green's function, just a correction. It will be shown later, as it is shown in paper II, that the effect of this correlation function of the electron becomes noticeable when the electron-phonon interaction is large in the range of the restriction imposed by the Lang-Firsov transformation [121], [93], [68] and mainly when the phonon mode of frequency ω_0 is excited by temperature. At low temperatures, the effects of the phonon correlation function, for instance the side bands in the density of states, are screened by the broadening of the electronic levels due to their coupling with the metallic leads. Moreover, the latter argument also suggests, that for spin polarized leads where the broadening electronic level is different for spin up and for spin down, the excited phonons will modulate largely the density of states for one spin specie much more than the other (See paper II). In the next section, the net effect of the Phonon correlation function on the electronic Green's function will be carefully derived, and few examples on the signatures of this effect on a physical system will be briefly discussed, more specifically for the single ion anisotropy case presented in paper II.

6.6 Vibrational Renormalization of the Electronic Green's Function

The renormalized Electronic Green's function for the physics described by an arbitrary Hamiltonian $\mathcal{H}$ reads:

$$G_{\sigma\sigma'}(t,t') = K_{\sigma\sigma'}(t,t')A(t,t'), \qquad (6.83)$$

with its Fourier transformation given by:

$$G_{\sigma\sigma'}(\omega) = \int K_{\sigma\sigma'}(t-t')A(t-t')e^{i\omega(t-t')}d(t-t'). \qquad (6.84)$$

To fully develop the above expression, let's look first at $A(t-t')$ in the following way:

$$A(t-t') = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\right)^2\left((1+n_B(\omega_0))\left(1-e^{-i\omega_0(t-t')}\right)+n_B(\omega_0)\left(1-e^{i\omega_0(t-t')}\right)\right)\right],$$

which after a simple expansion posterior to the evaluation of the present algebraic products and by factorizing $n_B(\omega_0)$ to the right, I arrived at the following result:

$$A(\tau) = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2\right]$$

$$\times exp\left[\left(\frac{\lambda}{\hbar\omega_0}\right)^2 n_B(\omega_0)\left(e^{-i\omega_0\tau}\left(\frac{n_B(\omega_0)+1}{n_B(\omega_0)}\right)+e^{i\omega_0\tau}\right)\right],$$

and by recalling that:

$$\frac{n_B(\omega_0)+1}{n_B(\omega_0)} = \frac{\frac{1}{e^{\beta\hbar\omega_0}-1}+1}{\frac{1}{e^{\beta\hbar\omega_0}-1}} = \frac{\frac{e^{\beta\hbar\omega_0}-1+1}{e^{\beta\hbar\omega_0}-1}}{\frac{1}{e^{\beta\hbar\omega_0}-1}} = e^{\beta\hbar\omega_0} \Rightarrow \sqrt{\frac{n_B(\omega_0)+1}{n_B(\omega_0)}} = e^{\beta\hbar\omega_0}/2,$$

I write:

$$A(\tau) = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2\right]exp\left[\left(\frac{\lambda}{\hbar\omega_0}\right)^2 n_B(\omega_0)\left(e^{\beta\hbar\omega_0}e^{-i\omega_0\tau}+e^{i\omega_0\tau}\right)\right].$$

$$(6.85)$$

A step further is take by noting that the term $n_B(\omega_0)e^{\beta\hbar\omega_0/2}$ reads:

$$n_B(\omega_0)e^{\beta\hbar\omega_0/2} = n_B(\omega_0)\sqrt{\frac{n_B(\omega_0)+1}{n_B(\omega_0)}} = \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)},$$

and after manipulating the term $e^{\beta\hbar\omega_0}e^{-i\omega_0\tau}+e^{i\omega_0\tau}$ in expression 6.85 such that:

$$e^{\beta\hbar\omega_0}e^{-i\omega_0\tau}+e^{i\omega_0\tau} = e^{\beta\hbar\omega_0/2}e^{\beta\hbar\omega_0/2}e^{-i\omega_0\tau}+e^{\beta\hbar\omega_0/2}e^{-\beta\hbar\omega_0/2}e^{i\omega_0\tau},$$

$$= e^{\beta\hbar\omega_0/2}\left(e^{\beta\hbar\omega_0/2}e^{-i\omega_0\tau}+e^{-\beta\hbar\omega_0/2}e^{i\omega_0\tau}\right), \qquad (6.86)$$

the Phonon correlation function yields:

$$A(\tau) = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2\right]$$
$$\times exp\left[\left(\frac{\lambda}{\hbar\omega_0}\right)^2\sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\left(e^{\beta\hbar\omega_0/2}e^{-i\omega_0\tau}+e^{-\beta\hbar\omega_0/2}e^{i\omega_0\tau}\right)\right].$$

$$(6.87)$$

I am at the moment one step away from a suitable result to proceed to calculate the Fourier transform proposed in expression 6.84. By invoking Euler's identity for the cosine function as $\cos\theta = \frac{1}{2}\left(e^{i\theta}+e^{-i\theta}\right)$, expression 6.87 can be further re-organize as follows:

$$A(\tau) = exp\left[-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2\right]$$
$$\times exp\left[2\left(\frac{\lambda}{\hbar\omega_0}\right)^2\sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\cos\left[\omega_0\left(\tau+i\beta\hbar/2\right)\right]\right],$$

and recalling the Jacobi-Anger expansion from expression 11.9:

$$e^{z\cos\theta} = \sum_{n=-\infty}^{+\infty} I_n(z)\,e^{in\theta},$$

$$(6.88)$$

then, $A(\tau)$ finally reads:

$$A(\tau) = e^{-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2}$$
$$\times \sum_{n=-\infty}^{+\infty} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2\sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right)e^{in\omega_0(\tau+i\beta\hbar/2)},$$

$$(6.89)$$

At the moment, the above result is replaced in expression 6.84, to be further elaborated as follows:

$$G_{\sigma\sigma'}(\omega) = \int K_{\sigma\sigma'}(\tau) A(\tau) e^{i\omega\tau} d\tau,$$

$$= \int K_{\sigma\sigma'}(\tau) e^{-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2}$$

$$\times \sum_{n=-\infty}^{+\infty} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right)$$

$$\times e^{in\omega_0\tau} e^{-n\omega_0\beta\hbar/2} e^{i\omega\tau} d\tau,$$

$$= e^{-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2} \sum_{n=-\infty}^{+\infty} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right)$$

$$\times \int K_{\sigma\sigma'}(\tau) e^{in\omega_0\tau} e^{-n\omega_0\beta\hbar/2} e^{i\omega\tau} d\tau,$$

$$= e^{-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2}$$

$$\times \sum_{n=-\infty}^{+\infty} e^{-n\omega_0\beta\hbar/2} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right)$$

$$\times \int K_{\sigma\sigma'}(\tau) e^{in\omega_0\tau} e^{i\omega\tau} d\tau,$$

arriving at the following expression for the total Green's function $G_{\sigma\sigma'}(\omega)$:

$$G_{\sigma\sigma'}(\omega) = e^{-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2}$$

$$\times \sum_{n=-\infty}^{+\infty} e^{-n\omega_0\beta\hbar/2} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right)$$

$$\times \int K_{\sigma\sigma'}(\tau) e^{i(\omega+n\omega_0)\tau} d\tau, \tag{6.90}$$

and recalling that:

$$\int K_{\sigma\sigma'}(\tau) e^{i(\omega+n\omega_0)\tau} d\tau = K_{\sigma\sigma'}(\omega\tau + n\omega_0),$$

$G_{\sigma\sigma'}(\omega)$ reads:

$$G_{\sigma\sigma'}(\omega) = e^{-\left(\frac{\lambda}{\hbar\omega_0}\sqrt{1+2n_B(\omega_0)}\right)^2}$$

$$\times \sum_{n=-\infty}^{+\infty} e^{-n\omega_0\beta\hbar/2} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right) K_{\sigma\sigma'}(\omega\tau + n\omega_0). \tag{6.91}$$

In the above equation, $K_{\sigma\sigma'}(\omega\tau + n\omega_0)$ is the electronic Green's function, $e^{-n\omega_0\beta\hbar/2} I_n\left(2\left(\frac{\lambda}{\hbar\omega_0}\right)^2 \sqrt{n_B(\omega_0)(n_B(\omega_0)+1)}\right)$ is the Bessel Harmonic factor (Phonon side band coefficient) and $G_{\sigma\sigma'}(\omega)$ is the total Green's function, renormalized by the phonon correlation function.

6.7 Electron-Electron Correlation vs Electron Phonon Interaction
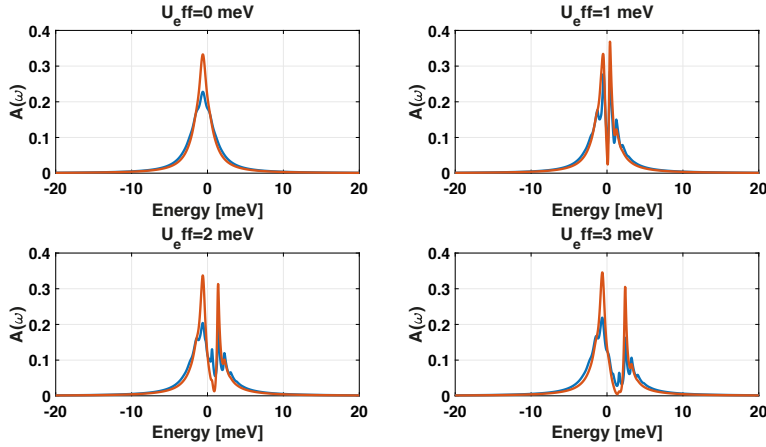
Figure 6.2. Density of states $A(\omega)$ for a single molecule magnet as presented in paper II, for $\overline{U} = 0$ meV (upper-left panel), $\overline{U} = 1$ meV (upper-right panel), $\overline{U} = 2$ meV (lower-left panel), $\overline{U} = 3$ meV (lower-right panel), for an electron-phonon coupling constant $\lambda = 0.7$ meV, for two different temperatures in the right lead, $T_R = 7.0$ K (in red) and $T_R = 10.0$ K (in blue), with $T_L = 3.0$ K. For larger temperatures, the Bessel side bands due to phonons in the density of states emerged.

Here, I have discussed the interplay among electrons, phonons and spins, making clear emphasis on the role of the electron-phonon interaction in the weak coupling limit on the electronic Green's function. Clearly, this effect increases as temperature grows in the system due to the excitation of single phonon mode density of states. In Fig. 6.2, it can be clearly seen the effect of: **1.** electron-electron correlation on the density of states as the lorentzian broadened peak, is split in what's known as the Hubbard bands as the effective electron-electron correlation energy increases from zero to 3 meV. **2.** the screening of the correlation energy is predicted by the application of the Lang-Firsov transformation, giving $\overline{U} = U - \frac{2\lambda^2}{\hbar\omega_0}$. This condition, means that given the Pauli exclusion principle where both electronic spin species repeal, molecular vibrations will bring the electrons closer to each other, hence reducing the repulsion among species and

inducing, at large values for the electron-phonon coupling, an effective attractive interaction, similar to the one emerging in conventional s-wave superconductivity. Since the condition derives from the approximation that the inelastic terms in the tunneling Hamiltonian are considered to be close to unity, posterior to the application of the Lang-Firsov transformation, this screening condition has to be analyzed with maximum care, because, in this limit, where the electron-phonon coupling is set to be small, attractive interactions might never emerge in a realistic context despite the prediction derived from the theory presented in this chapter. Nonetheless, it makes complete sense as argued, that molecular vibrations will bring electrons closer to each other, and hence, at stronger coupling limits, this screening condition might still applied. On the side of its ($\overline{U}$) effect on the Magnetic interactions, from the derivation of the non-equilibrium RKKY interaction in chapter 5, special care must be taken when the four-point propagator is decoupled under the effect of an effective electron-electron correlation, even in the low coupling limit (see paper II for detailed discussion).

7. Non-Equilibrium Multilevel Molecular Green's Functions

"On the Basis of Lorentz's theory, if we limit ourselves to a single spectral life, it suffices to assume that each atom or molecule contains a single moving electron."

Pieter Zeeman.

"Life...is a relationship between molecules."

Linus Pauling.

Magnetic Ad-Atoms adsorbed on surface (metallic) reflect characteristic trends in the differential conductance that resemble the magnetic or spin nature present in the molecule, when probed with a metallic tip, weather is non-magnetic, magnetic or superconducting. These molecular magnets have typical electronic structures that admit electron hopping in the ligand, on-site electron interaction, single nuclear vibration and localized spin moment couple via Kondo interaction. The non-equilibrium Green's functions, have been employed in the study of these physically-rich systems [94], [93], [67], [103], [102], [110], [122], where the Meir-Jauho-Wingreen [89] formalism is invoked, to determine transport characteristics through the molecule of interest, which will be expressive of the allowed processes within the molecule such as inelastic and elastic electron scattering [123], vibrational decoherence [62], [124], [102], [125], electron-electron interactions [126], [127], [48], [128] quantum interference [129], [130], [131], among others. Moreover, experiments on magnetic molecules adsorbed on surface and probed by an STM tip such as the one reported in [9], [2], [43], have evidenced signatures of their effective spin-spin interactions artificially engineered in the differential conductance. Moreover, theoretically, these experiments have been understood from the perspective of non-equilibrium Green's functions applied to single spin molecules [110], [132] and to a dimer of spins [67], [103], [102]. Systems with larger number of quantum dots/energy levels have been also considered from the optics of Keldysh Green's function, though spin trimers and larger chains of spins driven out of equilibrium have been rarely approached in the context of the

prediction of their magnetic interactions.

Here, I guide the reader through the derivation of a generalized multilevel equation of motion for the non-equilibrium molecular Green's function in the weak electron-phonon coupling and intermediate intra-molecule electron correlation energy limit. The solution of the equation of motion is then derived in the Fourier domain, for a single interacting vibrating molecule, for a dimer of spins, a trimer of spins and a dimer of spins coupled through a Benzene like molecule. These systems exemplified the multilevel molecular systems of interest in the context of this thesis. In this chapter I follow the conventions presented in chapter 6 with regards to the model Hamiltonian. Here in, I will consider a multilevel molecule described by a model Hamiltonian with its Fermionic and Bosonic Degrees of Freedom already decoupled from the Lang-Firsov transformation [116], detailed in chapter 6 and used in paper II of this dissertation.

7.1 Non-Interacting Multilevel Molecular Green's Function.

Recall the equation of motion for a single particle Green's function given by [65]:

$$i\hbar\frac{\partial G_{mn\sigma\sigma'}(t,t')}{\partial t} = \delta_{mn}\delta_{\sigma\sigma'}\delta(t-t') - \frac{i}{\hbar}\left\langle T_K\left[d_{m\sigma}(t),\overline{\mathcal{H}}\right]d_{n\sigma'}^{\dagger}(t')\right\rangle, \quad (7.1)$$

where the above commutator is evaluated based on the model given by expression 6.31. Note that in this chapter the notation has been modified slightly, as in chapter 6 the electronic Green's function was given by $K_{mn\sigma\sigma'}(t,t')$ and now is given by $G_{mn\sigma\sigma'}(t,t')$.
Then, to completely specify $G_{mn\sigma\sigma'}(t,t')$, the commutator $\left[d_{m\sigma}(t),\overline{\mathcal{H}}\right]$ has to be evaluated, which gives:

$$\left[d_{m\sigma}(t),\overline{\mathcal{H}}\right] = \bar{\epsilon}_{m\sigma}d_{m\sigma} + \sum_{m_1}\gamma_{mm_1}d_{m_1\sigma} + \sum_{\sigma_1}J_m d_{m\sigma_1}\boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\boldsymbol{S}_m(t)$$
$$+ \sum_{k}V_{mk\sigma}^* c_{k\sigma} + \sum_{q}V_{mq\sigma}^* c_{q\sigma} + \overline{U}_m d_{m\sigma}n_{m\bar{\sigma}}. \quad (7.2)$$

Replacing the evaluated commutator from expression 7.2 into expression 7.1, the following form for the equation of motion is achieved:

$$i\hbar \frac{\partial G_{mn\sigma\sigma'}(t,t')}{\partial t} = \delta_{mn}\delta_{\sigma\sigma'}\delta(t-t') + \bar{\epsilon}_{m\sigma}G_{mn\sigma\sigma'}(t,t') + \sum_{m_1}\gamma_{mm_1}G_{m_1 n\sigma\sigma'}(t,t')$$

$$+ \sum_{\sigma_1}J_m\boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\langle\boldsymbol{S}_m(t)\rangle G_{mn\sigma_1\sigma'}(t,t') + \overline{U}_m G_{mn\sigma\sigma',U}(t,t')$$

$$+ \sum_{k}V^*_{mk\sigma}H_{kn\sigma\sigma'}(t,t') + \sum_{q}V^*_{mq\sigma}H_{qn\sigma\sigma'}(t,t'), \qquad (7.3)$$

where the definitions for the molecular Green's function $G_{mn\sigma\sigma'}(t,t')$, the hybrid Green's function $H_{kn\sigma\sigma'}(t,t')$ and the interacting two particle Green's function $G_{mn\sigma\sigma',U}(t,t')$ have been used, as expressed below:

$$G_{mn\sigma\sigma'}(t,t') = -\frac{i}{\hbar}\left\langle T_K d_{m\sigma}(t)d^\dagger_{n\sigma'}(t')\right\rangle \qquad (7.4)$$

$$H_{(k,q)n\sigma\sigma'}(t,t') = -\frac{i}{\hbar}\left\langle T_K c_{(k,q)\sigma}(t)d^\dagger_{n\sigma'}(t')\right\rangle \qquad (7.5)$$

$$G_{mn\sigma\sigma',U}(t,t') = -\frac{i}{\hbar}\left\langle T_K d_{m\sigma}(t)n_{m\bar{\sigma}}(t)d^\dagger_{n\sigma'}(t').\right\rangle \qquad (7.6)$$

Note that in the derivation of expression 7.7, decoupling of the term $\left\langle d_{m\sigma_1}(t)\boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\boldsymbol{S}_m(t)d^\dagger_{n\sigma'}(t')\right\rangle$ was performed as is shown below:

$$\left\langle d_{m\sigma_1}(t)\boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\boldsymbol{S}_m(t)d^\dagger_{n\sigma'}(t')\right\rangle = \boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\langle\boldsymbol{S}_m(t)\rangle\left\langle d_{m\sigma_1}(t)d^\dagger_{n\sigma'}(t')\right\rangle. \qquad (7.7)$$

The Hybrid Green's functions are often written in terms of the couplings to the reservoirs, the local Green's function for the reservoirs $\mathcal{G}_{k\sigma}(t,t')$ and $\mathcal{G}_{q\sigma}(t,t')$ and in terms of the molecular Green's functions in the following way:

$$H_{kn\sigma\sigma'}(t,t') = \sum_{\mu}\int V_{\mu k\sigma}(\tau)\mathcal{G}_{k\sigma}(t,\tau)G_{\mu n\sigma\sigma'}(\tau,t')d\tau, \qquad (7.8)$$

$$H_{qn\sigma\sigma'}(t,t') = \sum_{\mu}\int V_{\mu q\sigma}(\tau)\mathcal{G}_{q\sigma}(t,\tau)G_{\mu n\sigma\sigma'}(\tau,t')d\tau. \qquad (7.9)$$

Next, expressions 7.8 and 7.9 (which were derived in appendix B yielding expressions 11.18 and 11.19) are replaced in equation 7.3 to give the

following equation of motion:

$$\left(i\hbar\frac{\partial}{\partial t} - \bar{\epsilon}_{m\sigma}\right)G_{mn\sigma\sigma'}(t,t') = \delta_{mn}\delta_{\sigma\sigma'}\delta(t-t') + \sum_{m_1}\gamma_{mm_1}G_{m_1n\sigma\sigma'}(t,t')$$

$$+ \sum_{\sigma_1}J_m\sigma_{\sigma\sigma_1}\cdot\langle S_m(t)\rangle G_{mn\sigma_1\sigma'}(t,t') + \bar{U}_m G_{mn\sigma\sigma',U}(t,t')$$

$$+ \sum_{k\mu}\int V_{\mu k\sigma}(\tau)V_{mk\sigma}^*(t)\mathcal{G}_{k\sigma}(t,\tau)G_{\mu n\sigma\sigma'}(\tau,t')d\tau$$

$$+ \sum_{q\mu}\int V_{\mu q\sigma}(\tau)V_{mq\sigma}^*(t)\mathcal{G}_{q\sigma}(t,\tau)G_{\mu n\sigma\sigma'}(\tau,t')d\tau. \qquad (7.10)$$

Moreover, by defining self-energies of the form [89]:

$$\Sigma_{m\mu\sigma\sigma}^{(L)}(t,t') = \sum_{k}V_{mk\sigma}^*(t)V_{\mu k\sigma}(t')\mathcal{G}_{k\sigma}(t,t'), \qquad (7.11)$$

$$\Sigma_{m\mu\sigma\sigma}^{(R)}(t,t') = \sum_{q}V_{mq\sigma}^*(t)V_{\mu q\sigma}(t')\mathcal{G}_{q\sigma}(t,t'). \qquad (7.12)$$

the equation of motion given by expression 7.10, now reads:

$$\left(i\hbar\frac{\partial}{\partial t} - \bar{\epsilon}_{m\sigma}\right)G_{mn\sigma\sigma'}(t,t') = \delta_{mn}\delta_{\sigma\sigma'}\delta(t-t') + \sum_{m_1}\gamma_{mm_1}G_{m_1n\sigma\sigma'}(t,t')$$

$$+ \sum_{\sigma_1}J_m\sigma_{\sigma\sigma_1}\cdot\langle S_m(t)\rangle G_{mn\sigma_1\sigma'}(t,t')$$

$$+ \bar{U}_m G_{mn\sigma\sigma',U}(t,t')$$

$$+ \sum_{\mu}\int \Sigma_{m\mu\sigma\sigma}^{(L)}(t,\tau)G_{\mu n\sigma\sigma'}(\tau,t')d\tau$$

$$+ \sum_{\mu}\int \Sigma_{m\mu\sigma\sigma}^{(R)}(t,\tau)G_{\mu n\sigma\sigma'}(\tau,t')d\tau, \qquad (7.13)$$

where $\mathcal{G}_{m\sigma}(t,t')$ satisfies:

$$\left(i\hbar\frac{\partial}{\partial t} - \bar{\epsilon}_{m\sigma}\right)\mathcal{G}_{m\sigma}(t,t') = \delta(t-t').$$

Now, I will perform the following variable swap: $t \to \tau$ in expression 7.13, then, multiply both sides of this expression by $\mathcal{G}_{m\sigma}(t,\tau)$ and the integrate

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with respect to τ to give:

$$
\begin{aligned}
\boldsymbol{G}_{mn\sigma\sigma'}(t,t') = &\int \delta_{mn}\delta_{\sigma\sigma'}\boldsymbol{G}_{m\sigma}(t,t') + \sum_{m_1}\gamma_{mm_1}\int \boldsymbol{G}_{m\sigma}(t,\tau)\boldsymbol{G}_{m_1n\sigma\sigma'}(\tau,t')d\tau \\
&+ \sum_{\sigma_1} J_m \int \boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\langle \boldsymbol{S}_m(\tau)\rangle \boldsymbol{G}_{m\sigma}(t,\tau)\boldsymbol{G}_{mn\sigma_1\sigma'}(\tau,t')d\tau \\
&+ \sum_{\mu}\int\int \boldsymbol{G}_{m\sigma}(t,\tau)\boldsymbol{\Sigma}_{m\mu\sigma\sigma}^{(L)}(\tau,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\tau'd\tau \\
&+ \sum_{\mu}\int\int \boldsymbol{G}_{m\sigma}(t,\tau)\boldsymbol{\Sigma}_{m\mu\sigma\sigma}^{(R)}(\tau,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\tau'd\tau \\
&+ \overline{U}_m \int \boldsymbol{G}_{m\sigma}(t,\tau)\boldsymbol{G}_{mn\sigma\sigma',U}(\tau,t')d\tau, \qquad\qquad (7.14)
\end{aligned}
$$

Next, one should as well defined an equation of motion for $\boldsymbol{G}_{mn\sigma\sigma',U}(t,t')$ which appears in expression 7.14.

7.2 Interacting Multilevel Molecular Green's Function

The interacting Green's function $\boldsymbol{G}_{mn\sigma\sigma',U}(t,t')$ was defined in expression 7.6. Moreover, the latter can be expanded as follows:

$$
\begin{aligned}
\boldsymbol{G}_{mn\sigma\sigma',U}(t,t') = &-\frac{i}{\hbar}\left\langle \boldsymbol{n}_{m\overline{\sigma}}\boldsymbol{d}_{m\sigma}(t)\boldsymbol{d}_{n\sigma'}^{\dagger}(t')\right\rangle\theta(t-t') \\
&+\frac{i}{\hbar}\left\langle \boldsymbol{d}_{n\sigma'}^{\dagger}(t')\boldsymbol{n}_{m\overline{\sigma}}\boldsymbol{d}_{m\sigma}(t)\right\rangle\theta(t'-t). \qquad (7.15)
\end{aligned}
$$

To proceed with the specification of the equation of motion for $\boldsymbol{G}_{mn\sigma\sigma',U}(t,t')$, expression 7.15 is differentiated yielding:

$$
\begin{aligned}
i\hbar\frac{\partial \boldsymbol{G}_{mn\sigma\sigma',U}(t,t')}{\partial t} = &\,\delta_{mn}\delta_{\sigma\sigma'}\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\rangle\delta(t-t') \\
&-\frac{i}{\hbar}\left\langle \boldsymbol{T}_K\left[\boldsymbol{n}_{m\overline{\sigma}}(t)\boldsymbol{d}_{m\sigma}(t),\overline{\mathcal{H}}\right]\boldsymbol{d}_{n\sigma'}^{\dagger}(t')\right\rangle. \qquad (7.16)
\end{aligned}
$$

Note that to solve for $\boldsymbol{G}_{mn\sigma\sigma',U}(t,t')$, the interacting commutator $\left[\boldsymbol{n}_{m\overline{\sigma}}(t)\boldsymbol{d}_{m\sigma}(t),\overline{\mathcal{H}}\right]$ must be evaluated. The latter was evaluated in the

Hubbard-I approximation[1], giving the result shown below:

$$\left[n_{m\bar{\sigma}}(t)d_{m\sigma}(t), \mathcal{H} \right] \approx \sum_{k} V^*_{mk\sigma} n_{m\bar{\sigma}}(t)c_{k\sigma} + \sum_{q} V^*_{mq\sigma} n_{m\bar{\sigma}}(t)c_{q\sigma}$$

$$+ \bar{\epsilon}_{m\sigma} n_{m\bar{\sigma}}(t)d_{m\sigma} + \overline{U}_m n_{m\bar{\sigma}}(t)d_{m\sigma}$$

$$+ J_m \sigma_{\sigma\sigma} \cdot S_m(t) n_{m\bar{\sigma}}(t)d_{m\sigma}. \quad (7.17)$$

Now, to arrive at a first glance on the equation of motion for the interacting Green's function, expression 7.17 is replaced onto expression 7.16, this procedure throws the primitive equation of motion given by:

$$i\hbar \frac{\partial G_{mn\sigma\sigma',U}(t,t')}{\partial t} = \delta_{mn}\delta_{\sigma\sigma'} \langle n_{m\bar{\sigma}}(t) \rangle \delta(t-t') + \bar{\epsilon}_{m\sigma} G_{mn\sigma\sigma',U}(t,t')$$

$$+ \sum_{k} V^*_{mk\sigma} \langle n_{m\bar{\sigma}}(t) \rangle H_{kn\sigma\sigma'}(t,t')$$

$$+ \sum_{q} V^*_{mq\sigma} \langle n_{m\bar{\sigma}}(t) \rangle H_{qn\sigma\sigma'}(t,t')$$

$$+ \overline{U}_m G_{mn\sigma\sigma',U}(t,t') + J_m \sigma_{\sigma\sigma} \cdot \left\langle S_m^{(z)} \right\rangle a_z G_{mn\sigma\sigma',U}(t,t'),$$

and hence, one can write the following preliminary form for the equation of motion for $G_{mn\sigma\sigma',U}(t,t')$:

$$\left(i\hbar \frac{\partial}{\partial t} - \bar{\epsilon}_{m\sigma} - \overline{U}_m - J_m \sigma_{\sigma\sigma} \left\langle S_m^{(z)} \right\rangle \right) G_{mn\sigma\sigma',U}(t,t') = \delta_{mn}\delta_{\sigma\sigma'} \langle n_{m\bar{\sigma}}(t) \rangle \delta(t-t')$$

$$+ \sum_{k} V^*_{mk\sigma} \langle n_{m\bar{\sigma}}(t) \rangle H_{kn\sigma\sigma'}(t,t') + \sum_{q} V^*_{mq\sigma} \langle n_{m\bar{\sigma}}(t) \rangle H_{qn\sigma\sigma'}(t,t'), \quad (7.18)$$

where I have invoked the definitions for the Green's functions $H_{(k,q)n\sigma\sigma'}(t,t')$ and $G_{mn\sigma\sigma',U}(t,t')$ from expressions 7.5 and 7.6 respectively, and applied the Hartree-Fock decoupling which is specified as follows:

$$\left\langle T_K n_{m\bar{\sigma}}(t)c_{(k,q)\sigma}(t)d^\dagger_{n\sigma'}(t') \right\rangle \approx \langle n_{m\bar{\sigma}}(t) \rangle \left\langle T_K c_{(k,q)\sigma}(t)d^\dagger_{n\sigma'}(t') \right\rangle.$$

To solve for the Green's function $G_{mn\sigma\sigma',U}(t,t')$, I rely on expressions 11.18 and 11.19 to substitute them for $H_{kn\sigma\sigma'}(t,t')$ and for $H_{qn\sigma\sigma'}(t,t')$, which gives the following equation of motion only in terms of the physics of the

---

[1]The Hubbard-I Approximation is a mean field technique that goes beyond Hartree-Fock mean Field Approximation. The details for this transformation can be found in ref. [133], where time dependent transport through intercating quantum dots is examined. In the context presented in this thesis, in chapter 5 of ref. [68], the approximation is discussed and in chapter 7 is put into context in a similar framework as the one discussed in chapter 6, lacking the spin degree of freedom and any magnetic nature in the molecule.

molecule and its self-energies:

$$\left(i\hbar\frac{\partial}{\partial t} - \bar{\epsilon}_{m\sigma} - \overline{U}_m - J_m\sigma_{\sigma\sigma}\left\langle S_m^{(z)}\right\rangle\right)\boldsymbol{G}_{mn\sigma\sigma',U}(t,t') = \delta_{mn}\delta_{\sigma\sigma'}\left\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\right\rangle\delta(t-t')$$

$$+ \sum_\mu \int \left\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\right\rangle \sum_{\boldsymbol{k}} V^*_{m\boldsymbol{k}\sigma}(t)\boldsymbol{G}_{\boldsymbol{k}\sigma}(t,\tau)V_{\mu\boldsymbol{k}\sigma}(\tau)\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau,t')d\tau$$

$$+ \sum_\mu \int \left\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\right\rangle \sum_{\boldsymbol{q}} V^*_{m\boldsymbol{q}\sigma}(t)\boldsymbol{G}_{\boldsymbol{q}\sigma}(t,\tau)V_{\mu\boldsymbol{q}\sigma}(\tau)\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau,t')d\tau,$$

$$(7.19)$$

and using expressions 7.11 and 7.12, the above expression can be re-cast in terms of the self-energies as:

$$\left(i\hbar\frac{\partial}{\partial t} - \bar{\epsilon}_{m\sigma} - \overline{U}_m - J_m\sigma_{\sigma\sigma}\left\langle S_m^{(z)}\right\rangle\right)\boldsymbol{G}_{mn\sigma\sigma',U}(t,t') = \delta_{mn}\delta_{\sigma\sigma'}\left\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\right\rangle\delta(t-t')$$

$$+ \sum_\mu \int \left\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\right\rangle \Sigma^{(L)}_{m\mu\sigma\sigma}(t,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\tau'$$

$$+ \sum_\mu \int \left\langle \boldsymbol{n}_{m\overline{\sigma}}(t)\right\rangle \Sigma^{(R)}_{m\mu\sigma\sigma}(t,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\tau'. \qquad (7.20)$$

Moreover, to solve for $\boldsymbol{G}_{mn\sigma\sigma',U}(t,t')$, one performs the variable swap $t \to \tau$ in expression 7.20 and multiplies from the left both sides of the expression by $\mathcal{G}_{mU}(t,\tau)$, which satisfies:

$$\left(i\hbar\frac{\partial}{\partial \tau} - \bar{\epsilon}_{m\sigma} - \overline{U}_m - J_m\sigma_{\sigma\sigma}\left\langle S_m^{(z)}\right\rangle\right)\mathcal{G}_{mU}(t,t') = \delta(t-t'),$$

hence giving:

$$\boldsymbol{G}_{mn\sigma\sigma',U}(t,t') = \delta_{mn}\delta_{\sigma\sigma'}\left\langle \boldsymbol{n}_{m\overline{\sigma}}(t')\right\rangle\mathcal{G}_{mU}(t,t')$$

$$+ \sum_{\alpha\mu} \int\int \mathcal{G}_{mU}(t,\tau)\left\langle \boldsymbol{n}_{m\overline{\sigma}}(\tau)\right\rangle\Sigma^{(\alpha)}_{m\mu\sigma\sigma}(\tau,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\tau d\tau'. \qquad (7.21)$$

7.3 Complete Interacting Multilevel Molecular Green's Function.

Here, I just simply replace expression 7.21 into equation 7.14, and then as a consequence the complete Green's function $\boldsymbol{G}_{mn\sigma\sigma'}(t,t')$ emerges and

gives:

$$
\begin{aligned}
\boldsymbol{G}_{mn\sigma\sigma'}(t,t') =&\; \delta_{mn}\delta_{\sigma\sigma'}\boldsymbol{\mathcal{G}}_{m\sigma}(t,t') + \sum_{m_1}\gamma_{mm_1}\int \boldsymbol{\mathcal{G}}_{m\sigma}(t,\tau)\boldsymbol{G}_{m_1 n\sigma\sigma'}(\tau,t')d\tau \\
&+ \sum_{\sigma_1}J_m\int \boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\langle \boldsymbol{S}_m(\tau)\rangle\boldsymbol{\mathcal{G}}_{m\sigma}(t,\tau)\boldsymbol{G}_{mn\sigma_1\sigma'}(\tau,t')d\tau \\
&+ \sum_{\alpha\mu}\int\int \boldsymbol{\mathcal{G}}_{m\sigma}(t,\tau)\boldsymbol{\Sigma}^{(\alpha)}_{m\mu\sigma\sigma}(\tau,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\tau'd\tau \\
&+ \overline{U}_m\delta_{mn}\delta_{\sigma\sigma'}\int \boldsymbol{\mathcal{G}}_{m\sigma}(t,\lambda)\langle \boldsymbol{n}_{m\overline{\sigma}}(t')\rangle\boldsymbol{\mathcal{G}}_{mU}(\lambda,t')d\lambda \\
&+ \overline{U}_m\sum_{\alpha\mu}\int\int\int \boldsymbol{\mathcal{G}}_{m\sigma}(t,\lambda)\boldsymbol{\mathcal{G}}_{mU}(\lambda,\tau)\langle \boldsymbol{n}_{m\overline{\sigma}}(\tau)\rangle \\
&\qquad\qquad \times\; \boldsymbol{\Sigma}^{(\alpha)}_{m\mu\sigma\sigma}(\tau,\tau')\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau',t')d\lambda d\tau d\tau'.
\end{aligned}
\tag{7.22}
$$

In the work presented in the appended papers, I usually make reference to the Retarded Green's function instead, which motivates me to write the retarded version of expression 7.22, by using the procedure of analytical continuation (see chapter 4), as follows:

$$
\begin{aligned}
\boldsymbol{G}^R_{mn\sigma\sigma'}(t,t') =&\; \delta_{mn}\delta_{\sigma\sigma'}\boldsymbol{\mathcal{G}}^R_{m\sigma}(t,t') + \sum_{m_1}\gamma_{mm_1}\int \boldsymbol{\mathcal{G}}^R_{m\sigma}(t,\tau)\boldsymbol{G}^R_{m_1 n\sigma\sigma'}(\tau,t')d\tau \\
&+ \sum_{\sigma_1}J_m\int \boldsymbol{\sigma}_{\sigma\sigma_1}\cdot\langle \boldsymbol{S}_m(\tau)\rangle\boldsymbol{\mathcal{G}}^R_{m\sigma}(t,\tau)\boldsymbol{G}^R_{mn\sigma_1\sigma'}(\tau,t')d\tau \\
&+ \sum_{\alpha\mu}\int\int \boldsymbol{\mathcal{G}}^R_{m\sigma}(t,\tau)\boldsymbol{\Sigma}^{R(\alpha)}_{m\mu\sigma\sigma}(\tau,\tau')\boldsymbol{G}^R_{\mu n\sigma\sigma'}(\tau',t')d\tau'd\tau \\
&+ \overline{U}_m\delta_{mn}\delta_{\sigma\sigma'}\int \boldsymbol{\mathcal{G}}^R_{m\sigma}(t,\lambda)\langle \boldsymbol{n}_{m\overline{\sigma}}(t')\rangle\boldsymbol{\mathcal{G}}^R_{mU}(\lambda,t')d\lambda \\
&+ \overline{U}_m\sum_{\alpha\mu}\int\int\int \boldsymbol{\mathcal{G}}^R_{m\sigma}(t,\lambda)\boldsymbol{\mathcal{G}}^R_{mU}(\lambda,\tau)\langle \boldsymbol{n}_{m\overline{\sigma}}(\tau)\rangle \\
&\qquad\qquad \times\; \boldsymbol{\Sigma}^{R(\alpha)}_{m\mu\sigma\sigma}(\tau,\tau')\boldsymbol{G}^R_{\mu n\sigma\sigma'}(\tau',t')d\lambda d\tau d\tau'.
\end{aligned}
\tag{7.23}
$$

This expression generates the Green's functions used to explore all the systems of molecules related to this thesis, such as spin dimers in paper I, single spin molecule magnets in paper II and IV and spin trimers in paper III. In the rest of this chapter, I will give an overview of the Green's function description of these systems, which will then be referred to in chapter 9.

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7.4 Single Spin, Single Level

In paper II, I address single spin unit molecular magnets, with regards to its uniaxial magnetic anisotropy as modulated by phonons, which has been defined in terms of the non-equilibrium Green's function in expression 5.57. This single molecule magnet is illustrated in figure 7.1.

As defined in the Meir-Jauho-Wingreen formalism [89], $\Sigma_{A\sigma\sigma}^{R(\alpha)}(\omega)$ was given
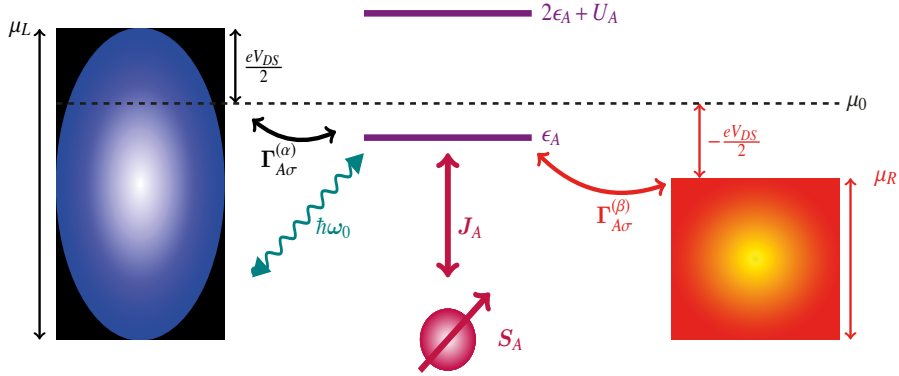
Figure 7.1. Single Spin Molecular Magnet: Single localized spin moment labeled as S_A, coupled through the Kondo interaction J_A to a single electronic level $\epsilon_{A\sigma} = \epsilon_{\sigma 0} \pm J_A \langle S_A \rangle$, with an associated electron-electron repulsion U_A. Spin up and Spin down electrons are coupled to a single vibration mode $\hbar\omega_0$ through a coupling constant λ (discussed in chapter 6). The electronic level $\epsilon_{A\sigma}$ is coupled to two metallic leads via interaction constants $\Gamma_\sigma^{(\alpha)}$ and $\Gamma_\sigma^{(\beta)}$, where α is associated with the left lead and β does is with the right lead. The left lead is shaded in blue suggesting that it is colder than the right lead shaded in red, this by convention. In the simulation reported in paper II, seldom, the temperatures in the right and left lead are in thermal equilibrium.

as shown below:

$$\Sigma_{A\sigma\sigma}^{R(\alpha)}(\omega) = \Lambda_{A\sigma}^{(\alpha)}(\omega) - \frac{i\mathbf{\Gamma}_{A\sigma}^{(\alpha)}(\omega)}{2}, \tag{7.24}$$

hence $G_{AA\sigma\sigma'}^{R}(\omega)$, from expression 7.23, and by using the definition given in expression 7.24, it reads:

$$G_{AA\sigma\sigma'}^{R}(\omega) = \frac{\delta_{\sigma\sigma'}\left(\hbar\omega - \epsilon_{A\sigma} - U_A\left(1 - \langle n_{A\bar{\sigma}} \rangle\right)\right)}{\left(\hbar\omega - \epsilon_{A\sigma} - \Lambda_\sigma(\omega) + \frac{i\mathbf{\Gamma}_\sigma(\omega)}{2}\right)\left(\hbar\omega - \epsilon_{A\sigma} - U_A\right) - U_A\langle n_{A\bar{\sigma}} \rangle\left(\Lambda_\sigma(\omega) - \frac{i\mathbf{\Gamma}_\sigma(\omega)}{2}\right)}. \tag{7.25}$$

Often, it is useful to calculate the real and imaginary parts of the Retarded Green's function. For this purpose it is convenient to express equation 7.25

as follows:

$$G^R_{\sigma\sigma'}(\omega) = \frac{\delta_{\sigma\sigma'} Q(\omega)}{(\hbar\omega - \epsilon_{A\sigma} - \Lambda_\sigma(\omega))(\hbar\omega - \epsilon_{A\sigma} - U_A) - U_A \langle n_{\overline{\sigma}} \rangle \Lambda_\sigma(\omega) + \frac{i\Gamma_\sigma(\omega)}{2} Q(\omega)},$$
(7.26)

where the parameters $\epsilon_{A\sigma}$, $\Lambda_\sigma(\omega)$, $\Gamma_\sigma(\omega)$, the dummy variable $Q(\omega)$ and the particle number $n_{A\overline{\sigma}}$ are defined as follows:

$$\epsilon_{A\sigma} = \epsilon_{\sigma 0} \pm J_A \langle S_A \rangle = \epsilon_{\sigma 0} + \sigma J_A \langle S_A \rangle$$
(7.27)

$$\Lambda_\sigma(\omega) = \Lambda^{(\alpha)}_{A\sigma}(\omega) + \Lambda^{(\beta)}_{A\sigma}(\omega);$$
(7.28)

$$\Gamma_\sigma(\omega) = \Gamma^{(\alpha)}_{A\sigma}(\omega) + \Gamma^{(\beta)}_{A\sigma}(\omega);$$
(7.29)

$$Q(\omega) = \hbar\omega - \epsilon_{A\sigma} - U_A (1 - \langle n_{A\overline{\sigma}} \rangle).$$
(7.30)

$$n_{A\overline{\sigma}} = \mathcal{IM} \int G^<_{AA\sigma\sigma}(\omega) \frac{d\hbar\omega}{2\pi}.$$
(7.31)

7.5 Two Spins, Two Levels

In the present section I will describe a dimer of spins coupled to a two level molecular structure and driven by two metallic leads. The coupling to the leads is represented by a pair of matrices given by:

$$\Gamma^{(\alpha)}_\sigma = \begin{bmatrix} \Gamma^{(\alpha)}_{A\sigma} & \Gamma^{(\alpha)}_{AB\sigma} \\ \Gamma^{(\alpha)}_{BA\sigma} & \Gamma^{(\alpha)}_{B\sigma} \end{bmatrix}, \quad \Gamma^{(\beta)}_\sigma = \begin{bmatrix} \Gamma^{(\beta)}_{A\sigma} & \Gamma^{(\beta)}_{AB\sigma} \\ \Gamma^{(\beta)}_{BA\sigma} & \Gamma^{(\beta)}_{B\sigma} \end{bmatrix}.$$
(7.32)

These matrices are defined in figure 7.2, which illustrates in general form, the system of interest.

The inverse of the molecular Green's function, can be constructed from expression 7.23, and its matrix representation (by specifying the site labels m and n), $\left[G^R(\omega) \right]^{-1}$ yields:

$$\left[G^R(\omega) \right]^{-1} = \begin{bmatrix} \hbar\omega - \epsilon_{A\sigma} + \frac{i}{2}\Gamma_{A\sigma} & -\gamma_{AB} + \frac{i}{2}\Gamma_{AB\sigma} \\ -\gamma_{BA} + \frac{i}{2}\Gamma_{BA\sigma} & \hbar\omega - \epsilon_{B\sigma} + \frac{i}{2}\Gamma_{B\sigma} \end{bmatrix}.$$
(7.33)

The above matrix representation (4×4, 2×2 in site space and 2×2 in spin space), can be easily inverted as a block diagonal matrix, giving the

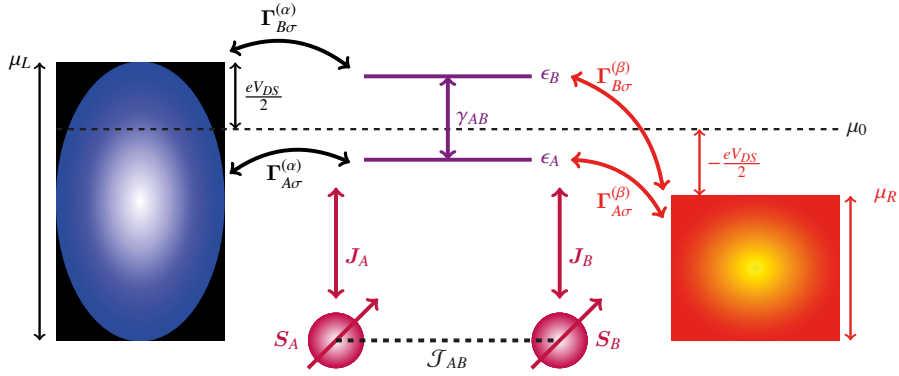*Figure 7.2.* Molecular Magnet Composed by a Dimer of Spins: Two Single localized spin moments labeled as S_A and S_B, coupled through the Kondo interaction J_A and J_B respectively to two single electronic levels $\epsilon_{m\sigma} = \epsilon_{m\sigma 0} \pm J_m \langle S_m \rangle$ (where $m = A, B$). Both electronic levels $\epsilon_{A\sigma}$ and $\epsilon_{B\sigma}$ are coupled to two metallic leads via interaction constants $\Gamma_{m\sigma}^{(\alpha)}$ and $\Gamma_{m\sigma}^{(\beta)}$, where α is associated with the left lead and β is associated with the right lead, for $m = A, B$. Levels $\epsilon_{A\sigma}$ and $\epsilon_{B\sigma}$ are coupled through the hybridization γ_{ab}, which determines the splitting between the bonding and anti-bonding levels of the molecule. The left lead is shaded in blue suggesting that is colder than the right lead shaded in red, this by convention. In the simulation reported in paper I, the variations in temperature given by $\Delta T = T_R - T_L$, are sometimes positive, sometimes negative (few cases), which suggests that blue goes to read and that red goes to blue when the sign of ΔT changes. The effective spin-spin interaction is labeled here as $\mathcal{J}_{AB}$. Lastly, the cross coupling terms of the energy levels with the leads, namely $\Gamma_{mn\sigma}^{(\alpha)}$ and $\Gamma_{mn\sigma}^{(\beta)}$ respectively, where $m = A, B$ and $n = A, B$, represent probability amplitudes for one electron to go from the energy level $\epsilon_{m\sigma}$ to the energy level $\epsilon_{n\sigma}$ through the tunneling either by the left lead (α) or by the right lead (β).

following expression:

$$G^R(\omega) = \frac{\begin{bmatrix} \hbar\omega - \epsilon_{B\sigma} + \frac{i}{2}\Gamma_{B\sigma} & \gamma_{AB} - \frac{i}{2}\Gamma_{AB\sigma} \\ \\ \gamma_{BA} - \frac{i}{2}\Gamma_{BA\sigma} & \hbar\omega - \epsilon_{A\sigma} + \frac{i}{2}\Gamma_{A\sigma} \end{bmatrix}}{\left(\hbar\omega - \epsilon_{A\sigma} + \frac{i}{2}\Gamma_{A\sigma}\right)\left(\hbar\omega - \epsilon_{B\sigma} + \frac{i}{2}\Gamma_{B\sigma}\right) - |t_{AB}|^2 \, e^{i\phi_{AB}}}, \qquad (7.34)$$

where the term $|t_{AB}|^2 e^{i\phi_{AB}}$ (for $\gamma_{AB} = \gamma_{BA}$) can be derived as follows:

$$\left(\gamma_{AB} - \frac{i}{2}\Gamma_{AB\sigma}\right)\left(\gamma_{BA} - \frac{i}{2}\Gamma_{BA\sigma}\right) = |\gamma_{AB}|^2 - \frac{i}{2}\left(\Gamma_{AB\sigma} + \Gamma_{BA\sigma}\right) - \frac{\Gamma_{AB\sigma}\Gamma_{BA\sigma}}{4}$$

$$= \sqrt{\left(|\gamma_{AB}|^2 - \frac{\Gamma_{AB\sigma}\Gamma_{BA\sigma}}{4}\right)^2 + |\gamma_{AB}|^2 \frac{(\Gamma_{AB\sigma} + \Gamma_{BA\sigma})^2}{4}}$$

$$\cdot exp\left[-i\arctan\left(\frac{2\gamma_{AB}\left(\Gamma_{AB\sigma} + \Gamma_{BA\sigma}\right)}{4|\gamma_{AB}|^2 - \Gamma_{AB\sigma}\Gamma_{BA\sigma}}\right)\right],$$

and in the particular case where $\Gamma_{AB\sigma} = \Gamma_{BA\sigma}$:

$$\left(\gamma_{AB} - \frac{i}{2}\Gamma_{AB\sigma}\right)\left(\gamma_{BA} - \frac{i}{2}\Gamma_{BA\sigma}\right)$$

$$= \sqrt{\left(|\gamma_{AB}|^2 + \frac{\Gamma_{AB\sigma}^2}{4}\right)^2} \cdot exp\left[-i\arctan\left(\frac{\gamma_{AB}\Gamma_{AB\sigma}}{|\gamma_{AB}|^2 - \frac{\Gamma_{AB\sigma}^2}{4}}\right)\right]$$

$$= |t_{AB}|^2 \cdot e^{-i\phi_{AB}}, \tag{7.35}$$

where $|t_{AB}|^2 = |\gamma_{AB}|^2 + \frac{\Gamma_{AB\sigma}^2}{4}$ and $\tan\phi_{AB} = -\frac{\gamma_{AB}\Gamma_{AB\sigma}}{|\gamma_{AB}|^2 - \frac{\Gamma_{AB\sigma}^2}{4}}$.

The phase ϕ_{AB} determines the overall sign of the density of states given by expression:

$$A(\omega) = -\frac{1}{\pi}\Im m\,\mathrm{Tr}\,G^R(\omega),$$

which underlines the fact that the molecule under consideration can not be over-occupied by the action of the metallic leads, which translates in the constraint $\gamma_{AB} \geq \frac{\Gamma_{AB\sigma}}{2}$.

In paper I, The system under consideration is a two level system where each of the electronic levels is singly coupled to one electrode (non-magnetic), hence $\Gamma_{AB\sigma} = \Gamma_{BA\sigma} = 0$, annihilating the possibility for quantum interference in the system, as discussed by [122]. After this simplification the Retarded Green's function for the system reads:

$$G^R(\omega) = \frac{\begin{bmatrix} \hbar\omega - \epsilon_{A\sigma} + \frac{i}{2}\Gamma_{B\sigma} & \gamma_{AB} \\ & \\ \gamma_{BA} & \hbar\omega - \epsilon_{A\sigma} + \frac{i}{2}\Gamma_{B\sigma} \end{bmatrix}}{\left(\hbar\omega - \epsilon_{A\sigma} + \frac{i}{2}\Gamma_{A\sigma}\right)\left(\hbar\omega - \epsilon_{B\sigma} + \frac{i}{2}\Gamma_{B\sigma}\right) - |t_{AB}|^2}. \tag{7.36}$$

For this configuration, the matrix representation for the coupling $\mathbf{\Gamma}_\sigma^{(\alpha)}$ and $\mathbf{\Gamma}_\sigma^{(\beta)}$ respectively reads:

$$\mathbf{\Gamma}_\sigma^{(\alpha)} = \begin{bmatrix} \Gamma_{A\sigma}^{(\alpha)} & 0 \\ 0 & 0 \end{bmatrix}, \quad \mathbf{\Gamma}_\sigma^{(\beta)} = \begin{bmatrix} 0 & 0 \\ 0 & \Gamma_{B\sigma}^{(\beta)} \end{bmatrix}, \tag{7.37}$$

and the resulting system is illustrated in figure 7.3
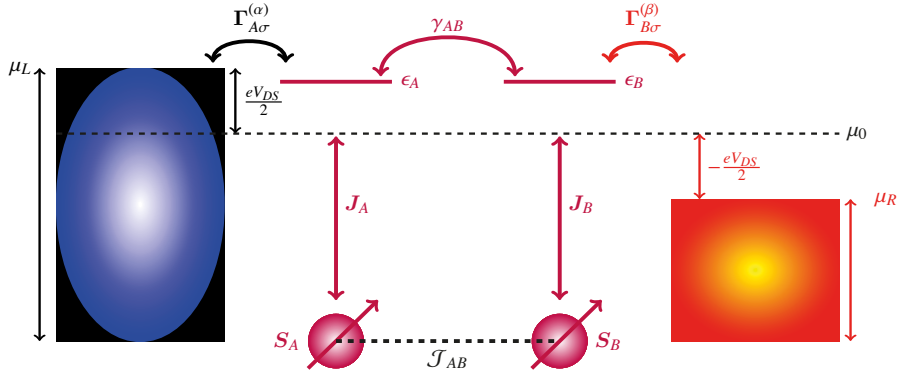
Figure 7.3. Molecular Magnet Composed by a Dimer of Spins Singly Coupled to Metallic Leads: The system described here, resembles the one shown in figure 7.2 in the case where each level is coupled only to one of the leads.

7.6 Three Spins, Three Levels

Here, I obtain the Retarded Green's function to describe the system shown in figure 7.4 from expression 7.23. This Green's function derives from the following expression:

$$G^{R}_{mn\sigma\sigma'}(\omega) = \delta_{mn}\delta_{\sigma\sigma'}\mathbb{G}^{R}_{m\sigma}(\omega) + \sum_{m_1}\gamma_{mm_1}\mathbb{G}^{R}_{m\sigma}(\omega)G^{R}_{m_1 n\sigma\sigma'}(\omega) +$$

$$J_m\boldsymbol{\sigma}^{(z)}_{\sigma\sigma}\left\langle \boldsymbol{S}^{(z)}_{m}\right\rangle \mathbb{G}^{R}_{m\sigma}(\omega)G^{R}_{mn\sigma_1\sigma'}(\omega) + \sum_{\mu\alpha}\mathbb{G}^{R}_{m\sigma}(\omega)\Sigma^{R(\alpha)}_{m\mu\sigma\sigma}(\omega)G^{R}_{\mu n\sigma\sigma'}(\omega). \quad (7.38)$$

In expression 7.38, $\mathbb{G}^{R}_{m\sigma}(\omega)$ is the bare electronic Green's function, $G^{R}_{mn\sigma\sigma'}(\omega)$ is the Green's function given coupling to the leads and effect of the spin and $\Sigma^{R(\alpha)}_{mn\sigma\sigma}(\omega)$ is the self-energy in retarded form[2], where α label the metallic contact associated with the latter.

After some algebraic manipulation, I may write the following equation of motion for the Green's function $G^{R}_{mn\sigma\sigma'}(\omega)$ as follows:

$$\left(\hbar\omega - \epsilon_{m\sigma} - J_m\boldsymbol{\sigma}^{(z)}_{\sigma\sigma}\langle S_m\rangle\right)G^{R}_{mn\sigma\sigma'}(\omega) = \delta_{mn}\delta_{\sigma\sigma'}$$

$$+ \sum_{m_1}\gamma_{mm_1}G^{R}_{m_1 n\sigma\sigma'}(\omega) + \sum_{\mu\alpha}\Sigma^{R(\alpha)}_{m\mu\sigma\sigma}(\omega)G^{R}_{\mu n\sigma\sigma'}(\omega),$$

$$(7.39)$$

---

[2]The retarded self-energy adopts here the usual form:

$$\Sigma^{R(\alpha)}_{mn\sigma\sigma}(\omega) = \boldsymbol{\Lambda}^{(\alpha)}_{mn\sigma\sigma}(\omega) - \frac{i}{2}\boldsymbol{\Gamma}^{(\alpha)}_{mn\sigma\sigma}(\omega).$$

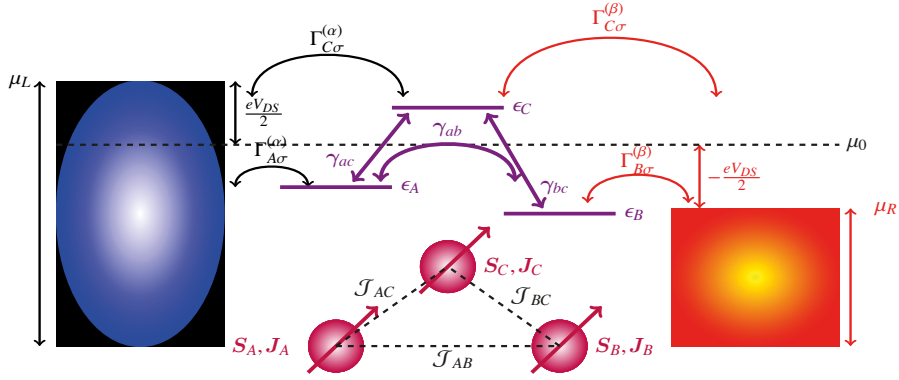*Figure 7.4.* Molecular Magnet Composed by a Trimer of Spins: This illustration describes a molecular trimer of electronic levels $\epsilon_{m\sigma}$, for $m = A, B, C$, each of them coupled to a local spin moment S_m through the Kondo interaction of strength J_m. Here, the Kondo interaction between the electronic level and the localized spin is not shown in arrow form as in figures 7.1, 7.2 and 7.3 due to lack of space and to keep clarity on where the interaction are and how they are labeled. The interaction γ_{mn}, for $m \neq n$, $m, n = a, b, c$, represents the hopping amplitude for an electron in level $\epsilon_{m\sigma}$ to undergo a transition to level $\epsilon_{n\sigma}$. This hopping amplitude is represented in matrix form by a symmetric tensor denoted as $[\gamma]$. The couplings to the leads, both left (α) and right (β), are represented by the matrix element $\Gamma_{mn\sigma\sigma}^{(\alpha,\beta)}$, and for the diagonal matrix elements ($m = n$), these couplings represent the tunneling amplitude for an electron in the left or right lead to transit into level $\epsilon_{m\sigma}$. The off-diagonal matrix elements not shown in the diagram, represent co-tunneling processes through different electronic levels.

which yields the following matrix expression for $\left[G_{mn\sigma\sigma'}^{R}(\omega) \right]^{-1}$:

$$\left[G_{mn\sigma\sigma'}^{R}(\omega) \right]^{-1} = \begin{bmatrix} \hbar\omega - \bar{\epsilon}_{A\sigma} + \frac{i}{2}\Gamma_{A\sigma} & -\gamma_{ab} & -\left(\gamma_{ac} - \frac{i}{2}\Gamma_{AC\sigma}\right) \\ \\ -\gamma_{ba} & \hbar\omega - \bar{\epsilon}_{B\sigma} + \frac{i}{2}\Gamma_{B\sigma} & -\left(\gamma_{bc} - \frac{i}{2}\Gamma_{BC\sigma}\right) \\ \\ -\left(\gamma_{ca} - \frac{i}{2}\Gamma_{CA\sigma}\right) & -\left(\gamma_{cb} - \frac{i}{2}\Gamma_{CB\sigma}\right) & \hbar\omega - \bar{\epsilon}_{C\sigma} + \frac{i}{2}\Gamma_{C\sigma}, \end{bmatrix}$$

(7.40)

where $\bar{\epsilon}_{m\sigma} = \epsilon_{m\sigma} + \Lambda_{m\sigma\sigma} + J_m \sigma_{\sigma\sigma}^{(z)} \langle S_m \rangle$, $\Lambda_{mn\sigma\sigma} = \Lambda_{mn\sigma\sigma}^{(\alpha)} + \Lambda_{mn\sigma\sigma}^{(\beta)}$, $\Gamma_{mn\sigma\sigma} = \Gamma_{mn\sigma\sigma}^{(\alpha)} + \Gamma_{mn\sigma\sigma}^{(\beta)}$.
Moreover, expression 7.40 can be written as a Dyson equation of the form:

$$G^{R}(\omega) = \left(\Omega - [\gamma] + \frac{i}{\hbar}\left(\Gamma_{\sigma\sigma}^{(\alpha)} + \Gamma_{\sigma\sigma}^{(\beta)} \right) \right)^{-1},$$

(7.41)

Where the matrices $\mathbf{\Omega}$, $[\gamma]$, $\mathbf{\Gamma}_{\sigma\sigma}^{(\alpha)}$ and $\mathbf{\Gamma}_{\sigma\sigma}^{(\beta)}$ are given by:

$$\mathbf{\Omega} = \begin{bmatrix} \bar{\epsilon}_{A\sigma} & 0 & 0 \\ 0 & \bar{\epsilon}_{B\sigma} & 0 \\ 0 & 0 & \bar{\epsilon}_{C\sigma} \end{bmatrix} \tag{7.42}$$

$$[\gamma] = \begin{bmatrix} 0 & \gamma_{ab} & \gamma_{ac} \\ \gamma_{ba} & 0 & \gamma_{bc} \\ \gamma_{ca} & \gamma_{cb} & 0 \end{bmatrix}, \tag{7.43}$$

$$\mathbf{\Gamma}_{\sigma\sigma}^{(\alpha)} = \begin{bmatrix} \Gamma_{A\sigma}^{(\alpha)} & 0 & \Gamma_{AC\sigma}^{(\alpha)} \\ 0 & 0 & 0 \\ \Gamma_{CA\sigma}^{(\alpha)} & 0 & \Gamma_{C\sigma}^{(\alpha)} \end{bmatrix} \tag{7.44}$$

$$\mathbf{\Gamma}_{\sigma\sigma}^{(\beta)} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \Gamma_{B\sigma}^{(\alpha)} & \Gamma_{BC\sigma}^{(\alpha)} \\ 0 & \Gamma_{CB\sigma}^{(\alpha)} & \Gamma_{C\sigma}^{(\alpha)} \end{bmatrix}. \tag{7.45}$$

The current set up arises as an architecture of fundamental importance in quantum engineering, extensively studied theoretically and experimentally. Here I pay special attention to the ability to commute between antiferomagnetic and ferromagnetic ground states with the aid of electric field control in the gate as demonstrated by [134] and by biasing the junction hosting the spin trimer [135]. It is desired to use a single electron source in order to account properly for interference effects within the molecular trimer. To achieve a single electron source from the STM tip, two methodologies can be explored: first, introducing electron-electron correlation in the electronic levels coupled to the STM tip or to the substrate, these levels will be singly occupied, hence the electrodes become a single electron source. Second, for highly spin polarized ferromagnetic leads, the tunneling probability of one electron either spin up or spin down from the leads, will force the system to either accept a spin up or spin down electron, but not both, hence, making the electrodes single electron sources. It is worthwhile to explore the solution with finite electron correlation energy in the orbitals overlapping with the STM tip wave function, which is already included in the formulation of this chapter, just by reconsidering expression 7.23.

7.7 Two Spins, Two Levels Coupled by a Through a Four Level Molecule

Here I extend the consideration from paper I, where a dimer of spins interacting through a two level molecule was studied. This extension consists in coupling the two electronic levels interacting with single spin moments, by a four level molecule exhibiting quantum interference with similar orbital organization as for the case of Benzene and other cyclic molecules. The system of interest is illustrated in figure 7.5. From expression 7.23, one
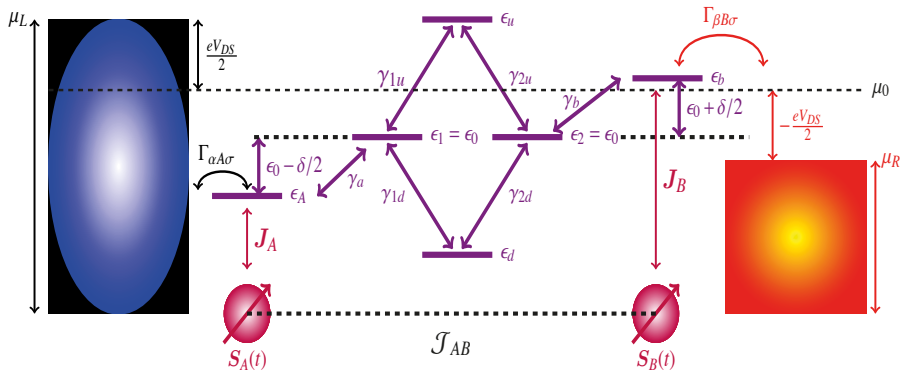
Figure 7.5. Molecular Magnet Composed by a Dimer of Spins Interacting through a Two Branch Electron Interferometer: This illustration describes a molecular trimer of electronic levels $\epsilon_{m\sigma}$, for $m = A, B, C$, each of them coupled to a local spin moment S_m through the Kondo interaction of strength J_m. Here, the Kondo interaction between the electronic level and the localized spin is not shown in arrow form as in figures 7.1, 7.2 and 7.3 due to lack of space and to keep clarity on where the interaction are and how they are labeled. The interaction γ_{mn}, for $m \neq n$, $m, n = a, b, c$, represents the hopping amplitude for an electron in level $\epsilon_{m\sigma}$ to undergo a transition to level $\epsilon_{n\sigma}$. This hopping amplitude is represented in matrix form by a symmetric tensor denoted as $[\gamma]$. The couplings to the leads, both left (α) and right (β), are represented by the matrix element $\mathbf{\Gamma}_{mn\sigma\sigma}^{(\alpha,\beta)}$, and for the diagonal matrix elements ($m = n$), these couplings represent the tunneling amplitude for an electron in the left or right lead to transit into level $\epsilon_{m\sigma}$. The off-diagonal matrix elements not shown in the diagram, represent co-tunneling processes through different electronic levels.

can obtain a generalized expression similar to expression 7.39 for the case of the spin trimer, which can be cast as a Dyson equation of the form:

$$G = \left(g_0^{-1} - [\gamma] + \frac{i}{2} \left(\Gamma^{(L)} + \Gamma^{(R)} \right) \right)^{-1}, \qquad (7.46)$$

$$g_0^{-1} = \begin{bmatrix} \hbar\omega - \bar{\epsilon}_{a\sigma} & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar\omega - \epsilon_{1\sigma} & 0 & 0 & 0 & 0 \\ 0 & 0 & \hbar\omega - \epsilon_{d\sigma} & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar\omega - \epsilon_{u\sigma} & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar\omega - \epsilon_{2\sigma} & 0 \\ 0 & 0 & 0 & 0 & 0 & \hbar\omega - \bar{\epsilon}_{b\sigma} \end{bmatrix}$$

(7.47)

$$[\gamma] = \begin{bmatrix} 0 & \gamma_a & 0 & 0 & 0 & 0 \\ \gamma_a & 0 & \gamma_{1d} & \gamma_{1u} & 0 & 0 \\ 0 & \gamma_{1d} & 0 & 0 & \gamma_{2d} & 0 \\ 0 & \gamma_{1u} & 0 & 0 & \gamma_{2u} & 0 \\ 0 & 0 & \gamma_{2d} & \gamma_{2u} & 0 & \gamma_b \\ 0 & 0 & 0 & 0 & \gamma_b & 0 \end{bmatrix}$$

(7.48)

$$\Gamma^{(L)} = \begin{bmatrix} \Gamma_{aa} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \quad \Gamma^{(R)} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \Gamma_{bb} \end{bmatrix}$$

(7.49)

where:

$$\bar{\epsilon}_{a\sigma} = \epsilon_{a\sigma} + J_a \langle S_a \rangle \sigma_{\sigma\sigma}^{(z)},$$

(7.50)

$$\bar{\epsilon}_{b\sigma} = \epsilon_{b\sigma} + J_b \langle S_b \rangle \sigma_{\sigma\sigma}^{(z)}$$

(7.51)

expressions 7.46, 7.47, 7.48, 7.49, 7.50 and 7.51 are used to make the predictions about the indirect exchange interactions among the spins, and the associated transport measurements. Also note that the use of colors in this expressions correspond to the use of colors in figure 7.5.

7.8 Final Comments

In this chapter I have attempted to familiarize the reader with the systems explored in the appended papers, making clear how the different ingredients in the system interact among themselves and with the reservoirs with the use of vivid colors that distinguish amongst. All of these, were built on the knowledge presented about a generalized equation of motion technique for an arbitrary number of electronic levels with an associated electron correlation energy. Orbital hybridization parameter is also included, which determines the amplitude with which an electron moves among these orbitals, and includes the coupling of the latter with localized

spin moments via the Kondo interaction, resembling the observations reported by A. A. Khajetoorians and Jens Wiebe *et.al* in [2]. Coupling to electron reservoirs is included through the Self-Energy, which I have simplified making the claim that, the associated Lamb-shift is negligible and the associated broadening is small though not negligible. The treatment of Phonons done by invoking the discussion made in chapter 6, is yet to be extended in this generalized formulation, to include the possibility for each level to couple to different vibration modes and with different strength, as well to include the possibility for direct and indirect (RKKY for Phonons) interactions among phonons, considering both electron and phonon reservoirs. For such advancement, the view point and the restrictions of the Lang-Firsov transformation will have to be revisited.

8. Quantum Coherence in Molecular Junctions

"There is an immense range of molecules out there. Surely we can make them do something more interesting than simply functioning as wires. I'm interested in the more exotic and dramatic electrical behaviors, and how we control the chemistry to make that happen. Highly insulating molecules are really interesting. In fact, any kind of extreme properties interest me."

Prof. Gemma Claire Solomon[1].

8.1 Why and How to Study Quantum Coherence in Magnetic Molecular Junctions.

The origin and nature of decoherence, or which is is the same, the inability to exhibit quantum interference, has been an intriguing question for now many years in different areas of physics, though it has been from the perspective of quantum optics that this quest has been usually tackled [78]. As quantum coherence is the ability of a system to exhibit quantum interference, when this ability is lost, the system of study goes from a coherent to a decoherent situation. For example, in areas such as quantum information theory, it is usually demanded to prepare maximally entangled states, and this task is intimately related with the persistence of coherence in the system [136],[137]. As an exemplifying thought, it is desirable to design a source of polarization entangled photon pairs from a bi-exciton configuration in a quantum dot [138]. As long as coherence persists in this system, this task could be achieved rather straight forward, but due to its coupling to the environment (electromagnetic radiation, laser fields, etc), the persistence of coherence in these type of systems poses a great challenge in its practical realization [139], with the constraint, for instance, in semiconductor quantum dots, that the sample fabrication becomes of crucial importance in these type of experiments [138], [140].

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[1]Source: http://chem.ku.dk/om/news/newslist/solomonuk/

In Molecular and condensed matter physics, the persistence of coherence, be it related to destructive or constructive quantum interference, has shown to play a significant role in systems like molecular junctions whose dimensionality enhances quantum effects [47], [141],[142],[5], such as coherent transport, in which case, dips and peaks in the electronic transmission emerges as a faithful signature of the presence of either type
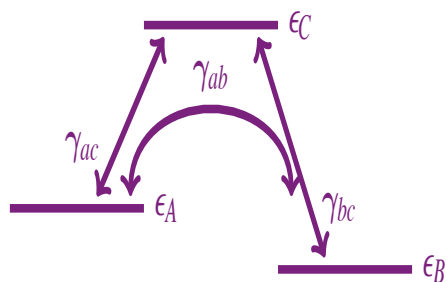

Figure 8.1. Set up proposed by [12] to Investigate the Effects of Quantum Interference in Charge Transport

of quantum interference manifestations [143], [144], [145], [146], [147], [148], [149], . Experimentally it has been know for quite some time now that the relation structure-function in molecular junctions with respect to quantum interference effects is more or less well described by the correlation between cross-conjugated molecules and destructive quantum interference, and the one claiming that, linear-conjugated complexes are related to the inability to host interference processes, though in a recent publication, Prof. Gemma Solomon and Collaborators argues from a theoretical point of view, against this generalized statement claiming that the connection between conjugation type in molecular systems and quantum interference is rather *"illusory"* [150]. In this thesis, following the argumentation by Valkenier [129], [151], [12] and by Bessis [152], I study the ability of a molecular junction hosting localized spin moments, such as $TbPc_2$ reported in [50], to exhibit electronic quantum interference, and host the effect of the localized magnetic moments present in the sample modify or modulate this ability, but more importantly, how these magnetic units interact via RKKY when the electronic structure of the molecule of interest undergoes a transition from quantum coherent transport to complete electronic decoherence. The latter, is a rather new aspect in the investigation of quantum coherent processes in molecular junctions, and in this thesis, I am proposing to put forward the debate on the usefulness to embed an electron interferometer in a molecular junction, through which, the localized magnetic moments can interact, and whether electronic quantum interference plays a role in the stability, control, manipulation and detection of quantum spin states, or whether it doesn't.

8.2 Theoretical Methods Used in the Description of Quantum Coherence

From the viewpoint of quantum optics, the Lindblad formalism for the density matrix has been extensively used [78], [136] and[137]. In condensed matter systems, this formalism has been was well explored [153], [154], [155], [156], [157], and some important drawbacks such as, its low effectiveness when treating problems in the strong coupling regime as compare to commonly reported approaches [158], the complications related to treat problems perturbatively [78], [159] and even, when it has been shown to perform well in comparison to what is expected, other methods such as non-equilibrium Green's functions reproduce a physical observable with a much better degree of assertiveness, this precisely in the non-Markovian regime, which is of fundamental importance in condensed matter [160]. As for quantum optics, the Markovian Lindblad equation has been shown reproduce experimental observations to a good degree of accuracy [78]. On the other hand, from the quantum master equation, the populations and coherences can be straight forward obtained, and the analysis of whether a system persists in a quantum coherent situation at a given time or not can be easily done [78],[154], [161], [157].

To merge the definitions, concepts and language from quantum optics and the formalism developed from condensed matter field theory [86], [88], into a common ground, few descriptions have been explored [154], [157]. In [162], a study of a quantum thermal transistor is presented, using a quite simplified approach, which provides great insight on the thermal evolution of the coherences and the populations defined for the system in the spirit of the quantum master equation. Moreover, as reported by Pedro Ribeiro *et.al* [154], it is well worth to explore the possibility of expressing the ladder operators in the quantum master equation in the context of Non-Equilibrium Green's functions, which are obtained in principle perturbatively, keeping in that way conventions from the density matrix as the system is evolved on the Keldysh contour as proposed in [79] (see section 4.2). Using this approach, typical systems studied in condensed matter physics were considered by P. Riveiro in [154], such as charge and energy flow in transport problems as well as the XY model for spin transport, where a measure for markovianity was defined, which may account for the limitations of the model.

Lastly, as it has been predicted theoretically [143], [12], [152] and demonstrated experimentally [163], [12], [134] molecular junctions are the perfect test bench to study quantum coherence and the effects of quantum decoherence in systems spanning physics at the nanometric length scale (that is, when the dimension of the junction where the molecule is embedded is

of the order of the coherence length of the wave functions of the conduction electrons) [124], [164], [157]. Moreover, Quantum interference could be as well studied from the standpoint of transport measurements [165], [166], [12], [167], [130],[147], [168],[169] and from thermoelectric response calculations and experiments performed in molecular junctions reported in [143], [153], [170], [151], [171]. Some of the observables of interest that can be used to either predict or to obtained a experimental evidence of quantum coherent effects in molecular junctions include transmission probabilities, the Seebeck coefficient, the Lorenz number, the Peltier coefficient and the Figure of Merit [147]. From these, signatures of whether coherence persists or is lost can be immediately determined, using the typical language from condensed matter field theory, the Keldysh formalism.

8.3 Quantum Interference and Decoherence Studies in Molecular Junctions.

As molecular junctions have paved the way to examine quantum interference from a charge and heat flow perspective, and controlled experiments (chemical, electrical and thermal) can be performed in such systems [135], [134], quantum coherence has been extensively studied in molecular junctions, establishing a correlation between structure and function from the standpoint of the ability to exhibit quantum interference within the molecular bridge embedded in a metallic junction [167], [151]. In [143], it was predicted that the transmission probability, the Seebeck coefficient and the Lorenz number can be used as signatures for destruction of quantum interference in molecules that exhibit quantum coherence effects. In this study the molecules examined were *isoprene*, *1,3-benzenedithiol* and *18-annulene*, and the dips in the transmission probability coincide with the peaks in the Seebeck coefficient and Lorenz number, suggesting that entropy driven processes are robust to quantum interference phenomena [143] (See chapter 9, section 9.2). Moreover, several experimental and computational studies and reviews on the field have reported the synthesis of linearly and cross conjugated organic molecules, as well as molecules exhibiting broken conjugation, and the study on these molecules with regards to quantum coherence [165], [129], [122], [172], [167], [151]. These studies demonstrated that the linear conjugated type of molecules in this case Anthracene-MT (Monothiolated) and Anthracene-DT (Dithiolated) exhibit robustness against quantum interference as for its transport properties [167], and that cross-conjugated molecules (Typically Anthraquinone-MT and Anthraquinone-DT) [129], as well as molecules with broken conjugation [151] shows that the transmission probability severely drops, suggesting the presence of destructive quantum interference processes in the molecular junction. This line of argumentation is strongly debated in

[150]. Other molecules typically investigated are the Oligo(Phenylene-Ethynylene) Mono and Dithiolated [173], [151], [131], which have been prepared and test to show the effect of the length of the chain on quantum interference in molecular junctions as well as to show the effect of conjugation type on this phenomena, establishing a well define correlation between cross-conjugation and quantum interference [151], at least in the systems under consideration. Additionally, it has been demonstrated that the main source of quantum decoherence in molecular junctions is the electron-phonon interaction [173], [146], which have been probed using interference effects in these type of systems and reported in [152].

From the standpoint of technological applications, some other studies that have demonstrated electrochemical and electrical control of the transmission in three-terminal devices, suggest that coherence controlled molecular junctions are a plausible realization, and that molecular junctions could serve as well as controlled nanoreactors [166], [134]. These studies, have provided important evidence that structure and function of the molecule embedded in the metallic junction can be modified by an

Figure 8.2. Decoherent Charge Transport: In the set up shown, when $\gamma_{ab} = 0$, the ability of the system to exhibit quantum interference is lost.

action of a gate signal, a bias voltage or temperature difference, and even electrochemically. The latter statement, serves as fuel to design a plan of action to determine whether quantum interference effects play a role in the dynamics of spin-spin interactions or not, by the action of gate fields or bias voltages.

On the theory front, interference effects in molecular junctions have been studied mainly using a hybrid between DFT and Non-Equilibrium Green's functions, as well as DFT+Σ methods, which have been reported in [174], [151], [147]. The Keldysh Green's function Technique from a model Hamiltonian, a technique widely used in transport studies at the nanscale [89] has been rarely used for this purpose in molecular junctions by itself, for biasing conditions far beyond equilibrium, in despite of its usefulness in the calculation of transmission and conductance as well as several Thermoelectric measures that complement the signatures for quantum interference effects present [175], [102]. These thermoelectric measurements, such as the ones defined for Boltzmann linear transport, namely the Seebeck coefficient, the Peltier coefficient, the electrical conductivity, the heat conductivity and the Lorenz number [176], can be well define in linear response from

the Landauer conductance using the Keldysh technique [143], [177],[178], [179], and beyond linear response, they can be defined in terms of differential conductivities [102]. In [jcpc], that is, in paper I, I explore the application of Non-equilibrium Green's functions to study energy and charge currents in a magnetic tunneling junction, defining the Seebeck coefficient for large bias voltages and large temperature gradients in terms of non-equilibrium differential conductivities, hence contributing to the application of the former in the systems of interest in the present chapter. Other available tools in the literature, are but not limited to, the scattering matrix theory [180], [181], the Floquet-Fourier formalism for the Green's function [182], [183], [181], Hierarchical equations of motion [160], [161], and finally, the technique which can be pretty much consider the theory of everything in condensed matter [86], namely[2] the Keldysh formalism for non-equilibrium Green's functions [105], [91], [68], [88], [104].

8.4 Review of Single Photon Interferometry

To put into context the idea of single electron interferometry, I will describe the processes of single photon interferometry as studied in quantum optics, and then I will ellaborate on my proposal on single electron interferometers using ferromagnetic-metallic tunneling junctions.

The typical set up of a single photon source, with a beam splitter and two photon detectors is shown in figure 8.3. In this set up, each detector has

$50 - 50$ Beam Splitter

$P(A) = \frac{1}{2}$

$P(B) = \frac{1}{2}$
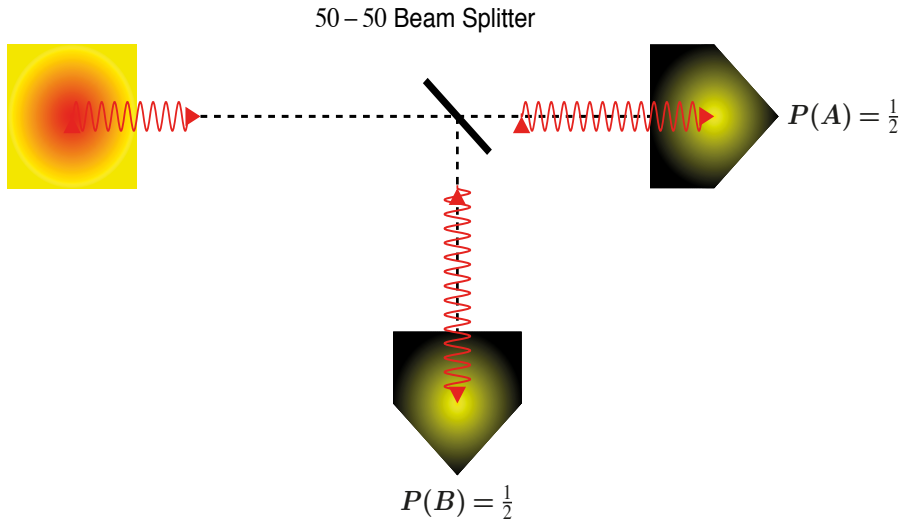
Figure 8.3. Single Photon Beam Splitter and Detection.

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[2]This claim has been made in chapter 11 of reference [86]

equal probability to click at the arival of the photon, and their paths are somwhat deterministic as there are no interefering pathways among photons.

For the case of the interferometer shown in figure 8.4, I show a single photon source, which is split and then recombined and it will certainly arrived at detector A (Detector B is shown to be blocked). If I perform a probabilistic
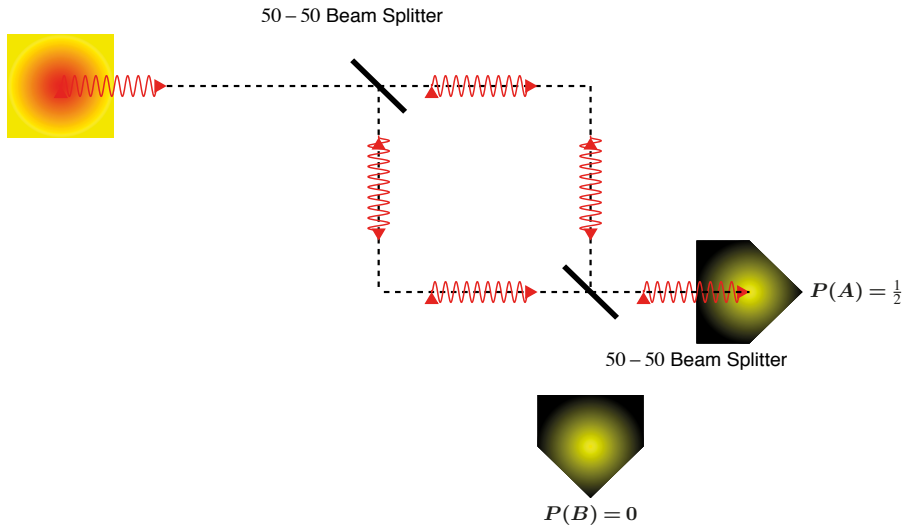
Figure 8.4. Single Photon Interferometer with Interfering Pathways: Classical Analysis.

analysis, taking into account the probability for each path and the probability for the detector (Detector A), It gives that the probability for detector A, is $P(A) = \frac{1}{2}$, which is clearly counter intuitive. The analysis is performed as follows:

$$P(A) = P(A|x)\,P(x) + P(A|y)\,P(y)$$

$P(A)$: Probability of detector A, $P(A|x)$: Probability that A fires given path x, $P(x)$: Probability of path x, $P(A|y)$: Probability that A fires given path y, $P(y)$: Probability of path y.

$$P(A) = P(A|x)\,P(x) + P(A|y)\,P(y) = \frac{1}{2}\frac{1}{2} + \frac{1}{2}\frac{1}{2} = \frac{1}{2}$$

$P(A)$: Probability of detector A, $P(A|x)$: Probability that A fires given path x, $P(x)$: Probability of path x, $P(A|y)$: Probability that A fires given path y, $P(y)$: Probability of path y.
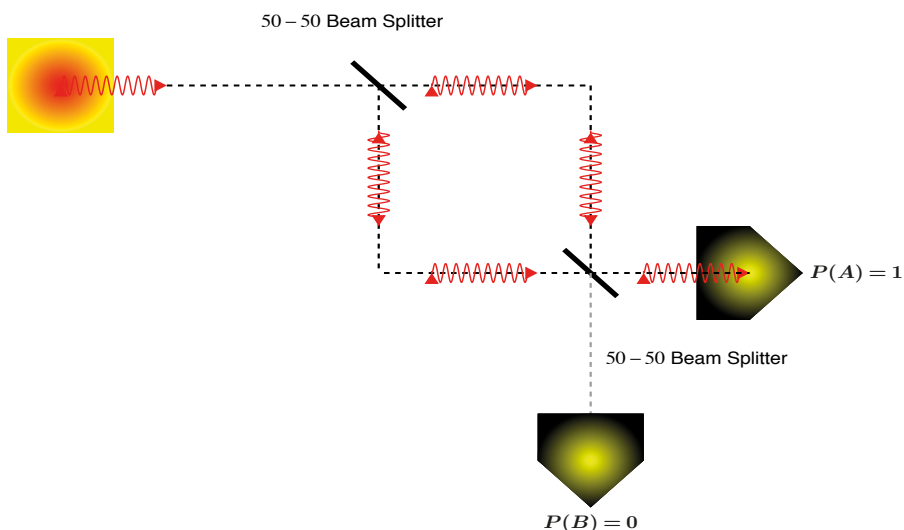
Figure 8.5. Single Photon Interferometer: Quantum Analysis Using the Addition of Probability Amplitudes or Wave Functions.

From the viewpoint of Quantum Mechanics, instead of adding probabilities, one adds wave-functions or probability amplitudes, as is shown below: Amplitudes:

$$\Psi(A) = \Psi(A|x)\Psi(x) + \Psi(A|y)\Psi(y), \qquad (8.1)$$

then, according to quantum theory of probabilities, $P(A)$, then reads:

$$\begin{aligned}
P(A) &= |\Psi(A)|^2 = \Psi(A)^\dagger \Psi(A) \\
&= (\Psi(A|x)\Psi(x) + \Psi(A|y)\Psi(y))^\dagger (\Psi(A|x)\Psi(x) + \Psi(A|y)\Psi(y)) \\
&= |\Psi(A|x)|^2 |\Psi(x)|^2 + |\Psi(A|y)|^2 |\Psi(y)|^2 \\
&\quad + \Psi(A|x)\Psi(x)\Psi(A|y)^\dagger \Psi(y)^\dagger + \Psi(A|x)^\dagger \Psi(x)^\dagger \Psi(A|y)\Psi(y) \\
&= P(A|x)P(x) + P(A|y)P(y) + \textsf{Interference}.
\end{aligned}$$

This interference , is unique to quantum mechanics, and it represents the redeeming quality of the latter with regards to novel technological applications such as quantum information theory and quantum engineering. In electron interferometry, where the wave function of this last one delocalizes along the interference path, the ability to exhibit quantum interference, has been shown of capital importance to understand a broad range of phenomena, such as transport and thermoelectrics, and my quest is to understand what is its interplay with the spin ordering within the molecular junction.

One more question arises in this type of set up, and is, what happens when the paths are not indistinguishable anymore? where there is a de-

gree of certainty on whether the photon takes one path or the other. To understand the implications of this context, I encourage the reader to consider the interferometer shown in figure 8.6, where the Gray box in the upper branch of the interferometer does not interact with the split photon. When a measurement probe is set on the upper branch, the wave function
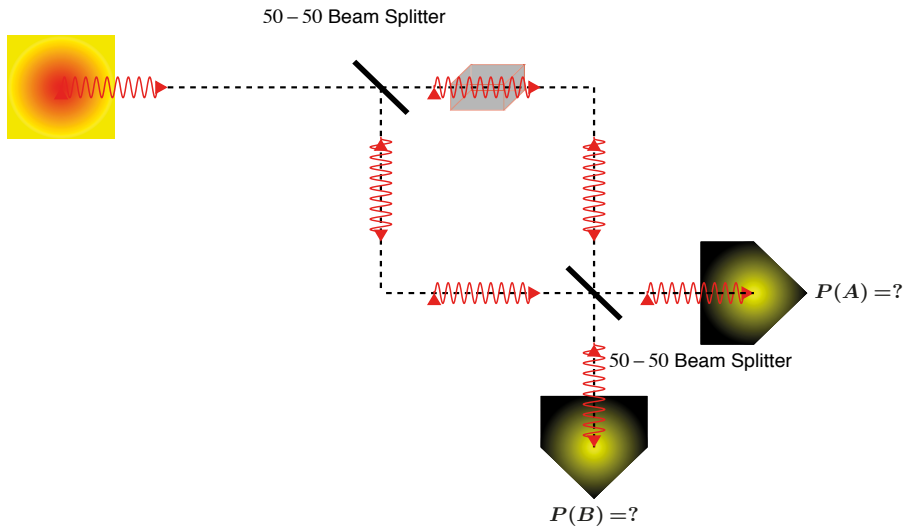
Figure 8.6. Single Photon Interferometer: No Measurement - Pathway uncertain

collapses and the paths the photon takes becomes distinguishable, hence the box clucks to become orange, as seen in figure 8.6. This is of capital importance to understand, since the probe (in orange), kills the ability of the system to exhibit quantum interference, therefore, undergoing a transition to a decoherent situation.

In electron interferometry, this situation can be triggered by Buttiker probes that induces dephasing, such as in the work presented by D. Seagal. In paper III, I show that the spin structure of a trimer competes with the dephasing mechanism, hence giving rise to destructive quantum interference as a consequence of the RKKY interaction.
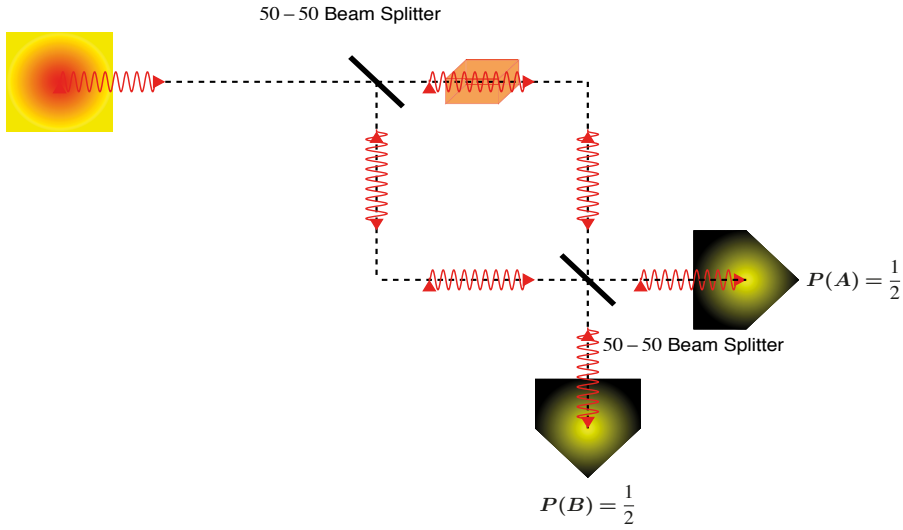
Figure 8.7. Single Photon Beam Splitter and Detection.

8.5 Aharonov-Bohm effect and Electron Interferometry

The Aharonov-Bohm effect was predicted in 1959 by Yakir Aharonov and David Bohm [184], where the effect of Gauge potentials on quantum mechanical observables was investigated. As oppose to classical theory, it was found that Gauge potentials from electrodynamics have a noticeable effect in quantum mechanics under the eye of electron interference, and the phase printed on the electron density after the electron beams are recombined is known as the Aharonov-Bohm phase and which is given by:

$$\Delta\Phi_{AB} = \frac{q\phi_M}{\hbar},\tag{8.2}$$

where q is the associated charge of the electron and ϕ_M is the magnetic flux that transverses the Aharonov-Ring in the region where the magnetic field density B is different than zero (see Fig. 8.8). In the next few lines, I will try to make sense of the Aharonov-Bohm effect as it is discussed in [75], and then, I will put it into context in molecular junctions specially the one shown in Fig. 7.5, where a phase is printed in the hybridization parameters γ_{1d} and γ_{2d}, such that: $\gamma_{1d}e^{-i\Phi_{1d}}$ and $\gamma_{2d}e^{-i\Phi_{2d}}$.

Now, suppose an electron is moving in an interferometer through a region where $B = 0$ and where $A \neq 0$, after the electron wave was split as shown in Fig. 8.8. In this context the time dependent Schrödinger equation

is writen as follows:

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\boldsymbol{\nabla} - q\boldsymbol{A}(\boldsymbol{r}) \right) + V(\boldsymbol{r},t) \right]\Psi_{AB}(\boldsymbol{r},t) = i\hbar\frac{\partial\Psi_{AB}(\boldsymbol{r},t)}{\partial t}, \qquad (8.3)$$

where $\Psi_{AB}(\boldsymbol{r},t)$ is the total wave function of the electron delocalized in the Aharonov-Bohm (AB) ring, $V(\boldsymbol{r},t)$ is the potential energy applied in the AB ring which may, or may not include an electric contribution of the form $q\phi_e$, being ϕ_e the electric scalar potential, and $\boldsymbol{A}(\boldsymbol{r})$ is the vector potential. By defining the AB wave function in terms of a phase factor in the following way:

$$\Psi_{AB}(\boldsymbol{r},t) = \psi(\boldsymbol{r},t)e^{ig(\boldsymbol{r})}, \qquad (8.4)$$

yielding the following time dependent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r},t) \right]\psi(\boldsymbol{r},t) = i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t}, \qquad (8.5)$$

where $g(\boldsymbol{r}) = \frac{q}{\hbar}\int \boldsymbol{A}(\boldsymbol{r}')\cdot d\boldsymbol{r}'$ and $\boldsymbol{\nabla}g(\boldsymbol{r}) = \frac{q}{\hbar}\boldsymbol{A}(\boldsymbol{r})$.
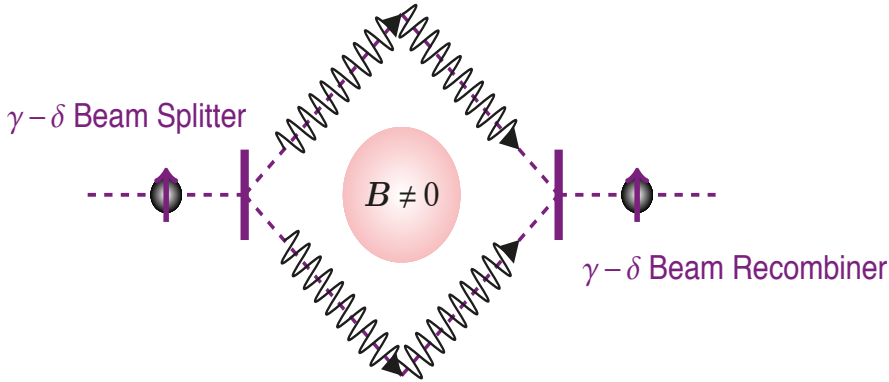
Figure 8.8. Aharonov-Bohm Interferometer: An incoming electron splits becoming delocalized in a region where the magnetic field $B = 0$, and then recombines, interfering constructively or destructively. The Aharonov-Bohm effect, predicts that the nature of this interference depends of the time-dependent potential felt by the electron in the ring where its delocalized.

Furthermore, $g(\boldsymbol{r})$ can be calculated for the particular AB geometry in the following way:

$$g(\boldsymbol{r}) = \frac{q}{\hbar}\int \boldsymbol{A}(\boldsymbol{r})\cdot d\boldsymbol{r} = \frac{q\phi_M}{2\pi\hbar}\int \left(\frac{1}{r}\boldsymbol{a}_\phi \right)\cdot\left(rd\phi\boldsymbol{a}_\phi \right),$$

$$= \pm\frac{q\phi_M}{2\hbar}. \qquad (8.6)$$

In the above expression, the sign of $g(r)$ depends on whether the direction of a_ϕ coincides with the circulation of $A(r)$ or not. The above reasoning should be straightforward for the audience with background in electrical engineering, with some support from refs. [75] and [16].

In the context of molecular junctions, the Aharonov-Bohm effect has been studied extensively mainly within double quantum dots Aharonov-Bohm interferometers in contact with electronic reservoirs [185, 157], or with nanowires exhibiting Spin-Orbit coupling hence providing a source for breaking time inversion symmetry in the system [186, 187, 188, 189, 190], among other related configurations. Experimentally, these topologies are supported by relevant findings reported in [191]. However, here I explore a different set up that has not been considered so far to the best of my knowledge, and definitely, has not been considered in the context of spin singlet - spin triplet formation via RKKY interaction.
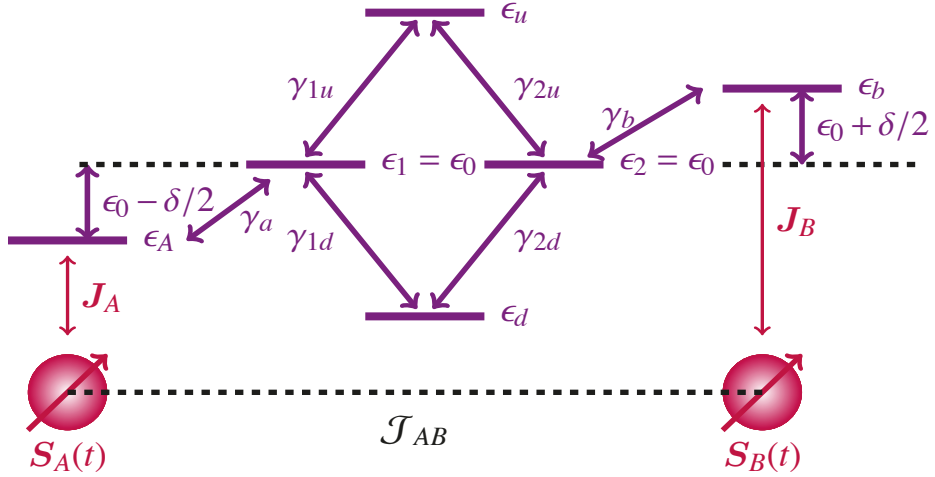
Figure 8.9. Two Spin RKKY Interfering Machine: Two electronic levels ϵ_A and ϵ_B are coupled to two magnetic units labeled as S_A and S_B via Kondo interaction constants J_A and J_B. Both magnetic units interact through the RKKY interaction where the electron bath is an Aharonov-Bohm like interferometer composed by two electronic beam splitters ϵ_1 and ϵ_2, and an upper and lower interferometer branch respectively labeled as ϵ_u and ϵ_d. A phase ϕ_{1d} is printed in the hybridization parameters γ_{1d} and γ_{2d}, which plays the role of an Aharonov-Bohm phase.

I considered the molecular junction illustrated in Fig. 7.5, where levels ϵ_A and ϵ_B that coupled to the left and right leads respectively, are Kondo coupled to two magnetic units that interact via RKKY. The latter and the former, play the role of electron source and sink. Levels ϵ_1 and ϵ_2 serve as electron beam splitters and/or electron recombiners. The molecule in between levels ϵ_A and ϵ_B is a Benzene like molecule with a simplified scheme of just

4 energy levels ϵ_1, ϵ_2, ϵ_u and ϵ_d, where level ϵ_u plays the role of the upper branch of an Aharonov-Bohm interferometer and conversely, level ϵ_d plays the role of the lower branch in an Aharonov Bohm interferometer. For completeness, I show in Fig. 8.9 the molecule of interest without coupling to the leads (This was discussed in chapter 7). To study the RKKY interaction between spins S_A and S_B, I propose a single electron-interferometer scheme. There are two available routes to do so. First, by guaranteeing that levels acting as source and sink are singly occupied, which can be done by associating an electron correlation energy with these levels. Second, by considering highly polarized metallic-ferromagnetic leads, which will guarantee that a single spin specie tunnels to and out from the molecule, hence, engineering a single electron interferometer. The proposed set up is shown in figure 8.10.
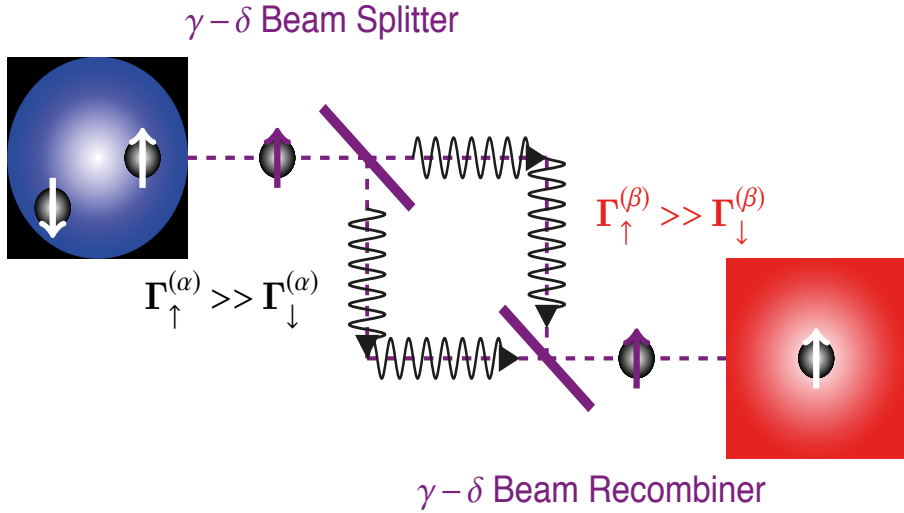
Figure 8.10. Single Electron Interferometer Embedded in a Metallic (Ferromagnetic) Tunneling Junction:.

Evaluation of the Heisenberg exchange interaction for the system depicted in Fig. 7.5 and 8.9, is evaluated through expression 5.55, by varying the printed phase ϕ_{1d} from $0 - \dfrac{2\pi}{3}$, showing the possibility to switch between singlet and triplet ground states by varying this phase (see Fig. 8.11). The results show that the entangled state can be control either by an applied bias voltage or more importantly, around zero-bias, by the printed phase on the hybridization parameters. This system is still under investigation, and I shall propose novel methods for electrical detection of the entangled state and product states.
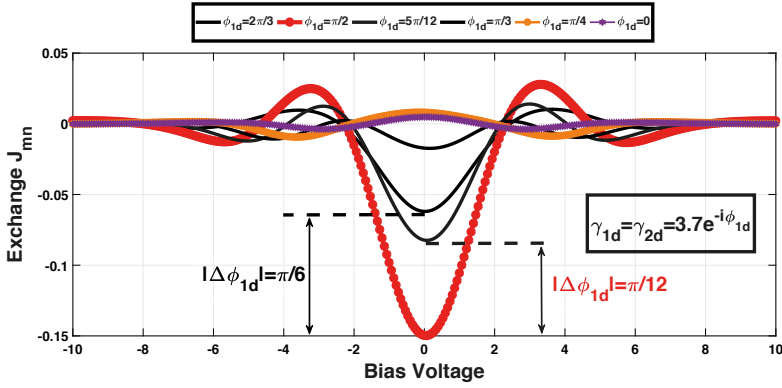
Figure 8.11. RKKY Heisenberg Exchange Interaction between spins S_A and S_B. The parameters used are: $\gamma_{1d} = \gamma_{2d} = 3.5e^{-i\phi_{1d}}$ meV, $\gamma_a = \gamma_b = 2$ meV, $\gamma_{1u} = \gamma_{2u} = 2.0$ meV, $\Gamma^{(\alpha)}_{A\sigma} = 5$ meV, $\Gamma^{(\beta)}_{B\sigma} = 5$ meV, $\rho^{(\alpha)} = 0.7$, $\rho^{(\beta)} = 0.7$, $J_A = 10$ meV, $J_B = 10$ meV. $\epsilon_A = \epsilon_B = \epsilon_1 = \epsilon_2 = 0$ meV, $\epsilon_u = 0.5$ meV, $\epsilon_d = -0.5$ meV.

8.6 Molecular Models in the Study of Quantum Interference

Here I consider three type of systems to make sense of electron interferometry in molecular junctions, to further extend the discussion to tripple quantum dots as interferometers. First a couple of electronic levels each singly coupled to a reservoir as illustrated in Fig. 7.2, two coupled electronic levels doubly coupled to both reservoirs, where off-diagonal elements of the broadening matrices are ignored, and a third type, where the off diagonal elements of the previous case are fully considered with dephasing induced among levels. The later and the former have the structure of the system discussed in Fig. 7.3. For the first case, the broadening matrices with respect to both leads are given by:

$$\mathbf{\Gamma}^{(L)} = \begin{bmatrix} \Gamma^{(L)}_{aa} & 0 \\ 0 & 0 \end{bmatrix}; \mathbf{\Gamma}^{(R)} = \begin{bmatrix} 0 & 0 \\ 0 & \Gamma^{(R)}_{bb} \end{bmatrix}. \tag{8.7}$$

As such, the transmission (as defined in 4.102) through the junction is evaluated as follows:

$$T_1(\epsilon) = \text{Tr}\left[\begin{bmatrix} \Gamma^{(L)}_{aa} & 0 \\ 0 & 0 \end{bmatrix}\begin{bmatrix} G^R_{aa}(\omega) & G^R_{ab}(\omega) \\ G^R_{ba}(\omega) & G^R_{bb}(\omega) \end{bmatrix}\begin{bmatrix} 0 & 0 \\ 0 & \Gamma^{(R)}_{bb} \end{bmatrix}\begin{bmatrix} G^A_{aa}(\omega) & G^A_{ab}(\omega) \\ G^A_{ba}(\omega) & G^A_{bb}(\omega) \end{bmatrix}\right],$$

$$= \text{Tr}\left[\begin{bmatrix} \Gamma^{(L)}_{aa}G^R_{aa}(\omega) & \Gamma^{(L)}_{aa}G^R_{ab}(\omega) \\ 0 & 0 \end{bmatrix}\begin{bmatrix} 0 & 0 \\ \Gamma^{(R)}_{bb}G^A_{ba}(\omega) & \Gamma^{(R)}_{bb}G^A_{bb}(\omega) \end{bmatrix}\right],$$

$$= \Gamma^{(L)}_{aa}\Gamma^{(R)}_{bb}G^R_{ab}(\omega)G^A_{ba}(\omega). \tag{8.8}$$

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Note that in this case, $\phi_{AB} = 0$. Furthermore, the characteristic polynomial of $T(\epsilon)$, that is, $q(\omega)$, can be simplified as follows:

$$
\begin{aligned}
q(\omega) &= \left[\left(\hbar\omega - \epsilon_{a\sigma} + \frac{i}{2}\Gamma_{aa\sigma}\right)\left(\hbar\omega - \epsilon_{b\sigma} + \frac{i}{2}\Gamma_{bb\sigma}\right) - |\gamma_{ab}|^2\right] \\
&\qquad \left[\left(\hbar\omega - \epsilon_{a\sigma} - \frac{i}{2}\Gamma_{aa\sigma}\right)\left(\hbar\omega - \epsilon_{b\sigma} - \frac{i}{2}\Gamma_{bb\sigma}\right) - |\gamma_{ab}|^2\right], \\
&= \left(\hbar\omega - \epsilon_{a\sigma} + \frac{i}{2}\Gamma_{aa\sigma}\right)\left(\hbar\omega - \epsilon_{a\sigma} - \frac{i}{2}\Gamma_{aa\sigma}\right) \\
&\qquad \times \left(\hbar\omega - \epsilon_{b\sigma} + \frac{i}{2}\Gamma_{bb\sigma}\right)\left(\hbar\omega - \epsilon_{b\sigma} - \frac{i}{2}\Gamma_{bb\sigma}\right) + |\gamma_{ab}|^4 \\
&\quad - |\gamma_{ab}|^2\left(\hbar\omega - \epsilon_{a\sigma} + \frac{i}{2}\Gamma_{aa\sigma}\right)\left(\hbar\omega - \epsilon_{b\sigma} + \frac{i}{2}\Gamma_{bb\sigma}\right) \\
&\qquad - |\gamma_{ab}|^2\left(\hbar\omega - \epsilon_{a\sigma} - \frac{i}{2}\Gamma_{aa\sigma}\right)\left(\hbar\omega - \epsilon_{b\sigma} - \frac{i}{2}\Gamma_{bb\sigma}\right), \\
&= \left[(\hbar\omega - \epsilon_{a\sigma})^2 + \frac{\Gamma_{aa\sigma}^2}{4}\right]\left[(\hbar\omega - \epsilon_{b\sigma})^2 + \frac{\Gamma_{bb\sigma}^2}{4}\right] \\
&\quad + |\gamma_{ab}|^4 - |\gamma_{ab}|^2\left[2(\hbar\omega - \epsilon_{a\sigma})(\hbar\omega - \epsilon_{b\sigma}) - \frac{\Gamma_{aa\sigma}\Gamma_{bb\sigma}}{2}\right], \\
&= (\hbar\omega - \epsilon_{0\sigma})^4 + \left[\frac{\Gamma_{aa\sigma}^2 + \Gamma_{bb\sigma}^2}{4}\right](\hbar\omega - \epsilon_{0\sigma})^2 + \frac{\Gamma_{aa\sigma}^2\Gamma_{bb\sigma}^2}{16} \\
&\quad - 2|\gamma_{ab}|^2(\hbar\omega - \epsilon_{0\sigma})^2 + |\gamma_{ab}|^2 + |\gamma_{ab}|^4 + |\gamma_{ab}|^2\frac{\Gamma_{aa\sigma}\Gamma_{bb\sigma}}{2}, \\
&= (\hbar\omega - \epsilon_{0\sigma})^4 + \left[\frac{\Gamma_{aa\sigma}^2 + \Gamma_{bb\sigma}^2}{4} - 2|\gamma_{ab}|^2\right](\hbar\omega - \epsilon_{0\sigma})^2 + \left(|\gamma_{ab}|^2 + \frac{\Gamma_{aa\sigma}\Gamma_{bb\sigma}}{4}\right)^2,
\end{aligned}
$$
(8.9)

where I have assumed $\epsilon_{a\sigma} = \epsilon_{b\sigma} = \epsilon_{0\sigma}$. Moreover, by replacing $G_{ab}^R(\omega)$ and $G_{ba}^A(\omega)$ from expression 7.34 (coupling to left lead is labeled here with L and the right lead is labeled with R) into expression 8.8, and by using expression 8.9, I may write $T(\epsilon)$ as follows:

$$
T(\epsilon) = \frac{\Gamma_{aa}^{(L)}\Gamma_{bb}^{(R)}|\gamma_{AB}|^2}{(\hbar\omega - \epsilon_{0\sigma})^4 + \left[\frac{\Gamma_{aa\sigma}^2 + \Gamma_{bb\sigma}^2}{4} - 2|\gamma_{ab}|^2\right](\hbar\omega - \epsilon_{0\sigma})^2 + \left(|\gamma_{ab}|^2 + \frac{\Gamma_{aa\sigma}\Gamma_{bb\sigma}}{4}\right)^2}.
$$
(8.10)

For the second case, the Landauer transmission (see expression 4.102) can be written as follows:

$$T_2(\epsilon) = \mathrm{Tr}\left[\left[\begin{array}{cc} \Gamma_{aa}^{(L)}G_{aa}^R(\omega) & \Gamma_{aa}^{(L)}G_{ab}^R(\omega) \\[2ex] \Gamma_{bb}^{(L)}G_{ba}^R(\omega) & \Gamma_{bb}^{(L)}G_{bb}^R(\omega) \end{array}\right]\left[\begin{array}{cc} \Gamma_{aa}^{(R)}G_{aa}^A(\omega) & \Gamma_{aa}^{(R)}G_{ab}^A(\omega) \\[2ex] \Gamma_{bb}^{(R)}G_{ba}^A(\omega) & \Gamma_{bb}^{(R)}G_{bb}^A(\omega) \end{array}\right]\right],$$

$$= \Gamma_{aa}^{(L)}\Gamma_{aa}^{(R)}|G_{aa}^R(\omega)|^2 + \Gamma_{bb}^{(L)}\Gamma_{bb}^{(R)}|G_{bb}^R(\omega)|^2$$

$$+ \left[\Gamma_{aa}^{(L)}\Gamma_{bb}^{(R)} + \Gamma_{aa}^{(R)}\Gamma_{bb}^{(L)}\right]G_{ab}^R(\omega)G_{ba}^A(\omega). \tag{8.11}$$

Using Eq. 7.34 on Eq. 8.11, the Landauer transmission for this case reads:

$$T_2(\epsilon) = \frac{\alpha\,(\hbar\omega - \epsilon_{0\sigma})^2 + \beta}{(\hbar\omega - \epsilon_{0\sigma})^4 + \left[\frac{\Gamma_{aa\sigma}^2 + \Gamma_{bb\sigma}^2}{4} - 2|\gamma_{ab}|^2\right](\hbar\omega - \epsilon_{0\sigma})^2 + \left(|\gamma_{ab}|^2 + \frac{\Gamma_{aa\sigma}\Gamma_{bb\sigma}}{4}\right)^2}, \tag{8.12}$$

where α and β are given by:

$$\alpha = \Gamma_{aa}^{(L)}\Gamma_{aa}^{(R)} + \Gamma_{bb}^{(L)}\Gamma_{bb}^{(R)}, \tag{8.13}$$

$$\beta = \left[\frac{\Gamma_{aa}^{(L)}\Gamma_{aa}^{(R)}}{4}\left(\Gamma_{bb\sigma}^{(L)} + \Gamma_{bb\sigma}^{(R)}\right)^2 + \frac{\Gamma_{bb}^{(L)}\Gamma_{bb}^{(R)}}{4}\left(\Gamma_{aa\sigma}^{(L)} + \Gamma_{aa\sigma}^{(R)}\right)^2\right]$$

$$+ \left(\Gamma_{aa}^{(L)}\Gamma_{bb}^{(R)} + \Gamma_{aa}^{(R)}\Gamma_{bb}^{(L)}\right)|\gamma_{ab}|^2. \tag{8.14}$$

Similarly, for the third case, the Landauer transmission can be evaluated using the following broadening matrices:

$$\mathbf{\Gamma}^{(L)} = \left[\begin{array}{cc} \Gamma_{aa}^{(L)} & \Gamma_{ab}^{(L)} \\[2ex] \Gamma_{ba}^{(L)} & \Gamma_{bb}^{(L)} \end{array}\right] ; \mathbf{\Gamma}^{(R)} = \left[\begin{array}{cc} \Gamma_{aa}^{(R)} & \Gamma_{ab}^{(R)} \\[2ex] \Gamma_{ba}^{(R)} & \Gamma_{bb}^{(R)} \end{array}\right], \tag{8.15}$$

where the off diagonal elements of the matrices $\mathbf{\Gamma}^{(L)}$ and $\mathbf{\Gamma}^{(R)}$ are given by the following relation:

$$\Gamma_{mm\sigma}^{(\chi)} = 2\pi\sum_{\mathbf{k}}\delta(\epsilon - \epsilon_{\mathbf{k}\sigma})|v_{m\mathbf{k}\sigma}|^2, \tag{8.16}$$

$$\Gamma_{mn\sigma}^{(\chi)} = e^{-i(\phi_m - \phi_n)}\cdot 2\pi\sum_{\mathbf{k}}\delta(\epsilon - \epsilon_{\mathbf{k}\sigma})|v_{m\mathbf{k}\sigma}||v_{n\mathbf{k}\sigma}|. \tag{8.17}$$

The couplings $v_{m\mathbf{k}\sigma}$ and $v_{n\mathbf{k}\sigma}^*$ appearing in Eqs. 8.16 and 8.17, are complex in nature, and therefore, they can express both of them as an amplitude times a phase factor of the form $v_{m\mathbf{k}\sigma} = |v_{m\mathbf{k}\sigma}|e^{-i\phi_m}$ and $v_{m\mathbf{k}\sigma}^* = |v_{m\mathbf{k}\sigma}|e^{i\phi_m}$, where phases ϕ_m and ϕ_n determine the strength of the dephasing between levels m and n. The transmission for this case is evaluated numerically, given the number of terms contained in the latter, making its display more

confusing than enlightening. Fig. 8.12 shows a comparison among plots for transmission $T_3(\epsilon)$ corresponding to several values for γ_{ab}. In Fig. 8.13, I compare all three models, showing the emergence of destructive quantum interference for model represented by the transmission $T_3(\epsilon)$.
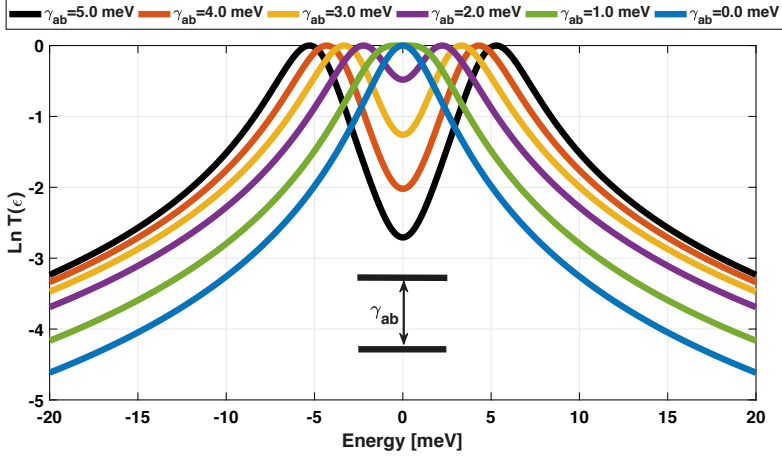
Figure 8.12. Transmission $T_3(\epsilon)$ for several values of the hybridization γ_{ab}. As γ_{ab} increases, the transmission dip around resonance is enhanced, and therefore destructive quantum interference is signed on $T_3(\epsilon)$.
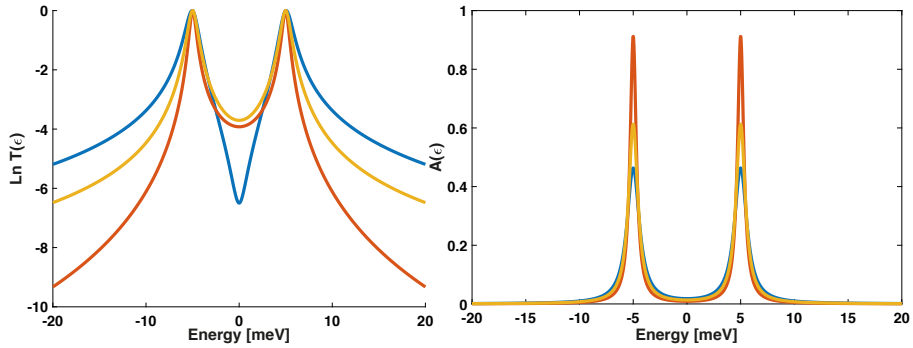
Figure 8.13. Left Panel: Comparison among transmission probabilities $T_1(\epsilon)$, $T_2(\epsilon)$ and $T_3(\epsilon)$, emerging from the models with diagonal self-energies both singly (In Red) and doubly coupled (In Yellow) levels to the reservoirs, and doubly coupled levels to the reservoirs including dephasing (blue). The spectral function $A(\epsilon)$ is shown in the right panel, where the color conventions follow up the ones for the left panel.

In this thesis, I explore a model that in principle combines the character-istics of the models giving rise to transmission probabilities $T_1(\epsilon)$, $T_2(\epsilon)$ and $T_3(\epsilon)$, namely a triple quantum dot model as described in chapter 7 and as

illustrated in figure 7.4. In [12], the triple quantum dot is considered with the aim of studying quantum coherence in molecular junctions. Fig. 8.14, shows the transmission for the three cases of study consider in [12], hence demonstrating the ability to induce or lift destructive quantum interference by modulating the hybridization γ_{ab}, as demonstrated experimentally by van der Zant *et.al* in [192].
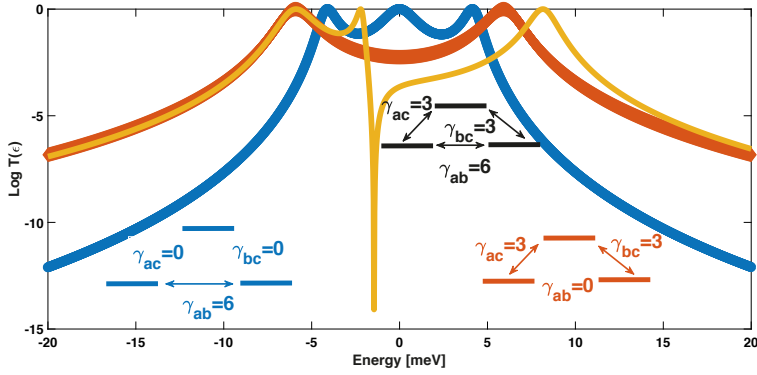
Figure 8.14. Transmission Probabilities for the triple quantum dot shown in Fig. 7.4, under three different test configurations shown in blue ($\gamma_{ab} = 6meV$, $\gamma_{ac} = \gamma_{bc} = 0meV$), red ($\gamma_{ab} = 0meV$, $\gamma_{ac} = \gamma_{bc} = 3meV$) and black (with yellows stripes in the plot) ($\gamma_{ab} = 6meV$, $\gamma_{ac} = \gamma_{bc} = 3meV$). The configurations shown in blue and red exhibit no possibility for destructive quantum interference while black shows a clear signature of the presence of quantum coherent transport in the system, this in accordance with the model studied in [12].

In paper III, I consider a triple quantum dot where each of the energy levels is coupled via Kondo interaction to single spin units that order ferromagnetically, anti-ferromagnetically or as a combination of them, hence, affecting the degree, strength and nature of quantum interference in the system. This is confirmed in Fig. 8.15 where the modulation of the hybridization γ_{ab} from 0 meV to 6 meV only induces destructive quantum interference for a particular symmetry of spin ordering in the molecule, shown in Fig. 7.4. This modulation shows its effect on the spin ordering in Fig. 8.17 where the region in which all contour plots are either positive or negative exhibit either anti or ferromagnetic ordering respectively. Therefore, is assertive to claim that lifting or inducing a certain form of quantum coherence in the triple dot system induces a particular spin ordering, what I refer to here as coherence induced switching dynamics between frustrated nanomagnets all-ferromagnetic nanomagnets. This commutation can also be achieved by the action of a gate field V_G or a bias voltage V_{DS}, as shown in Fig. 8.18.
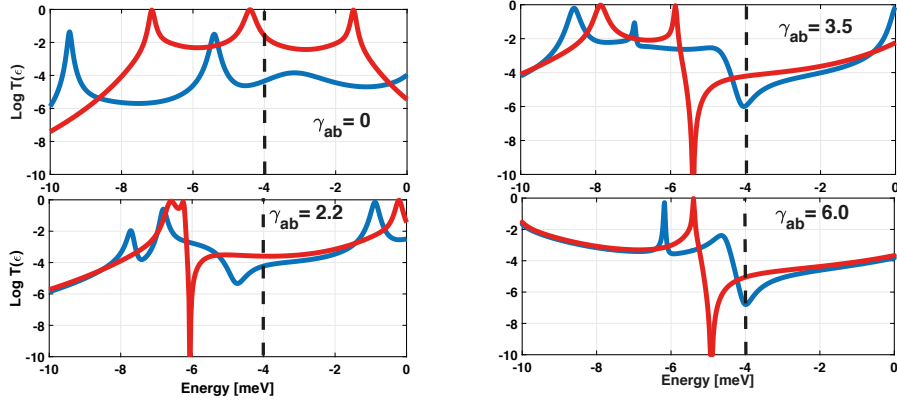
Figure 8.15. Transmission Probability for a Spin Trimer Driven Out of Equilibrium: A comparision is shown between the transmission probabilities through the junction of interest when there is spin ordering effect (effect) and where the isn't (red). This study is performed for $V_G = -4.0 \ meV$ (dashed in blacked).
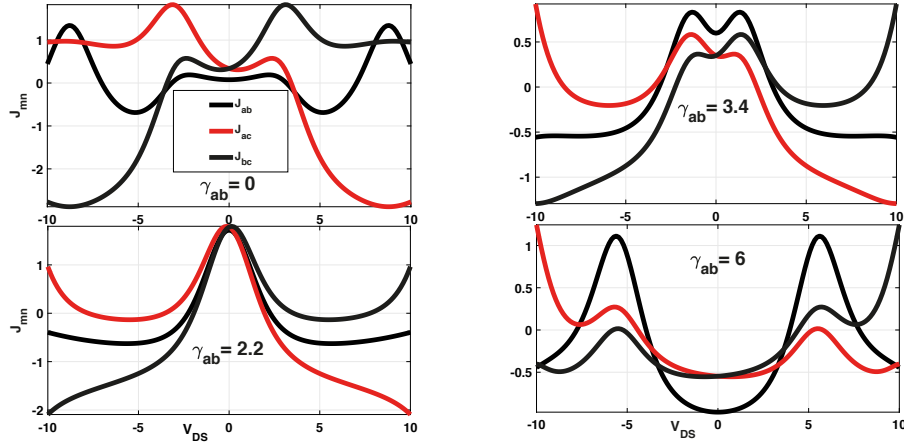
Figure 8.16. Effective Exchange Interactions $\mathcal{J}_{ab}$, $\mathcal{J}_{ac}$ and $\mathcal{J}_{bc}$ as a function of bias voltage for different values of the modulated parameter γ_{ab} $(0, 2.2, 3.4, 6.0 \ [meV])$.
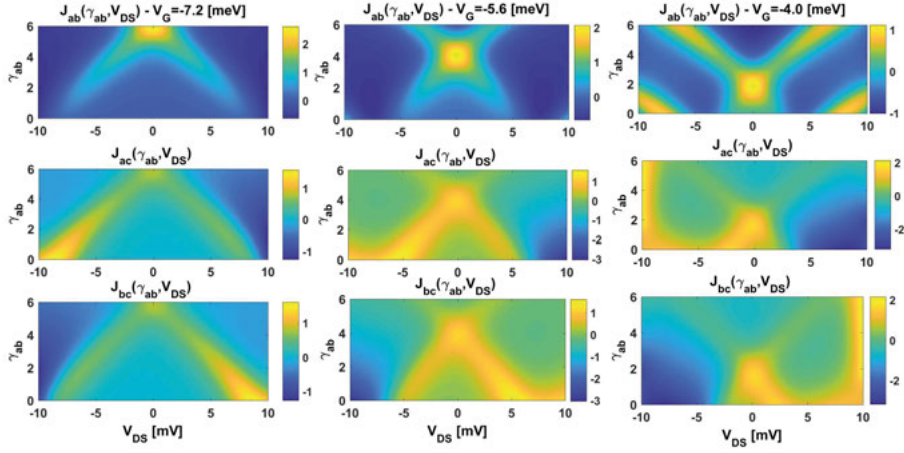
Figure 8.17. Magnetic $V_{DS}-V_G$ diagram. Shows regions where anti-ferromagnetic ordering arises (coincidence in yellow) and other ones where ferromagnetic ordering does it so (coincidence in blue). The panels are arranged in vertical order for different values of the parameter γ_{ab}.
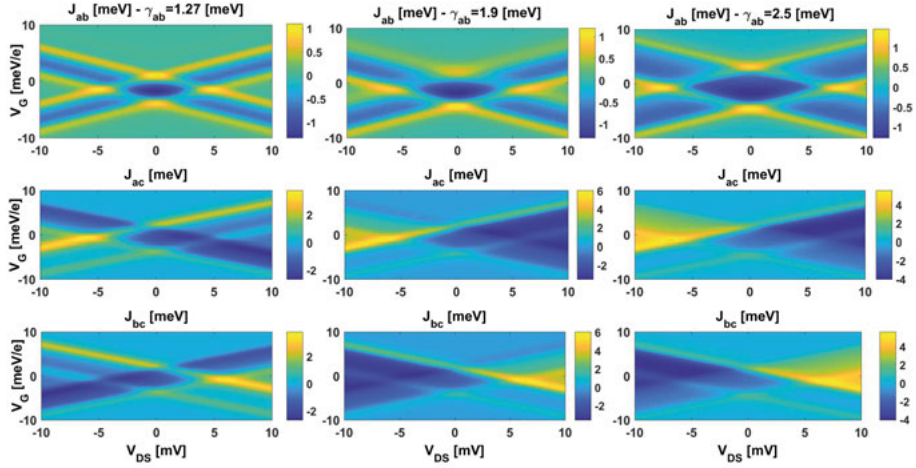
Figure 8.18. Magnetic $V_{DS}-V_G$ diagram. Shows regions where anti-ferromagnetic ordering arises (coincidence in yellow) and other ones where ferromagnetic ordering does it so (coincidence in blue). The panels are arranged in vertical order for different values of the parameter γ_{ab}.

8.7 Concluding Remarks

Here I provide a substantial overview of the literature on quantum coherent effects in molecular junction, I provide some thought about the Aharonov-Bohm effect and I develop some notions for understanding molecular junc-

tions as a single electron interferometer and compare with single photon interferometer for providing some context with regards to the ingredients of the interferometry machine and the interesting questions that may be asked. I discuss a novel possibility for combining effective spin-spin interactions and a complete AB interferometer, and the effect on a AB-like phase of the formation of singlet-triplet states, and hence, the effect on the degree of entanglement of the spin system. Then, I provide some arguments about the signatures of quantum interference emerging in the transmission of three different configurations of double dot junctions, and I argue that the triple quantum dot provides a further advantage to observe quantum interference of destructive nature, and how this behavior can be modified by the modulation of one of the hybridization parameters in the electronic background, hence showing a transition between the typical behavior of linear conjugated molecules to cross conjugated molecules with regards to its quantum coherent ability. Lastly, the interplay between spin ordering and interference effects signed in the transmission probability is considered, showing a clear effect of the order and its influence on electron localization and delocalization, on the emergent signatures of quantum interference observed in the transmission profile.

Part III:
Contribution

"I will mention the lovingkindness of the LORD and the praises of the LORD, according to all that the LORD has bestowed on us, and the great goodness towards the house of Israel, which He has bestowed on them according to His mercies, according to the multitude of His lovingkindness"

Isaiah $63:7$

Here, I will briefly report on the main results that account for my original contribution to the field of study, done in collaboration with Prof. Jonas Fransson (papers I, II, III and IV) and with the Doctoral candidate Henning Hammar (II, III and IV). I have also collaborated with Prof. Erik Sjöqvist (paper III).

9. Results and Contribution

"I am the vine; you are the branches. If you remain in me and I in you, you will bear much fruit; apart from me you can do nothing"

Gospel According to Yohannan (John) 15:5.

9.1 Comprehensive Summary of Results in Reported Papers

I strongly believe that the best in which knowledge is spread, is through the clear connection of the central ideas that effectively split the time framework where the scientific construction takes place. As an example of this line of thought, when discussing any magnetism related idea, one should refer to the contributions by James Clerk Maxwell, Heinrich Hertz and Niels Bohr and connected thoroughly with those from Heisenberg, Kasuda, Yosida and Kondo, and place the scientific discussion of interest with precision, within this framework, which will give the engaged community an idea of the impact and relevance of the debate one wants to put forward. In this very same way, A. A. Khajetorians and collaborators, when their atom by atom tailoring of nanomagnets was presented to the community, they felt that it was of capital importance to contextualize the audience with the efforts to achieve reasonable control over the magnetic exchange interactions at the atomic level, and how a convergence site with the development of scanning tunneling microscopy gave birth to the possibility of engineering precise magnetic exchange interactions in transition metal ions adsorbed on surface. The impossibility to comprehend their message, it can be due to, purely, a lack of understanding of how questions regarding the physics of ions exhibiting a localized magnetic moments in metals emerged. Reasoning with a similar philosophy, Piers Coleman introduces the concept of a localized spin moment in metals emerging from ions like, transition metal ions, by connecting the contributions from the early 20th century experimentalists that study electrical resistivity in Gold, Copper and Lead with Magnetic impurities, with those from the experimentalists in the late 1950's that had much precise control over the purity of metals and with the theoretical explanation of the observation of anomalies due to the impurity mainly by P. Anderson, J. Kondo and K. Wilson, and from there,

Coleman elaborates on what he believes the future directions in impurity physics and heavy Fermion science are.

From a likewise viewpoint, in the present thesis I focus my efforts in conveying three points that will convince the readers about the relevance of my work. First, I argue about the importance of studying magnetism and how this view has evolved throughout the history changing dramatically the way we live and making our existence in the Earth planet unlikely, if all of the sudden magnetism would disappear. Currently, the studies of magnetism keep changing our lives and provide a never ending fuel to keep making progress towards the control and manipulation of its manifestations in low dimensional physics, hoping that the consequences will be as influential for our society, as they were in the past 250 years, both world wide and locally. Secondly, I try to convince the reader about the relevance of understanding how magnetism in matter and its manifestations became a challenge, how this challenges were address by the more curious physicists of the time (Heisenberg, Landau, Langevin, Anderson, Kondo), and how these ideas lead to the study of localized magnetic moments (impurities) in metals. Thirdly and Lastly, I make a big effort to claim, that the current trends in magnetism at the molecular level, more specifically, the design of magnetic interactions among magnetic impurities (localized moments) on adsorbates, is a direct consequence of the convergence of the events stated in point two and the novel experimental probing and control methods at the atomic scale emerging from the 1980's namely, Scanning tunneling Microscopy (STM) and Atomic Force Microscopy AFM. My work on *Probing Magnetism at the Atomic Scale*, is a rather novel platform, in which the recent experimental efforts in understanding the effective interactions among localized magnetic moments in metals probed by STM or AFM tips, can be viewed from the perspective of molecular tunneling junctions, and from the analysis tools supplied by the *non-equilibrium quantum statistical mechanical theory*, meaningful results can be obtained, that resemble transport and spectroscopic experimental measurements, well account for in the recent progress made in the field.

Through the papers included in my thesis, you will encounter one published paper I, 1 submitted paper II, and two pre-prints III and IV. My contribution with original work on the area of study, centers in the paradigm of molecular junction systems, with localized magnetic moments embedded within it, approaching problems from single vibrating ion anisotropy electrically controlled, to multi-partite driven spin systems, dynamic effects in spin driven energy currents in single molecule magnets, and to electronic quantum interference driven magnetic order, both in spin dimers and trimers. In I, the heat and energy transport is addressed in a dimer of spins coupled to a two level electronic system, where each energy level of the represented

molecule, couples to a non-magnetic lead. In the framework of the non-equilibrium Green's function and the Meir-Jauho-Wingreen formalism (See chapter 4), I predict the behavior of the energy current in the system at different spin regimes, namely, singlet, triple and four fold configurations, and I show that in the singlet state where the magnetic moments localized the electron wavefunction in each of the electronic levels, despite of the charge current being negligible, the energy current persists, hence, confirming the predictions by Bergfield about entropy driven processes against coherence driven processes in molecular junctions. In paper II, I address the problem on single vibrating ion anisotropy in the interacting regime and argue that, when the molecular magnet under consideration is driven electrically and thermally, this property is modulated and commutes between easy plane and easy axis configurations, and the temperature excited-phonons, besides screening the electron-electron correlation, it induces a locking behavior in the anisotropy that reduces the magnitude of the latter though increases its relative stability, desired property in the single molecule magnet experiments with the tendency to serve as quantum information units. Lastly, when the electron-electron correlation increases beyond the screening limit imposed by the phonons, the behavior of the single ion anisotropy becomes strongly localized in the bias voltage - gate voltage plane, behavior induced by the sharp particle number variations due to the presence of Hubbard bands in the density of states. In paper III, the coherent manipulation of a trimer of spins grated onto molecules adsorbed on non-magnetic metal hosts is considered, where the electronic levels in the molecule are such that quantum interference can be engineered and the commutation between frustrated spin geometries and complete spin ferromagnetic ordered is studied, this, by the action of an STM tip, resembling novel experimental set ups. For completeness, I provide possible transport signatures that will serve as a tool to detect and to control the spin states, which motivate the design of robust quantum circuits based on the three-spin Greenberger-Horne-Zeilinger state. Moreover, in paper IV, I contribute to the work of Henning Hammar, done in the scope of time varying dynamics in driven single molecule magnets, where we evaluate the effect of the different time scales of the spin dynamics in the purely spin driven energy current through the magnet, done with the aid of the continuous time Wavelet transform. The promising results obtained, set the basis for spin dynamics driven cooling of metallic thin layers and on the counterpart, we present ground breaking results in the efforts made to design spin states robust against decoherence and entropy related instabilities.

The contribution of the work I aim to present in this thesis, promises, to pave the way for conceiving novel architectures for spin based quantum engineering based on all electro-thermal control, and possibly, to propose ground breaking experiments aiming at exploring phonon/photon based

engineered RKKY interaction in nanomagnets, which will provide additional means for controlling, manipulating and detecting non-classical quantum states.

9.2 Paper I: *Charge Transport and Entropy Production Rate in Magnetically Active Molecular Dimer*.
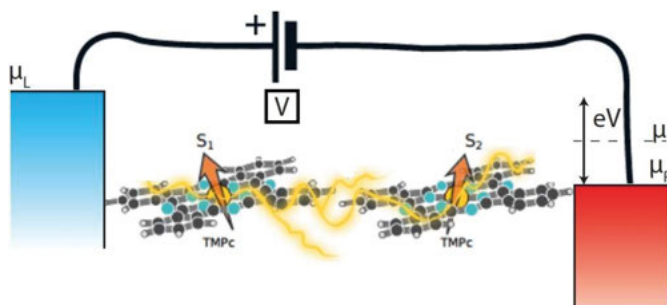
Figure 9.1. Dimer of Spins hosted by a Linearly Conjugated Molecule Embedeed in a Molecular Junction.

In paper I I approached the problem of heat transport and thermoelectric response functions such as the Seebeck coefficient in paramagnetic molecules comprising to spin units embedded in two level molecules resembling, for instance, Phthalocianine or Porphyrin complexes. I would like to concentrate in this section on a result that is of appealing importance to me, which is the detection of an entangled state (bi-partite entanglement) by means of particle and heat currents, verified by theoretical predictions on the RKKY effective exchange interaction among magnetic units and the spin occupation number, that is, the spin populations as a function of the applied bias in the junction. In Fig. 9.2, it was detected that for different gating conditions, for small bias where the spins in the dimer exhibit bi-partite entanglement (See the effective exchange interaction in Fig. 9.4, positive for singlet configuration, negative for the triplet), the heat current decays to at least an order of magnitude larger compared with the decay of the charge current (see Fig. 9.3). The heat current is an entropy driven process, robust to quantum coherent effects, hence, in the impossibility for the charge current to serve as a detecting mechanism for the entangled state in the system, the order of magnitude larger that the heat current exhibits serves as means of detection in this case, leaving the question open
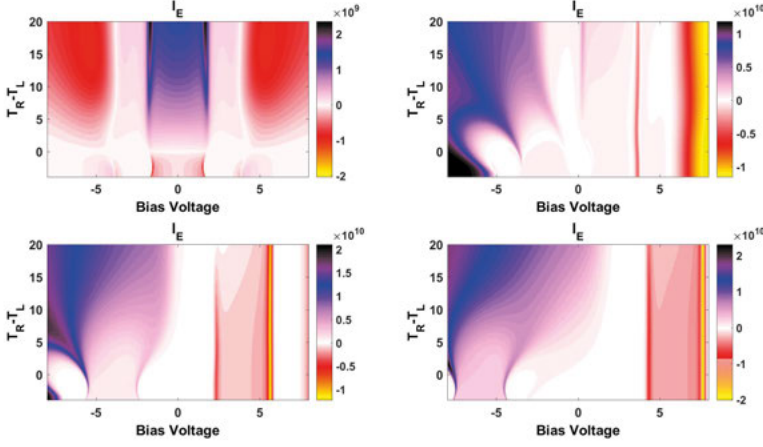
Figure 9.2. Energy Current for 4 different gating conditions: $\epsilon_0 - \mu_0 = 0 \ \ meV$, $\epsilon_0 - \mu_0 = 1 \ \ meV$, $\epsilon_0 - \mu_0 = 2 \ \ meV$ and $\epsilon_0 - \mu_0 = 3 \ \ meV$

whether is useful to have such mechanism or not, taking into account that heat currents are not observable [193].
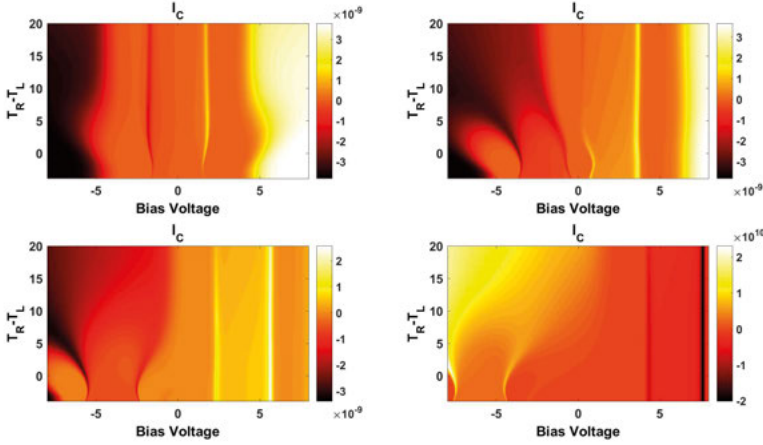
Figure 9.3. Charge Current for 4 different gating conditions: $\epsilon_0 - \mu_0 = 0 \ \ meV$, $\epsilon_0 - \mu_0 = 1 \ \ meV$, $\epsilon_0 - \mu_0 = 2 \ \ meV$ and $\epsilon_0 - \mu_0 = 3 \ \ meV$

In Fig. 9.4, the effective RKKY interaction among spins in the dimer is shown. Switching between a singlet and a triplet state is possible by the coordinate application of a bias, which varies with the application of the gate field. Robustness against temperature variations in the junction is discussed in paper I. This results is unappealingly interesting to me as it provides meaningful prediction of the way in which entanglement, and

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hence, quantum information processes can be modulated by the application of a bias voltage in the absence of a magnetic field.
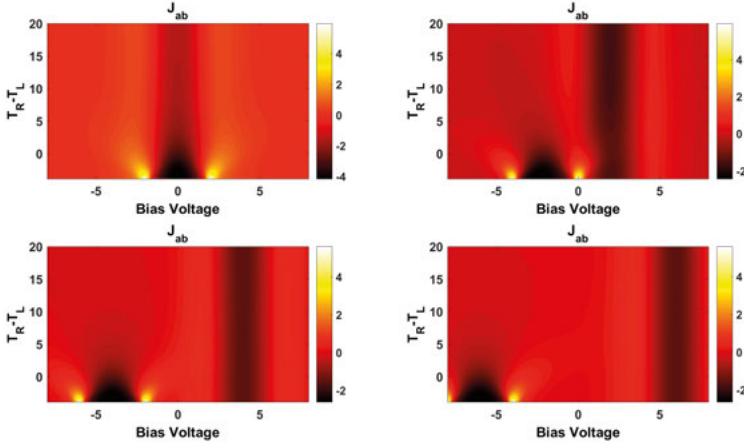
Figure 9.4. Effective Exchange Interaction $\mathcal{J}_{ab}$ for 4 different gating conditions: $\epsilon_0 - \mu_0 = 0 \ meV$, $\epsilon_0 - \mu_0 = 1 \ meV$, $\epsilon_0 - \mu_0 = 2 \ meV$ and $\epsilon_0 - \mu_0 = 3 \ meV$

9.3 Paper II: *Electronically Mediated Magnetic Anisotropy in Vibrating Magnetic Molecules.*

9.3.1 Conventions and Restrictions

In this paper, I considered a model of a single molecule magnet as compare to the one presented in [110, 194], where a single electronic level ϵ_σ vibrating at a frequency $\hbar\omega_0$ coupled to ferromagnetic leads, is interacting with a spin moment via the Kondo interaction. The interaction strength of the coupling between the electrons in the single level and the single phonon mode is denoted as λ.

Here, the Hamiltonian of the system is given by 9.1, where the individual model Hamiltonians specified in expressions 9.2, 9.3 and 9.4. The system is illustrated in figure 7.1, and the parameters are defined according to the

convention established in chapter 7.

$$\mathcal{H} = \mathcal{H}_C + \mathcal{H}_{Mol} + \mathcal{H}_T, \tag{9.1}$$

$$\mathcal{H}_C = \sum_{\alpha \boldsymbol{k}\sigma} \epsilon_{\boldsymbol{k}\sigma\alpha}(t) c^{\dagger}_{\boldsymbol{k}\sigma\alpha}(t) c_{\boldsymbol{k}\sigma\alpha}(t) \tag{9.2}$$

$$\mathcal{H}_{Mol} = \sum_{\sigma} \epsilon_{\sigma} d^{\dagger}_{\sigma} d_{\sigma} + U n_{\uparrow} n_{\downarrow} + \hbar\omega_0 a^{\dagger} a$$

$$+ \sum_{\sigma} \lambda d^{\dagger}_{\sigma} d_{\sigma} \left(a^{\dagger} + a \right) + J s_e(t) \cdot S(t) - g\mu_B S(t) \cdot B(t), \tag{9.3}$$

$$\mathcal{H}_T = \sum_{\alpha \boldsymbol{k}\sigma} V_{\boldsymbol{k}\sigma\alpha}(t) c^{\dagger}_{\boldsymbol{k}\sigma\alpha}(t) d_{\sigma}(t) + V^{*}_{\boldsymbol{k}\sigma\alpha}(t) d^{\dagger}_{\sigma}(t) c_{\boldsymbol{k}\sigma\alpha}(t) \tag{9.4}$$

The model represented by expression 9.1 can be diagonalized by the application of the Lang-Firsov transformation [116] as described in chapter 6, which decouples the Fermionic degrees of freedom ($d_{\sigma}(t)$, $d^{\dagger}_{\sigma'}(t)$) and the Bosonic degrees of freedom (a, $a^{\dagger}$) present in the molecular Hamiltonian given by expression 9.3, at the expense of renormalizing the tunneling Hamiltonian defined by expression 9.4, where the operators $d_{\sigma}(t)$, $d^{\dagger}_{\sigma'}(t)$ are transformed as $d_{\sigma}(t) \rightarrow \overline{d}_{\sigma}(t) = d_{\sigma}(t)\chi(t)$ and $d^{\dagger}_{\sigma'}(t) \rightarrow \overline{d}^{\dagger}_{\sigma'}(t) = d^{\dagger}_{\sigma'}(t')\chi^{\dagger}(t')$, hence the Green's function reads in consequence as follows:

$$\overline{G}_{\sigma\sigma'}(t,t') = -\frac{i}{\hbar} \left\langle T_K \overline{d}_{\sigma}(t) \overline{d}^{\dagger}_{\sigma'}(t') \right\rangle \rightarrow$$

$$\overline{G}_{\sigma\sigma'}(t,t') = -\frac{i}{\hbar} \left\langle T_K d_{\sigma}(t) \chi(t) d^{\dagger}_{\sigma'}(t') \chi^{\dagger}(t') \right\rangle$$

$$\approx -\frac{i}{\hbar} \left\langle T_K d_{\sigma}(t) d^{\dagger}_{\sigma'}(t') \right\rangle \left\langle \chi(t) \chi^{\dagger}(t') \right\rangle,$$

and by defining:

$$G_{\sigma\sigma'}(t,t') = -\frac{i}{\hbar} \left\langle T_K d_{\sigma}(t) d^{\dagger}_{\sigma'}(t') \right\rangle; \tag{9.5}$$

$$A(t,t') = \left\langle \chi(t) \chi^{\dagger}(t') \right\rangle, \tag{9.6}$$

we write:

$$\overline{G}_{\sigma\sigma'}(t,t') \approx G_{\sigma\sigma'}(t,t') A(t,t'), \tag{9.7}$$

where $G_{\sigma\sigma'}(t,t')$ is the renormalized electronic Green's function and $A(t,t')$ is the vibrational correlation function, which accounts for the corrections of the electronic propagator due to electron-phonon coupling.

The renormalized model Hamiltonian now reads (Accordingly with the ex-

position of concepts done in chapter 6):

$$\overline{\mathcal{H}} = \overline{\mathcal{H}}_C + \overline{\mathcal{H}}_{Mol} + \overline{\mathcal{H}}_T, \tag{9.8}$$

$$\overline{\mathcal{H}}_C = \mathcal{H}_C = \sum_{\alpha k\sigma} \epsilon_{k\sigma\alpha} c_{k\sigma\alpha}^\dagger c_{k\sigma\alpha}, \tag{9.9}$$

$$\overline{\mathcal{H}}_T = \sum_{\alpha k\sigma} V_{k\sigma\alpha} c_{k\sigma\alpha}^\dagger d_\sigma \chi + V_{k\sigma\alpha}^* d_\sigma^\dagger \chi^\dagger c_{k\sigma\alpha}, \tag{9.10}$$

$$\overline{\mathcal{H}}_{Mol} = \sum_\sigma \overline{\epsilon}_\sigma d_\sigma^\dagger d_\sigma + \overline{U} n_\uparrow n_\downarrow + \hbar\omega a^\dagger a$$

$$+ J s_e(t) \cdot S(t) - g\mu_B S(t) \cdot B(t). \tag{9.11}$$

The limitation of the model described by expressions 9.8, 9.9, 9.10 and 9.11 relies on the restrictions imposed by Hewson and Newns in [195] on the parameters λ, $\hbar\omega_0$ and $\Gamma = \sum_{\alpha\sigma} \Gamma_\sigma^{(\alpha)}$, which are given by the following expressions:

$$\left(\frac{\lambda}{\hbar\omega_0}\right) < 1 < \frac{\Gamma}{2\hbar\omega_0} e^{-(\lambda/\hbar\omega_0)^2}, \tag{9.12}$$

$$\hbar\omega_0 < \left|\epsilon_\sigma - \frac{\lambda^2}{\hbar\omega_0}\right|, \tag{9.13}$$

$$\frac{2\lambda^2}{\hbar\omega_0} < \Gamma. \tag{9.14}$$

The approximate solution space we propose to fulfill the restrictions given by expressions 9.12, 9.13 and 9.14 is given by inequalities $\lambda = \frac{1}{6}\Gamma$ and $\hbar\omega_0 = \frac{1}{5}\Gamma = \frac{6}{5}\Gamma$, and as such, the range of validity of the energy level ϵ_σ which also satisfies restriction given by equation 9.14, is $-\infty < \epsilon_\sigma < -0.06 \bigcup 0.35 < \epsilon_\sigma < +\infty$. The results presented in paper II, should be examine from the viewpoint of this description.

9.3.2 Summary of Results

In the paper I described the effect of the electron-phonon coupling λ on the magnetic uniaxial anisotropy of the molecule in the range imposed by the restrictions discussed earlier, where the electron-electron correlation is screened by the effect of the vibrations, such that the effective electron-electron interaction is equal to zero. It was shown that when the single phonon mode is sufficiently excited thermally, the electron-phonon interaction drives the anisotropy to a regime where the change in sign is not possible neither by gating nor by biasing the junction. As a consequence, the

molecule is locked to its high spin ground state upon the excitation of the single phonon mode, exhibiting the inability to commute between ground states. At the stake of increasing the electron-electron correlation strength, a finite effective electron-electron interaction emerges, and, the uniaxial magnetic anisotropy is reduced and quenched for broad ranges of the gate and bias signals, though the locking effect induced by the electron-phonon interaction persists when the phonons intake sufficient thermal energy and for gate and bias fields producing non-zero anisotropy energies.

9.4 Paper III: *Quantum Coherence Driven Magnetic Ordering in Biased Three Level Organometallic Molecules.*

9.4.1 Solving the Spin Hamiltonian

In paper III, as a result of the effective spin-spin interaction, mediated by the Non-equilibrium RKKY through the electronic structure of the molecule connecting all three localized moments, the Following spin Hamiltonian emerges (see expression 5.54 in chapter 5):

$$\mathcal{H}_{spin} = \mathcal{J}_{AB}\boldsymbol{S}_A \cdot \boldsymbol{S}_B + \mathcal{J}_{AC}\boldsymbol{S}_A \cdot \boldsymbol{S}_C + \mathcal{J}_{BC}\boldsymbol{S}_B \cdot \boldsymbol{S}_C, \qquad (9.15)$$

where $\mathcal{J}_{mn}$ was derived in chapter 5, giving expression 5.55.
The spin dot product in expression 9.15 can be expanded as a complete Hilbert space as follows:

$$\boldsymbol{S}_A \cdot \boldsymbol{S}_B = S_{Ax} \otimes S_{Bx} \otimes \mathbb{I} + S_{Ay} \otimes S_{By} \otimes \mathbb{I}_{2\times2} + S_{Az} \otimes S_{Bz} \otimes \mathbb{I}_{2\times2}, \qquad (9.16)$$

$$\boldsymbol{S}_B \cdot \boldsymbol{S}_c = \mathbb{I}_{2\times2} \otimes S_{Bx} \otimes S_{Cx} + \mathbb{I}_{2\times2} \otimes S_{By} \otimes S_{Cy} + \mathbb{I}_{2\times2} \otimes S_{Bz} \otimes S_{Cz}, \qquad (9.17)$$

$$\boldsymbol{S}_A \cdot \boldsymbol{S}_C = S_{Ax} \otimes \mathbb{I}_{2\times2} \otimes S_{Cx} + S_{Ay} \otimes \mathbb{I}_{2\times2} S_{Cy} + S_{Az} \otimes \mathbb{I}_{2\times2} \otimes S_{Cz}, \qquad (9.18)$$

where the operators S_{ix}, S_{iy} and S_{iz} for a spin $\dfrac{1}{2}$ degree of freedom are given by:

$$S_{ix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad S_{iy} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad S_{iz} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

and the index i labels the spin in the trimer.
In matrix form, expressions 9.16, 9.17 and 9.18 read:

$$
S_A \cdot S_B =
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 & 2 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 2 & 0 & 0 \\
0 & 0 & 2 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{bmatrix}
\tag{9.19}
$$

$$
S_A \cdot S_C =
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 2 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 2 & 0 \\
0 & 2 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{bmatrix},
\tag{9.20}
$$

$$
S_B \cdot S_C =
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 2 & 0 & 0 & 0 & 0 & 0 \\
0 & 2 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 2 & 0 \\
0 & 0 & 0 & 0 & 0 & 2 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{bmatrix}
\tag{9.21}
$$

Expressions 9.19, 9.20 and 9.21, are replaced into expression 9.15, with the aim of writing the effective Hamiltonian $\mathcal{H}_{spin}$, in matrix form, as follows:

$$
\mathcal{H}_{spin} =
\begin{bmatrix}
\mathcal{J}_{+++} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \mathcal{J}_{+--} & 2\mathcal{J}_{BC} & 0 & 2\mathcal{J}_{AC} & 0 & 0 & 0 \\
0 & 2\mathcal{J}_{BC} & \mathcal{J}_{-+-} & 0 & 2\mathcal{J}_{AB} & 0 & 0 & 0 \\
0 & 0 & 0 & \mathcal{J}_{--+} & 0 & 2\mathcal{J}_{AB} & 2\mathcal{J}_{AC} & 0 \\
0 & 2\mathcal{J}_{AC} & 2\mathcal{J}_{AB} & 0 & \mathcal{J}_{--+} & 0 & 0 & 0 \\
0 & 0 & 0 & 2\mathcal{J}_{AB} & 0 & \mathcal{J}_{-+-} & 2\mathcal{J}_{BC} & 0 \\
0 & 0 & 0 & 2\mathcal{J}_{AC} & 0 & 2\mathcal{J}_{BC} & \mathcal{J}_{+--} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{J}_{+++}
\end{bmatrix}
\tag{9.22}
$$

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where the terms in expression 9.22 are defined in the expressions below:

$$\mathcal{J}_{+++} = \mathcal{J}_{AB} + \mathcal{J}_{AC} + \mathcal{J}_{BC}, \tag{9.23}$$

$$\mathcal{J}_{+--} = \mathcal{J}_{AB} - \mathcal{J}_{AC} - \mathcal{J}_{BC}, \tag{9.24}$$

$$\mathcal{J}_{--+} = -\mathcal{J}_{AB} - \mathcal{J}_{AC} + \mathcal{J}_{BC}, \tag{9.25}$$

$$\mathcal{J}_{-+-} = -\mathcal{J}_{AB} + \mathcal{J}_{AC} - \mathcal{J}_{BC}. \tag{9.26}$$

When the system under study is driven by ferromagnetic leads (see illustration on figure 7.4), the effective Hamiltonian given by expression 9.15, fully adopts the form of expression 5.54, where the Dzyaloshinskii-Moriya interaction and the Ising Tensor contributions now play a significant role. This effective Hamiltonian, under this conditions reads:

$$\begin{aligned}
\mathcal{H}_{spin} = \mathcal{J}_{AB}\boldsymbol{S}_A \cdot \boldsymbol{S}_B &+ \mathcal{J}_{AC}\boldsymbol{S}_A \cdot \boldsymbol{S}_C + \mathcal{J}_{BC}\boldsymbol{S}_B \cdot \boldsymbol{S}_C \\
&+ \boldsymbol{D}_{AB} \cdot \boldsymbol{S}_A \times \boldsymbol{S}_B + \boldsymbol{D}_{AC} \cdot \boldsymbol{S}_A \times \boldsymbol{S}_C + \boldsymbol{D}_{BC} \cdot \boldsymbol{S}_B \times \boldsymbol{S}_C \\
&+ \mathbb{I}_{AA}\left(\boldsymbol{S}_A^{(z)}\right)^2 + \mathbb{I}_{BB}\left(\boldsymbol{S}_B^{(z)}\right)^2 + \mathbb{I}_{CC}\left(\boldsymbol{S}_C^{(z)}\right)^2. \tag{9.27}
\end{aligned}$$

Moreover, the aim in this context is to evaluate the spin expectation values of the form $\langle \boldsymbol{S}_m \rangle$, for $m = a, b, c$, to then feed them into the retarded Green's function or in the inverse retarded Green's function as calculated in chapter 7 for the configuration shown in Fig. 7.4. To move forward in that department, I employ the definition of the thermal expectation value given by (see chapter 4):

$$\langle \boldsymbol{S}_m \rangle = \frac{1}{\mathcal{Z}_s} \mathbb{TR}\left[e^{-\beta \mathcal{H}_{spin}} \boldsymbol{S}_{m\perp} \right], \tag{9.28}$$

where the operator $\boldsymbol{S}_{m\perp}$, is the projection of the total spin operator onto the Hilbert space of spin $\boldsymbol{S}_m$, and $\mathcal{Z}_s$ is the partition function of the spin sub-system. Additionally, to fully determine the formation of Quartet and Doublet states for the antiferromagnetic and ferromagnetic ordering case, we calculate the elements of the spin density matrix ρ_{spin} in a diagonal basis as follows:

$$\rho_{spin} = \frac{e^{-\beta \bar{\mathcal{H}}_{spin}}}{\mathcal{Z}_s}, \tag{9.29}$$

where $\bar{\mathcal{H}}_{spin}$ is the Hamiltonian described in Eq. 9.22 in diagonal basis.
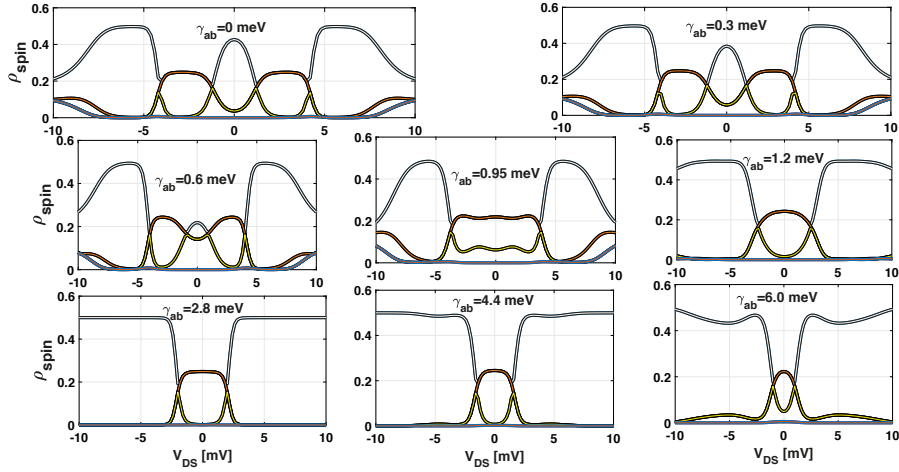
Figure 9.5. Spin Eigen Value Problem - $8-$Dimensional Hilbert Space

The ambition is to, associate each of the configurations (quartets and doublets, depending whether there is an anti-ferromagnetic state or a ferromagnetic state [69]) shown in Fig. 9.5 to either an entangled 3-partite state or a bipartite entangled 3-qubit state, or to a quasi-classical product state, hence demonstrating the means for control of the degrees of entanglement via localization in the $V_{DS} - V_G$ magnetic diagram (see paper III).

9.5 Paper IV: *Spin-dependent heat signatures of single-molecule spin dynamics.*

It has been well understood, that the heat transport in matter obeys a given number of mechanisms in which the electronic and vibrational play a fundamental role. Uchida *et.al* [196], has investigated extensively the heat carried by the accumulation of spin in ferromagnetic metals [197], [198] and ferromagnetic insulators [199] as well as in paramagnetic materials [200], where the electrical potential between the regions of accumulation remains the same, suggesting that there is no charge current flowing through the physical system of interest, and leaving the responsibility of the heat flow to the spin current uniquely. In this context, the Onsager formulation for thermo-electricity can be re-formulated in terms of charge, spin and heat currents [201], [202], which shall be related through the thermoelectric response coefficients to charge bias, spin bias and temperature bias, where these coefficients are the Seebeck coefficient, the Peltier coefficient, the electrical conductivity, the thermal conductivity, the spin conductivity, the thermo-spin conductivity, the spin-Seebeck coefficient and the spin-Peltier coefficient [203]. Here, we made some progress in the phenomenon of

purely spin-driven energy transport in a biased single molecule magnet, where using a spin analog of Eq. 4.117, the time-resolved energy current is evaluated, and spin dynamics signatures are observed in the latter. This promising result sets the basis for high performance thermo-spin cooling in molecular magnets, and paves the way to design bipartite entanglement molecular machines driven by time-dependent fields of high robustness against spin decoherence [204] (See Fig. 9.6).
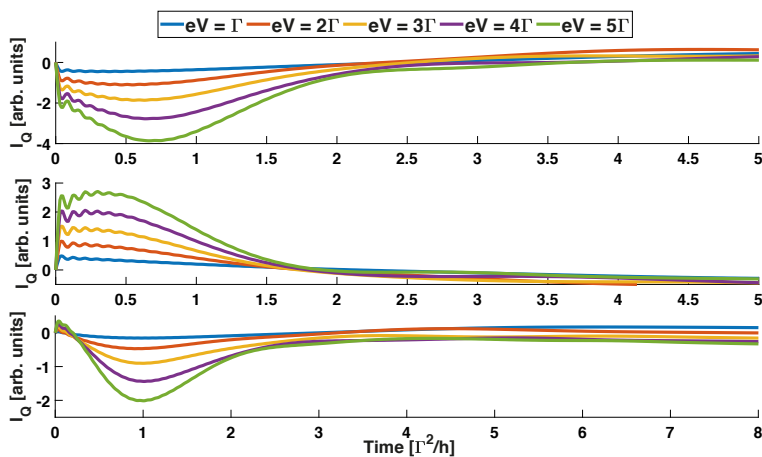

Figure 9.6. Charge, spin and Total Heat Flow in the time Dependent Driven Single Molecule Magnet

10. Svensk sammanfattning

Vetenskap utformas genom att noga utreda och utveckla centrala idéer genom längre tid av vetenskapligt arbete och åtskilliga individuella bidrag. Teorin och kunskapen om magnetism, som är en central del av denna avhandling, har under åren utvecklats där signifikanta bidrag har gjorts av James Clerk Maxwell, Heinrich Hertz and Niels Bohr kopplat till de bidrag av Heisenberg, Kasuda, Yosida och Kondo. Detta tillsammans med ett engagerat kollegium av forskare har fört den vetenskapliga diskussionen vidare genom noga studier av de fysikaliska koncept som magnetism inkluderar. De tidigaste försöken inkluderar en klassisk bild av magnetism, något som sedan utökades till att inbegripa en kvantmekaniska effekter och kollektiva fenomen. Fokus var att med statistisk fysik och mångkropparsteori beskriva faserna av de olika material som experimentellt gick att observera och därmed beskriva magnetism som helhet.

Experiment påsenare tid har möjliggjort atomär kontroll av enstaka atomer och molekyler. Detta har gjort att det varit av stor vikt att utveckla en förståelse och kontroll av magnetisk växelverkan i nanosystem. Fältet öppnade för möjligheterna att med hjälp av sveptunnelmikroskop noggrant kontrollera magnetisk växelverkan mellan atomer som är absorberade påen yta. Den vetenskapliga bakgrund dessa observationer är tidigare insikter om fysiken kring joner med magnetiska moment och magnetiska orenheter i material. Piers Coleman introducerade konceptet av ett lokaliserat magnetiskt moment som en effektiv beskrivning av en orenhet bestående av en övergångsmetallsatom. Denna effektiva beskrivning gjordes utifrån att koppla de experimentella observationerna av magnetiska orenheters påverkan påguld, koppar och blys resistans med de teoretiska observationerna av diverse anomaliteter kopplade till orenheter gjorda av P. Anderson, J. Kondo och K. Wilson. Från detta la Coleman fram sina idéer om vad som borde vara den framtida inriktningen inom fysiken kring orenheter och tunga fermioner.

Denna avhandling utgår från ett liknande synsätt och utgår från tre punkter för att övertyga läsaren om avhandlingens relevans. Först motiveras det varför det är viktigt att studera magnetism, hur synsättet påmagnetism utvecklas genom åren och hur vår existens påjorden inte skulle vara möjlig om all magnetism plötsligt försvann. För tillfället påverkar vår kunskap om magnetism och kontrollen av de relaterade fenomenen dagligen våra liv. Förhoppningen är att den nuvarande och framtida forskningen inom

förståelsen och kontrollen av magnetism i lågdimensionell fysik kan fortsatt påverka vårt samhälle, liksom de senaste 250 årens upptäckter inom magnetism har gjort. Därefter introduceras konceptet om varför det är relevant att förståmagnetism i material och de utmaningar som uppstått genom åren. Dessa utmaningar har noga behandlats av de aktiva fysikerna under denna tid (Heisenberg, Landau, Langevin, Anderson, Kondo) och ledde sedan fram till studien av magnetisk växelverkan mellan magnetiska orenheter/moment i material. Slutligen motiveras att dagens trend i magnetism påmolekylär nivåoch försök att kontrollera magnetisk växelverkan mellan lokaliserade magnetiska moment är en direkt konsekvens av de nya experimentella metoderna för kontroll av system påatomär nivå. Dessa metoder inkluderar sveptunnelsmikroskopi och atomkraftsmikroskopi som utvecklades på80-talet. Dessa verktyg har använts för att experimentellt förståden effektiva växelverkan mellan lokala magnetiska moment och mangetism i nanosystem. Med hjälp av icke-jämvikts statistik kvantfysik går det att beskriva mycket av de observationer som sker i dessa system och man har gjort flera relevanta framsteg inom olika områden (exempelvis växling av cooper par, stark spinn-fonon koppling, anisotropi av enskilda atomer, stark anisotropi, m.m.).

De artiklar som läggs fram i denna avhandling inkluderar; en publicerad artikel I, tvåinskickade artiklar II, III och tvåförberedda artiklar IV. Bidraget i avhandlingen till det relevanta fältet centreras kring molekylära system i tunnelövergångar med lokaliserade magnetiska moment. De inkluderar elektriskt kontrollerade vibrerande anisotropa system, drivna spinnsystem, dynamiska effekter i spinndrivna energiströmmar i molekylära magneter och elektrisk interferensdriven magnetisk ordning i spinn dimerer och trimerer. I artikel I undersöks värme- och energitransport i en dimer av lokala magnetiska moment kopplad till ett elektroniskt tvåenergysystem i en tunnelövergång mellan omagnetiska kontakter. Genom att använda ickejämvikts Greens funktioner och Meir-Jauho-Wingreen formalism härleds beteendet av energiströmmen för olika spinnregimer. Resultaten visar påatt i singlettillstånd existerar en ändlig energiström trots en i stort sett försvinnande laddningsström. Detta bekräftar Bergfields utsagor om att processerna i molekylära överg{aangar är entropidrivna. I artikel II analyseras en vibrerande anisotropisk jon som interagerar med en molekylär magnet. Detta system drivs ur jämvikt med hjälp av termisk och elektrisk gradient. Genom denna kontroll kan man ändra systemets anisotropi från en föredragen riktning i planet eller en ut ur planet till den andra. Vidare visas att temperaturexiterade fononer både skärmar elektron-elektron interaktion och låser anisotropin i olika konfigurationer, något som är ett önskvärt fenomen för att bygga kvantinformationssystem. Slutligen visas att med ökande elektron-elektron korrelation blir anisotropin starkt lokaliserad till småspänningsskillnader pågrund av närvaron av Hubbardband i tillståndtätheten.

I artikel III analyseras koherent manipulation av en trimer av spinn lokaliserade i en icke-magnetisk metall. I detta system analyseras kvantinterferens mellan de lokala elektroniska nivåerna, frustrerade spinngeometrier och ferromagnetisk ordning. De relevanta transportsignaturerna för systemet tas fram och kan användas i verktyg för att kontrollera och läsa av spinntillstånd och motivera en design av robusta kvantkretsar baserade påtrespinns Greenberger-Horne-Zeilinger-tillstånd. I artikel IV analyseras den tidsberoende dynamiken av en driven magnetisk molekyl med fokus påspinndynamikens effekt påden spinnberoende energiströmmen. Resultaten visar påspinndynamisk driven kyling av molekylära magneter och metalliska tunnfilmer och robusta spinntillstånd mot dekoherens och entropidrivna processer.

De arbeten som tas upp i denna avhandling tyder påatt leda till möjligheten att ta fram nya arkitekturen för spinnbaserade kvantkretsar baserade påelektro-termisk kontroll. Utöver detta är förhoppningen att arbetet i denna avhandling kan leda till nya experiment med fokus påatt utreda fonon-/fotonkontrollerad växelverkan i nanomagneter som ytterligare verktyg för att kontrollera och läsa av kvanttillstånd.

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Appendix A.
Additional Relevant Derivations

Exchanging Creation and Annihilation Operators in Exponential Form

Here, I am considering the simplification of the term $e^{\Lambda a^{\dagger}} e^{\Lambda' a} e^{-\Lambda a^{\dagger}}$. I proceed in the following way:

$$e^{\Lambda a^{\dagger}} e^{\Lambda' a} e^{-\Lambda a^{\dagger}} = e^{\Lambda a^{\dagger}} \left(\sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda' a)^k \right) e^{-\Lambda a^{\dagger}},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k e^{\Lambda a^{\dagger}} a^k e^{-\Lambda a^{\dagger}},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k \left(a^k + \left[\Lambda a^{\dagger}, a^k \right] + \frac{1}{2!} \left[\Lambda a^{\dagger}, \left[\Lambda a^{\dagger}, a^k \right] \right] + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k \left(a^k + \Lambda(-1)k a^{k-1} + \frac{1}{2!} \left[\Lambda a^{\dagger}, \Lambda(-1)k a^{k-1} \right] + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k \left(a^k + \Lambda(-1)k a^{k-1} + \frac{1}{2!} \Lambda^2(-1)^2 k(k-1) a^{k-2} + \cdots \right),$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k \sum_{n=0}^{k} (-1)^n \frac{k!}{n!(k-n)!} \Lambda^n a^{k-n},$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k \sum_{n=0}^{k} \binom{k}{n} (-\Lambda)^n a^{k-n} = \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda')^k (a - \Lambda)^k,$$

$$= \sum_{k=0}^{+\infty} \frac{1}{k!} (\Lambda' a - \Lambda \Lambda')^k,$$

then, arriving at the following result:

$$e^{\Lambda a^{\dagger}} e^{\Lambda' a} e^{-\Lambda a^{\dagger}} = e^{-\Lambda \Lambda'} e^{\Lambda' a}. \tag{11.1}$$

Where I have used:

$$\underbrace{\left[a^{\dagger}, \cdots \left[a^{\dagger}, \left[a^{\dagger}, \left[a^{\dagger}, a^k \right] \right] \right] \right]}_{n\ a^{\dagger}\text{'s}} = (-1)^n \frac{k!}{(k-(n+1))!} a^{k-n} = (-1)^n \frac{\partial^n a^k}{\partial a^n},$$

given that $\left[a^{\dagger}, a^k\right] = -ka^{k-1}$.

Eigenvalues of Creation and Annihilation operators in Exponential form

Let's consider an annihilation operator a acting on the state $|n\rangle$, which translates to:

$$a|n\rangle = \sqrt{n}|n\rangle, \tag{11.2}$$

then $a^2|n\rangle$ and $a^3|n\rangle$ can be obtained as follows:

$$a^2|n\rangle = \sqrt{n}a|n-1\rangle = \sqrt{n(n-1)}|n-2\rangle,$$

$$= \sqrt{\frac{n!}{(n-2)!}}|n-2\rangle, \tag{11.3}$$

$$a^3|n\rangle = \sqrt{n}a^2|n-1\rangle = \sqrt{n(n-1)}a|n-2\rangle = \sqrt{n(n-1)(n-2)}|n-3\rangle,$$

$$= \sqrt{\frac{n!}{(n-3)!}}|n-3\rangle, \tag{11.4}$$

and in general the term $a^m|n\rangle$ can be calculated as follows:

$$a^m|n\rangle = \sqrt{n}a^{m-1}|n-1\rangle = \sqrt{n(n-1)}a^{m-2}|n-2\rangle$$

$$= \sqrt{n(n-1)(n-2)}a^{m-3}|n-3\rangle$$

$$= \cdots = \sqrt{n(n-1)(n-2)\cdots(n-(m-2))}a^{m-(m-1)}|n-(m-1)\rangle,$$

$$= \sqrt{n(n-1)(n-2)\cdots(n-(m-2))(n-(m-1))}|n-m\rangle$$

then, I am allowed write the above result as follows:

$$a^m|n\rangle = \sqrt{\frac{n!}{(n-m)!}}|n-m\rangle, \tag{11.5}$$

with the restriction $n \geq m$.

From the above result, one can proceed to calculate $e^{\phi(t)a}|n\rangle$ as follows:

$$e^{\phi(t)a}|n\rangle = \sum_{k=0}^{+\infty} \frac{1}{k!}[\phi(t)]^k a^k|n\rangle = \sum_{k=0}^{n} \frac{1}{k!}[\phi(t)]^k \sqrt{\frac{n!}{(n-k)!}}|n-k\rangle, \tag{11.6}$$

and for the case of $\langle n|e^{-\phi^*(t)a^{\dagger}}$ we write:

$$\langle n|e^{-\phi^*(t)a^{\dagger}} = \sum_{q=0}^{+\infty}\langle n|\left[a^{\dagger}\right]^q \frac{1}{q!}(-1)^q[\phi^*(t)]^q,$$

$$= \sum_{q=0}^{n}\langle n-q|\sqrt{\frac{n!}{(n-q)!}}\frac{1}{q!}(-1)^q[\phi^*(t)]^q. \tag{11.7}$$

From expressions 11.6 and 11.7, one can calculate expectation values of the form $\langle n|e^{-\phi^*(t)a^\dagger}e^{\phi(t)a}|n\rangle$, in the following way:

$$\langle n|e^{-\phi^*(t)a^\dagger}e^{\phi(t)a}|n\rangle = \sum_{q=0}^{n}\langle n-q|\sqrt{\frac{n!}{(n-q)!}}\frac{1}{q!}(-1)^q[\phi^*(t)]^q$$

$$\times \sum_{k=0}^{n}\frac{1}{k!}[\phi(t)]^k\sqrt{\frac{n!}{(n-k)!}}|n-k\rangle,$$

$$= \sum_{k=0}^{n}\sum_{q=0}^{n}\frac{1}{q!}(-1)^q\sqrt{\frac{n!}{(n-q)!}}\sqrt{\frac{n!}{(n-k)!}}\frac{1}{k!}\langle n-q|[\phi^*(t)]^q[\phi(t)]^k|n-k\rangle,$$

$$= \sum_{k=0}^{n}\sum_{q=0}^{n}\frac{1}{q!}(-1)^q\sqrt{\frac{n!}{(n-q)!}}\sqrt{\frac{n!}{(n-k)!}}\frac{1}{k!}[\phi^*(t)]^q[\phi(t)]^k\langle n-q|n-k\rangle,$$

$$= \sum_{k=0}^{n}\sum_{q=0}^{+\infty}\frac{1}{q!}\frac{1}{k!}(-1)^q\frac{n!}{\sqrt{(n-k)!(n-q)!}}[\phi^*(t)]^q[\phi(t)]^k\delta_{qk},$$

$$= \sum_{k=0}^{n}\frac{1}{k!}\frac{1}{k!}(-1)^k\frac{n!}{(n-k)!}|\phi(t)|^{2k},$$

hence, we write the above result as follows:

$$\langle n|e^{-\phi^*(t)a^\dagger}e^{\phi(t)a}|n\rangle = \sum_{k=0}^{n}\frac{(-1)^k}{k!}\frac{n!}{k!(n-k)!}|\phi(t)|^{2k} = \mathcal{L}_n\left(|\phi(t)|^2\right), \qquad (11.8)$$

Jacobi-Anger Expansion

First let's consider the term:

$$e^{z\cos\theta} = e^{z\left(\frac{e^{i\theta}+e^{-i\theta}}{2}\right)} = e^{\frac{z}{2}e^{i\theta}}e^{\frac{z}{2}e^{-i\theta}},$$

and by Taylor expanding both exponentials, we may write:

$$e^{z\cos\theta} = e^{\frac{z}{2}e^{i\theta}}e^{\frac{z}{2}e^{-i\theta}} = \sum_{m=0}^{+\infty}\frac{1}{m!}\left(\frac{z}{2}\right)^m e^{im\theta}\sum_{n=0}^{+\infty}\frac{1}{n!}\left(\frac{z}{2}\right)^n e^{-in\theta}$$

$$= \sum_{m=0}^{+\infty}\sum_{n=0}^{+\infty}\frac{1}{m!n!}\left(\frac{z}{2}\right)^{m+n}e^{i(m-n)\theta},$$

and by defining $\ell = m - n$, m can be substituted by $\ell + n$. By noting that for $m \to +\infty$, $\ell \to +\infty$, and when $m = 0$, $\ell = -n$ (either $n = 0$ or $n = +\infty$, so

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we choose the value that gives the minimum ℓ, that is, $\ell = -n \to -\infty$.), the evaluation of $e^{z\cos\theta}$ proceeds as follows:

$$e^{z\cos\theta} = \sum_{m=0}^{+\infty}\sum_{n=0}^{+\infty} \frac{1}{m!n!} \left(\frac{z}{2}\right)^{m+n} e^{i(m-n)\theta} = \sum_{\ell=-n}^{+\infty}\sum_{n=0}^{+\infty} \frac{1}{(n+\ell)!n!} \left(\frac{z}{2}\right)^{n+\ell+n} e^{i\ell\theta}$$

$$= \sum_{\ell=-\infty}^{+\infty}\sum_{n=0}^{+\infty} \frac{1}{n!(n+\ell)!} \left(\frac{z}{2}\right)^{2n+\ell} e^{i\ell\theta},$$

and recalling the definition of the modified Bessel function we finally arrive at[1]:

$$e^{z\cos\theta} = \sum_{\ell=-\infty}^{+\infty} I_\ell(z) e^{i\ell\theta}. \tag{11.9}$$

Important Result on Complex Integration

Considering integrals of the form:

$$\int_{-\infty}^{t} e^{ix(t-\tau)} d\tau,$$

by using the following substitution:

$$t - \tau = s; \quad ds = -d\tau; \quad \tau \to -\infty \Rightarrow s \to +\infty; \quad \tau \to t \Rightarrow s \to 0;$$

then:

$$\int_{-\infty}^{t} e^{ix(t-\tau)} d\tau = -\int_{+\infty}^{0} e^{ixs} ds = \lim_{\delta\to 0} \int_{0}^{+\infty} e^{i(x+i\delta)s} ds,$$

$$= \lim_{\delta\to 0} \left[\frac{e^{i(x+i\delta)s}}{i(x+i\delta)} \right]_{0}^{\infty}$$

$$= \lim_{\delta\to 0} \lim_{s\to +\infty} \frac{e^{ixs}e^{-\delta s} - 1}{i(x+i\delta)} = -\frac{1}{i(x+i\delta)},$$

therefore, in compact form, it gives:

$$(-i) \int_{-\infty}^{t} e^{ix(t-\tau)} d\tau = \frac{1}{x+i\delta} \tag{11.10}$$

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[1] See Derivation in Video Format at the Youtube Channel: Juan David Jaramillo

Appendix B.
Derivation of Hybridized Non-Equilibrium Green's Functions

Metal-Molecule Hybridization

Recall expression 6.31 as the model Hamiltonian for a multilevel molecular complex, which reads:

$$\mathcal{H} = \mathcal{H}_{Leads} + \mathcal{H}_T + \mathcal{H}_{mol}^{(e)} + \mathcal{H}_{mol}^{(vib)} + \mathcal{H}_{mol}^{(e-vib)} + \mathcal{H}_{mol}^{(spin)}.$$

The task that concerns this section is the derivation of a closed form for the hybrid Green's function $H_{kn\sigma\sigma'}(t,t')$ and $H_{qn\sigma\sigma'}(t,t')$. These objects characterize the quantum mechanical tunneling processes between a metallic contact and a molecular complex, that can be represented by an arbitrary number of levels.

Consider the Green's function given by:

$$
\begin{aligned}
H_{kn\sigma\sigma'}(t,t') &= -\frac{i}{\hbar}\left\langle \mathcal{T}_C c_{k\sigma}(t) d_{n\sigma'}^{\dagger}(t') \right\rangle \\
&= -\frac{i}{\hbar}\left\langle c_{k\sigma}(t) d_{n\sigma'}^{\dagger}(t') \right\rangle \theta(t-t') + \frac{i}{\hbar}\left\langle d_{n\sigma'}^{\dagger}(t') c_{k\sigma}(t) \right\rangle \theta(t'-t),
\end{aligned}
\tag{11.11}
$$

and it's derivative with respect to time can be calculated in the following way:

$$
\begin{aligned}
\frac{\partial H_{kn\sigma\sigma'}(t,t')}{\partial t} &= \frac{\partial}{\partial t}\left[-\frac{i}{\hbar}\left\langle c_{k\sigma}(t) d_{n\sigma'}^{\dagger}(t') \right\rangle \theta(t-t') + \frac{i}{\hbar}\left\langle d_{n\sigma'}^{\dagger}(t') c_{k\sigma}(t) \right\rangle \theta(t'-t) \right], \\
&= -\frac{i}{\hbar}\left\langle \frac{\partial c_{k\sigma}(t)}{\partial t} d_{n\sigma'}^{\dagger}(t') \right\rangle \theta(t-t') + \frac{i}{\hbar}\left\langle d_{n\sigma'}^{\dagger}(t') \frac{\partial c_{k\sigma}(t)}{\partial t} \right\rangle \theta(t'-t) \\
&\quad - \frac{i}{\hbar}\left\langle c_{k\sigma}(t) d_{n\sigma'}^{\dagger}(t') \right\rangle \delta(t-t') - \frac{i}{\hbar}\left\langle d_{n\sigma'}^{\dagger}(t') c_{k\sigma}(t) \right\rangle \delta(t'-t), \\
&= -\frac{i}{\hbar}\left\langle \mathcal{T}_C \frac{\partial c_{k\sigma}(t)}{\partial t} d_{n\sigma'}^{\dagger}(t') \right\rangle - \frac{i}{\hbar}\left\langle \{ c_{k\sigma}(t), d_{n\sigma'}^{\dagger}(t') \} \right\rangle \delta(t-t'),
\end{aligned}
$$

and multiplying both sides of the above expression by $i\hbar$, we arrive at:

$$
i\hbar\frac{\partial H_{kn\sigma\sigma'}(t,t')}{\partial t} = -\frac{i}{\hbar}\left\langle \mathcal{T}_C (i\hbar)\frac{\partial c_{k\sigma}(t)}{\partial t} d_{n\sigma'}^{\dagger}(t') \right\rangle = -\frac{i}{\hbar}\left\langle \mathcal{T}_C \left[c_{k\sigma}(t), \mathcal{H} \right] d_{n\sigma'}^{\dagger}(t') \right\rangle,
\tag{11.12}
$$

using the result $\{c_{k\sigma}(t), d^{\dagger}_{n\sigma'}(t')\} = 0$ and $i\hbar\dfrac{dA_H(t)}{dt} = [A_H(t), \mathcal{H}]$.

From expression 11.12, it becomes clear that to completely specify $H_{kn\sigma\sigma'}(t,t')$ the commutator $[c_{k\sigma}(t), \mathcal{H}]$ shall be calculated, done in the following way:

$$[c_{k\sigma}(t), \mathcal{H}] = [c_{k\sigma}(t), \mathcal{H}_{Leads} + \mathcal{H}_T] = [c_{k\sigma}(t), \mathcal{H}_{Leads}] + [c_{k\sigma}(t), \mathcal{H}_T],$$

$$= \left[c_{k\sigma}(t), \sum_{k'\sigma'} \epsilon_{k'\sigma} c^{\dagger}_{k'\sigma'} c_{k'\sigma'}\right] + \left[c_{k\sigma}(t), \sum_{mk'\sigma'} V_{mk\sigma} c^{\dagger}_{k'\sigma'} d_{m\sigma'}\right],$$

$$= \sum_{k'\sigma'} \epsilon_{k'\sigma'} \left[c_{k\sigma}(t), c^{\dagger}_{k'\sigma'} c_{k'\sigma'}\right] + \sum_{mk'\sigma'} V_{mk'\sigma'} \left[c_{k\sigma}(t), c^{\dagger}_{k'\sigma'} d_{m\sigma'}\right],$$

$$= \sum_{k'\sigma'} \epsilon_{k'\sigma'} \{c_{k\sigma}(t), c^{\dagger}_{k'\sigma'}\} c_{k'\sigma'} + \sum_{mk'\sigma'} V_{mk'\sigma'} \{c_{k\sigma}(t), c^{\dagger}_{k'\sigma'}\} d_{m\sigma'},$$

$$= \sum_{k'\sigma'} \epsilon_{k'\sigma'} \delta_{kk'} \delta_{\sigma\sigma'} c_{k'\sigma'} + \sum_{mk'\sigma'} V_{mk'\sigma'} \delta_{kk'} \delta_{\sigma\sigma'} d_{m\sigma'},$$

which then gives:

$$[c_{k\sigma}(t), \mathcal{H}] = \epsilon_{k\sigma} c_{k\sigma} + \sum_{m} V_{mk\sigma} d_{m\sigma}. \qquad (11.13)$$

To derive the above equations we have made use of expression 6.32 and 6.33 which specify model Hamiltonians $\mathcal{H}_{Leads}$ and $\mathcal{H}_T$. Now, we replace expression 11.13 into expression 11.12, and we do the following procedure:

$$i\hbar\frac{\partial H_{kn\sigma\sigma'}(t,t')}{\partial t} = -\frac{i}{\hbar}\left\langle \mathcal{T}_C [c_{k\sigma}(t), \mathcal{H}] d^{\dagger}_{n\sigma'}(t')\right\rangle$$

$$= -\frac{i}{\hbar}\left\langle \mathcal{T}_C \left(\epsilon_{k\sigma} c_{k\sigma} + \sum_{m} V_{mk\sigma} d_{m\sigma}\right) d^{\dagger}_{n\sigma'}(t')\right\rangle,$$

$$= \epsilon_{k\sigma}\left[-\frac{i}{\hbar}\left\langle \mathcal{T}_C c_{k\sigma}(t) d^{\dagger}_{n\sigma'}(t')\right\rangle\right]$$

$$+ \sum_{\mu} V_{\mu k\sigma}\left[-\frac{i}{\hbar}\left\langle \mathcal{T}_C d_{\mu\sigma}(t) d^{\dagger}_{n\sigma'}(t')\right\rangle\right]$$

$$= \epsilon_{k\sigma} H_{kn\sigma\sigma'}(t,t') + \sum_{\mu} V_{\mu k\sigma} G_{\mu n\sigma\sigma'}(t,t'),$$

and the above result allows us to write the equation of motion for $H_{kn\sigma\sigma'}(t,t')$ in the following way:

$$\left(i\hbar\frac{\partial}{\partial t} - \epsilon_{k\sigma}\right) H_{kn\sigma\sigma'}(t,t') = \sum_{\mu} V_{\mu k\sigma}(t) G_{\mu n\sigma\sigma'}(t,t'), \qquad (11.14)$$

where:

$$\left(i\hbar \frac{\partial}{\partial t} - \epsilon_{\boldsymbol{k}\sigma}\right)\mathcal{G}_{\boldsymbol{k}\sigma}(t,t') = \delta(t,t').$$ (11.15)

Moreover, by making the variable swap $t \to \tau$ in expression 11.14

$$\left(i\hbar \frac{\partial}{\partial \tau} - \epsilon_{\boldsymbol{k}\sigma}\right)\boldsymbol{H}_{\boldsymbol{k}n\sigma\sigma'}(\tau,t') = \sum_{\mu} V_{\mu\boldsymbol{k}\sigma}(\tau)\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau,t'),$$ (11.16)

and by multiplying the above expression by $\mathcal{G}_{\boldsymbol{k}\sigma}(t,\tau)$ and integrating with respect to τ:

$$\int \mathcal{G}_{\boldsymbol{k}\sigma}(t,\tau)\left(i\hbar \frac{\partial}{\partial \tau} - \epsilon_{\boldsymbol{k}\sigma}\right)\boldsymbol{H}_{\boldsymbol{k}n\sigma\sigma'}(\tau,t')d\tau = \int \delta(t-\tau)\boldsymbol{H}_{\boldsymbol{k}n\sigma\sigma'}(\tau,t')d\tau$$

$$= \sum_{\mu} \int V_{\mu\boldsymbol{k}\sigma}(\tau)\mathcal{G}_{\boldsymbol{k}\sigma}(t,\tau)\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau,t')d\tau, \quad (11.17)$$

and we may finally write:

$$\boldsymbol{H}_{\boldsymbol{k}n\sigma\sigma'}(t,t') = \sum_{\mu} \int V_{\mu\boldsymbol{k}\sigma}(\tau)\mathcal{G}_{\boldsymbol{k}\sigma}(t,\tau)\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau,t')d\tau,$$ (11.18)

and for $\mathcal{G}_{\boldsymbol{q}\sigma n}(t,t')$:

$$\boldsymbol{H}_{\boldsymbol{q}n\sigma\sigma'}(t,t') = \sum_{\mu} \int V_{\mu\boldsymbol{q}\sigma}(\tau)\mathcal{G}_{\boldsymbol{q}\sigma}(t,\tau)\boldsymbol{G}_{\mu n\sigma\sigma'}(\tau,t')d\tau.$$ (11.19)

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