Time Evolution in Open Quantum Systems - From Exciton Dynamics to Charge Transport

by

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Abstract

The research work presented in this thesis concerns the improvement of several theoretical techniques for describing quantum systems coupled to fermionic or bosonic reservoirs. The validity of the aforementioned developments is then numerically investigated to obtain the time-dependent quantum transport of charges or excitons through molecular junctions or aggregates, respectively. The former are single or a short chain of conducting, conjugated molecules wedged between two inert electrodes, acting as active circuit elements, while the latter can be comprehended as light absorbing pigments containing conjugated chains residing within fluctuating protein environments. The model used to describe the quantum transport is a linear chain or aggregates of tight-binding sites coupled to external fermionic or bosonic baths.

The three main formalisms that are presented in this work include quantum master equations (QME), in second order perturbation theory in the system-reservoir coupling, the hierarchical equations of motion (HEOM) scheme for multi-particle bosonic systems as well as a scheme based on time-dependent nonequilibrium Green’s functions (NEGF) for non-interacting fermionic systems. The NEGF scheme for time-dependent quantum transport of charge provides the time-dependent current through the systems of sites as well as the on-site population dynamics, while the QME and HEOM schemes for energy transfer dynamics deliver information only about the population or occupation number dynamics for systems coupled to bosonic baths.

The studied approaches usually assume that the corresponding bath correlation functions or environmental self-energies can be regarded as a weighted sum of exponentials. If, however, the environment is accurately described only by a highly complex spectral density or if it has very low temperature, this approach becomes highly inefficient. To this end a scheme based on a Chebyshev expansion of the correlation functions or self-energies is presented along with a rigorous derivation of the respective quantum master equations within second-order perturbation theory, the time-dependent nonequilibrium Green’s function based equations of motion and the hierarchical equations of motion. Furthermore, the relative strengths and limitations of the Chebyshev expansion-based scheme are discussed. The predominant improvements to existing methods brought about by the Chebyshev expansion include the ability of this approach to simulate exactly, highly non-trivial (containing many gaps and spikes) and arbitrary forms of the environmental influence and temperatures without any additional numerical effort as compared to trivial (smooth with no discontinuities) environmental effects. For charge transport systems, this allows for the incorporation of the actual spectral density of the electronic bath beyond the wide band approximation, while for energy transfer systems, one is enabled to treat numerically or experimentally
obtained spectral densities, crucial for the accurate calculation of dissipation dynamics in, for instance, light harvesting systems.

For the numerical investigation, the aforementioned schemes were programmed and benchmarked against other well-established approaches for the single resonant level for charge transport systems and two-level model systems for energy transport systems. Moreover, the main advantage of Chebyshev-based NEGF scheme is expressed by numerical simulations performed for a realistic system-reservoir scenario, namely for double stranded DNA molecule surrounded by a fluctuating environment in contact with fermionic leads that represent energy profiles of realistic leads. The Chebyshev expansion enables the usage of any kind of lead spectral densities, ranging from numerical over experimental to analytical. This is especially useful for the case of energy transport systems as well since the spectral energy profiles obtained from experimental results can be directly incorporated within Chebyshev based schemes.
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Chapter 1

Introduction

1.1 Motivation

The continued advancement of and increase in the range of capabilities of electronic devices in recent decades has been achieved by scaling down the size of silicon dioxide based integrated circuit components which consequently scales up the density of components per chip. This scaling up of packaging density or functions per chip follows Moore’s law [1]. But as charge leakage due to quantum tunneling appears when the minimum feature size in transistors reduces to a few nanometers, a size comparable to the mean free path of charge carriers, quantum mechanical effects can no longer be neglected. Although new architectural techniques such as 3D microchip design can uphold Moore’s law, lithographic techniques face a fundamental barrier to scaling.

As early as the 1950’s with the invention of the transistor, the development of integrated circuits and the subsequent difficulty with regards to radical miniaturization of the existing electronic components, Arthur von Hippel, a physicist of German origin, formulated the bottom-up approach that he termed as molecular engineering [2, 3]. This idea of molecular scale electronics reappeared later in the 1970’s at IBM due to Ari Aviram, who worked on the theory of electron transfer through single organic molecules with Mark Ratner and published, in 1974, the often-cited paper on molecular rectifiers [4]. The bottom-up approach forms the basic principle by which electronic components may be built using individual molecules. The underlying idea is to assemble elementary elements to form complex structures, as opposed to the top-down approach where microscopic circuit components are carved out of the macroscopic bulk using lithography techniques. The bottom-up approach [5] allows the manipulation of molecules on the nanometer scale to construct device architectures with predetermined electronic, mechanical or chemical properties based on the properties of the molecules utilized. Molecules have been used to construct active and passive circuit components (switches, diodes, resistors, and LEDs [6].). Molecular electronic devices could allow for a range of advantages such as reduced manufacturing complexity and the possibility to automate device manufacture using self-assembly techniques, leading to lowered costs. Moreover, the smaller feature size leads to a higher density of devices packed per unit area or volume, allowing easier scaling and lower power consumption. For example, data could potentially be stored on DNA with a density approximately $10^{12}$ times that of the currently available DRAMs [7]. While
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it still seems rather unlikely that molecular electronics will replace silicon-based electronics anytime soon, it can assume a supplementary position. For example, new functionalities may be tailored using the properties of individual molecules that may not be possible to implement in traditional solid state electronics. The importance of molecular electronics lies in the fact that in recent years it has developed into a field of research where many fundamental questions regarding quantum phenomena can be investigated.

On the other hand, beyond silicon-based semiconductor technology, the use of organic materials in electronics and optoelectronics applications have attracted a lot of attention in recent decades, with successful products such as the liquid-crystal display, organic light-emitting-diode displays, and photoreceptors in electrophotography already in the market. Organic photovoltaic devices, chemical sensors and plastic transistors, for example, are rapidly developing. In fact, organic molecules may also be used to build molecular scale devices with specifically tailored functionalities. The few nanometer scale structure that combines the advantages of using organic compounds to build electronic devices and molecular electronics is the molecular wire, the length scales of which range from about 3 to 30 nm. Molecular wires have attracted substantial interest in recent years as they fall in the scale where the transition between different transport mechanisms is expected to occur [8–12]. Relevant systems where different transport mechanisms appear include self assembly monolayers of conjugated oligomers and π-stacked systems such as the DNA [11], which provide an effective medium for charge transport [13]. Conjugated organic molecules such as polyenes (general formula: \(C_nH_{n+2}\)) are specially relevant for building molecular wires as they contain multiple single and double bonds appearing in an alternating fashion. The alternating single-double bonds cause the wave function of the π-system to be delocalized, or in other words extend over the whole molecule, thus aiding conduction. Due to the nature of the chemical bonds they possess, conjugated organic molecules display semiconducting behaviour, with band gaps more than about 1.5 eV, (band gap in silicon is 1.1 eV at room temperature). In such molecules, the valence band, or π band, is normally filled with electrons while the conduction band, or π* band is normally empty [7]. Although unaltered strands of DNA behave as wide band-gap semiconductors [14, 15], the conductivity characteristic of the DNA double helix remains a dubious issue, especially in experimental work, because it is affected by environmental factors such as water and ions trapped among the DNA strands. Thorough understanding of charge transport and of the effects of excess localized charges at specific bases has wide range implications for protein binding to DNA molecules within cells, DNA sequencing and DNA-based biosensors [16].

Experimental transport measurements on single-molecular electronics built using organic molecules show important physical effects such as Kondo resonance [17] as well as Coulomb Blockade [17, 18]. Properties corresponding to such effects are actually designed by chemical synthesis, for example, by attaching different functional groups to the conducting molecule. More complex structures such as the molecular crossbar [19] may be obtained by forming a kind of an extended ticktacktoe board from molecular wires and having individual molecular devices wedged in between the junctions. Both memory [20] and logic components may be experimentally produced utilizing single molecules or molecular wires to construct electronic circuits [21, 22].

The transport of electrons or charge through single molecules or molecular wires presents an im-
important problem in the field of molecular electronics since conduction properties are the most relevant for electronic applications. In the above-mentioned structure, in general, a molecule is wedged between two conducting electrodes. Such metal-molecule-metal formations [23] have been extensively studied as potential building blocks for molecular scale integrated circuits. The current across this molecular junction or wire depends on the applied bias voltage. More sophisticated devices may be formed by simple modifications of the molecular wire. For example, a gate voltage may be attached in such a way as to cause a shift the energy levels of the molecule, forming a molecular transistor. The conductance properties of molecular wires are influenced by a multitude of factors including, but not limited to, the band structure of the electrodes, electronic structure of the molecule and the molecule-lead coupling i.e. the surrounding environment of the molecule in the form of solvent molecules or ions, for instance.

A major relevant issue is with regard to attaching the molecule to the external leads. This is usually achieved by covalently binding the molecule to the electrodes using functional groups known as anchoring groups. For organic molecules typical linkers consist of -S-H terminal anchor groups. These have been shown to provide good mechanical stability, especially when contacting gold electrodes [24]. An essential technology in this case is the development of few nanometer gap metallic electrodes capable of holding small molecules formed by mechanical break junction techniques [25, 26]. The gap width of electrodes is tunable enabling reproducible construction of molecular junctions with stable molecule-electrode contacts [25].

It's not only in electronic devices where quantum effects may be present. Quantum phenomena are prevalent and play an important role in many biological processes [27]. The sense of smell, for example, is claimed to be a quantum process based on phonon-assisted tunneling [28]. In fact, one of the most important processes in nature involving quantum effects is Photosynthesis that has been extensively studied during the last few decades [29,30]. Research shows that quantum mechanical coherence forms an integral part of the process of photosynthesis [31–35], although this view has become controversial now due results shown in recent research [36,37]. Current understanding of the energy transfer dynamics confirms that the excitons are delocalized over their closest neighboring sites, but quantum coherence is considered to play a negligible role in the exciton transfer dynamics because it usually has a decay time of a few tens of femtoseconds [37].

Green plants, certain kinds of bacteria and algae, all capture and convert sunlight to chemical energy through photosynthetic machinery generally composed of aggregates of light absorbing pigments or light-harvesting antenna complexes and reaction centers (RC). The system composing the pigments which are surrounded by a protein environment is called a light harvesting complex (LHC). The pigments and the reaction center are arranged so as to direct the incoming energy towards the respective reaction centers where the energy conversion takes place. The process of light harvesting starts with the absorption of photons from the sunlight by, for example, chlorophyll pigments embedded within a protein environment provided that the energy of the captured photon is equal to that of the allowed electronic transition. The photons are absorbed in the form of an excitation from the ground state of the pigment molecules. If the molecule which is excited has neighbouring molecules which are near enough, the excitation energy may be transmitted to the neighbours via electromagnetic interactions. In the step that follows, the electronic excitations (or excitons) are used to facilitate charge separation. This conversion occurs at
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the reaction center (RC). The charge separation, or proton gradient, is then basically used to drive chemical reactions. Due to the energy transfer process therein being highly efficient [30] the quantum efficiency of the natural light-harvesting process is extremely high (> 95%).

Due to the way the pigments are packed, the strength of the electronic interactions inside the molecular aggregate or the network of cooperating pigments varies from weak to strong. This distribution is necessary for efficient light harvesting. If a certain group of pigments has strong (compared to the environmental coupling) inter-molecular couplings then the spread of the electronic excitation is coherent [38, 39]. In contrast, in pigment groups weakly coupled to each other the electronic excitation is shared incoherently or the excitation transfer process is random [40, 41]. The theoretical treatment of the former process of excitation dynamics is possible using a range of approaches discussed in this work.
1.2 Theoretical Methods

Charge transport through single molecular junctions or small chains of molecules forms an elementary case of quantum transport in molecular scale structures [42, 43]. The molecular junction may be subject to external fields or perturbations, e.g., electromagnetic fields (e.g., laser) and electrostatic fields such as fluctuating solvent effects. The resulting time-dependent fluctuations in the charge transport through molecular junctions constitutes a rapidly advancing field of research, [44–53] aided substantially in the recent years by experimental advancements that are able to reliably fabricate such systems [54–61]. Theoretical tools for simulating molecular scale systems not only facilitate the computation of transport quantities like current and population dynamics but also help us to understand the fundamental principles needed to manufacture, at large scale, single molecule or nanoscale electronics [62–68].

The scattering approach developed by Landauer and Büttiker [69, 70] provides a basic but useful insight into the electron dynamics of nanoscale systems, although recent developments have shown their drawbacks [71]. While scattering approaches [72] are usually limited to time-independent setups, time-dependent effects can be accounted for by using more rigorously quantum formalisms such as quantum master equations (QME) theories [73–76], hierarchical equation of motion schemes [77, 78] and time dependent nonequilibrium Green’s functions (NEGF) methods [65, 79–87]. Whereas QMEs derived in perturbation theory are, in general, restricted to dealing with only weak molecule-lead coupling strengths, the NEGF formalism has no such restrictions and is able to deal with any magnitude of the coupling strength. The strong coupling regime is important since many interesting quantum phenomena occur only within it, including Coulomb blockade, current hysteresis, negative differential resistance and chemical reactions [88]. In this thesis we take as the starting point the TD-NEGF approach in Ref. 82 and 89. This approach has found usage in the examination of many realistic systems [45, 90–93]. While in general the exponential function is utilized for building the equations of motion (EOM) in the NEGF scheme, in this work we use the Chebyshev expansion to formulate a completely different set EOMs. This expansion uses Chebyshev polynomials and bessel functions to form numerically tractable forms of the self-energies within the NEGF scheme or the correlation functions within QME or HEOM schemes.

Essentially the same EOMs as described for the above charge transport scenarios may also be utilized to calculate excitation energy (exciton) transfer in dissipative systems, such as molecular aggregates, where each aggregate is assumed to be attached to its own independent bath. The main difference is that while in the case of fermionic systems the relevant particles travel from and to the electrodes that represent the bath or the environment, in the case of bosonic baths only the dissipation of energy from the system is considered. Additionally, the fermionic and bosonic particle distributions are described by the Fermi and the Bose-Einstein functions, respectively. For the fermionic case the model utilized in this work assumes that only the first and the last site of the molecular wire is attached to the reservoirs while for the bosonic case each site is assumed to have its own individual reservoir. Moreover, while the NEGF scheme for fermionic systems neglects inter-particle interactions such as electron-electron interactions without loss of accuracy of the resultant observables, the schemes describing time evolution in bosonic systems here make no such assumptions and can account for particle correlation effects.

Furthermore, just as in the fermionic case where the total system is factorized or dissociated into a re-
duced system (i.e., the molecule) and its environment (i.e., the reservoir electrodes) one can understand, for bosonic systems, for instance, photons as the environment surrounding the system, i.e., the molecular aggregate composed of the light harvesting complexes coupled to a (protein) environment. The environmental effects can be incorporated into the system via, for example, perturbative approaches like the Redfield theory [94] or QME developed in second-order perturbation theory [95]. Even though such schemes are relevant to a range of system sizes, their limitation to weak coupling regimes makes them susceptible to missing out on pertinent effects of the system-bath interaction. Therefore, an accurate description of the excitation dynamics necessitates that the environment and the system-environment coupling be treated in a nonperturbative manner such that the complete range of environmental effects may be incorporated in the system-bath coupling. This is possible using exact methods like path integral approaches, though such schemes are numerically unfeasible for larger systems [96,97]. The system-bath interaction may also be treated in an exact manner by using the hierarchical equations of motion (HEOM) approach, originally developed by Kubo and Tanimura [98]. Although the HEOM is computationally expensive if the size of the system is large, recent improvements to the HEOM scheme that use graphical processing units (GPUs) to calculate the time evolution of the auxiliary operators present in the HEOM scheme in a parallel and distributive manner render it efficient for the investigation of energy transfer in larger systems, for instance, light-harvesting complexes [99–101].

Another commonality between the bosonic [102,103] and fermionic [75] systems is the usage of an exponential decomposition scheme that enables the expansion of the correlation functions or self-energies of the reservoirs in terms of sums of weighted exponential functions. This is achieved by decomposing the environmental spectral density contained within the self-energies or correlation functions in terms of Lorentzian functions, and, moreover, expanding the Fermi function in terms of poles using, for example, the Ozaki scheme [104–106]. This approach has been utilized extensively for building complete sets of ordinary differential equations: QME [75,102,103], HEOM [107] as well as NEGF-based equations of motion [82]. A marked disadvantage of this approach is that a sum of Lorentzian functions is not able to accurately and efficiently mimic complicated molecule-lead couplings or spectral densities. Additionally, the expansion of the Fermi function becomes numerically unfeasible at very low temperatures due to the Fermi function approaching a step-function like form. On the other hand, the Chebyshev expansion that is utilized in this work allows for the construction of coupled EOMs based on properties of the derivatives of the bessel functions and does not have the above-mentioned limitations exhibited by the exponential decomposition scheme. Furthermore, the Chebyshev decomposition enables simulating systems at arbitrarily low temperatures without additional numerical demands. Moreover, the Chebyshev scheme is able to incorporate numerical and experimental spectral densities or environmental effects without any approximations, and, most importantly, the simulation of the most non-trivial spectral densities can be achieved at no extra computational cost as compared to highly trivial spectral densities. The Chebyshev expansion may be applied to treat both fermionic as well as bosonic systems and allows the incorporation of environmental effects exactly i.e., within EOMs built using the Chebyshev approach there is no requirement for any kind of decomposition of the Fermi function or the spectral densities, any kind of numerically or analytically tractable expressions for which may be utilized.

Such a Chebyshev expansion has been previously utilized in other propagation schemes like wave
packet propagation [108–111]. In recent years Tian and Chen [112] applied the Chebyshev spectral decomposition to formulate the single-particle hierarchical equation of motion by employing the Jacobi-Anger identity to expand the relevant quantities in terms of Chebyshev polynomials. For the single particle or non-interacting case, these equations are equivalent to the TD-NEGF scheme for the RSDM (Reduced Single-particle Density Matrix). In previous studies regarding fermionic [113] as well as bosonic [95] systems (latter presented in this thesis in Chapter 4), we have shown the use of Chebyshev polynomials and Bessel functions to develop differential equations in the QME framework based on a particular property of the Bessel functions of the first kind. The same trick as in the above studies was applied in Ref: 114 to decompose the self-energies of the electrodes within the NEGF framework. In this work we also present the Chebyshev scheme to decompose the correlation functions of the environment within the HEOM scheme. These works are discussed in Chapter 3 and 4, respectively.

Finally, a notable limitation of the Chebyshev scheme is the scaling of the computational or numerical demands with the time period that is being simulated. Basically, the scheme breaks down at a certain point in time depending on the number of polynomials utilized in the expansion of the self-energies or the correlation functions. However, the breakdown point is easily calculatable and observable in the results, and places no restrictions on the accuracy of the scheme before the break down point has occurred.
1.3 Experimental Methods

The determination of properties, such as the electrical conductance, of molecular scale electronic devices is highly challenging. In recent decades, though, researchers in the field of molecular electronics are able to employ scanning probe microscopy (SPM) techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to construct molecular scale components. For the experimental measurement of conductance of the molecules (e.g. DNA), the molecules need be to wedged securely in between two electrodes in a reliable as well as reproducible fashion. A range of techniques allow the manufacture of molecular junctions, including mechanical break junctions [25], electrochemical deposition [115], electromigration [26], electron beam lithography [116] and scanning probe techniques (SPT) [117]. In experiments involving SPT setups, scanning tunneling microscope (STM) or atomic force microscope (AFM) are utilized [?], 117. When using an STM, the molecule is laid out on or adsorbed onto a substrate layer thereby forming one of the electrodes. The STM tip acts as the other electrode. This tip-molecule coupling is weak and the contact formed is not precise or well-defined, whereas the substrate-molecule coupling is strong. Consequently, the substrate exerts a greater influence on the properties of the molecule. Due to this limitation this technique is not deemed suitable for the measurement of absolute conductance. One way to reduce this problem is to embed the conducting molecule into a matrix of another, often less conducting molecule.

A molecular junction may also be realized using breakjunction techniques [25] such as mechanically controlled break junction technique (MCBJ) [118–120], the scanning tunneling microscopy break junctions (STM-BJ) technique [120–122] or the conductive probe AFM break junction (CPAFM-BJ) technique [120] which allow a direct current measurement. In STM-BJ, electric current is used to maneuver the position of the STM tip, which is repeatedly brought in and out of contact with the substrate electrode. By constructing conductance histograms in large numbers (usually 1000s) of conductance versus tip displacement tracks that are formed during tip retraction the conductance of a single molecules may be identified. These methods involve weaker and more equally balanced couplings to the electrodes as compared to SPT. The STM-BJ technique is currently the most widely-used experimental method to measure single molecule conductance [120, 123]. A similar CPAFM-BJ technique [123, 124] uses a metal-coated AFM tip as one of the electrodes and consists of a force signal detector which is controlled by a laser. The tip position here is force controlled. A similar conductance histogram to the above can be constructed to determine single-molecule conductance. Such experiments along with computational results allow for improvements in understanding of electron transport in molecular junctions.

For experiments regarding light harvesting systems: The information about the energy transfer process may be experimentally obtained by 2 dimensional spectroscopy techniques [125, 126]. In such experiments aggregates of, for example, Fenna-Matthews-Olsen (FMO) pigment-protein complex are targetted by a total of four laser pulses distributed in time. The initial two pulses generate electronic excitations in the FMO complex. Pulse number three probes the system after a certain delay while the function of the last pulse is to act as a reference for the outgoing signal. This enables the calculation of the signal phase [126,127]. Repeated measurements for a range of delay times are then used to calculate
the energy transfer dynamics. The resultant 2D map of the population (and thus energy transfer) dynamics allows identification of coherent energy transfer dynamics [33]. This possible coherence may be exploited for the regulation of the energy transfer process to develop applications including artificial light harvesting devices [128] and new generations of solar cells. Recent experimental studies using the polarization-controlled electronic 2D spectroscopy [36] and photon echo optical 2D spectroscopy [37] of the FMO complex show no evidence of long-lived electronic quantum coherence, rather the coherence is shown to decay on a time-scale of tens of femtoseconds. This rapid dephasing of the electronic coherences present the view that coherence plays a negligible role in photoactive complexes [36,37].
1.4 Thesis description

This thesis is organized as follows. Chapter 2 provides a discussion regarding the tight-binding model used for the description of the molecular wire sandwiched between two fermionic reservoirs and molecular aggregates within fluctuating protein environments coupled to heat or phonon (bosonic) baths. As such, the basic theoretical background concepts needed to study charge and exciton dynamics in molecular scale systems embedded in a fluctuating environment, and the system-bath Hamiltonian for such charge and energy transfer systems are presented. Next, the density operator based quantum description of an open system is presented, followed by the concept of decomposition of the composite system into the reduced system and the environment [76] components. Subsequently the correlation functions as well as self-energies are introduced, which are responsible for correlating the system and the environment. The former as well as the latter may be formulated in terms of Chebyshev polynomials within the scheme known as the Chebyshev expansion scheme, which is presented thereafter and its application to propagation schemes is introduced. In this thesis we work exclusively with Chebyshev decomposition which is applied to expand the reservoir self energies or correlation functions in terms of Chebyshev polynomials and bessel functions. This scheme is also contrasted with the exponential spectral decomposition scheme. It is noted that the Chebyshev approach does not involve an expansion of the Fermi function and incorporates the Fermi function and the spectral density without any approximations. Specifically, it is the exponential term in the self energies or the correlation functions which decomposed in terms of a series of Chebyshev polynomials and bessel functions using the Jacobi-Anger identity. Consequently, one gets an efficient performance at low temperatures, where the steepness of the Fermi function makes a series expansion numerically unfeasible. This is followed by an introduction to the Green’s functions and other relevant quantities utilized within the time-dependent nonequilibrium Green’s function approach for quantum transport for uncorrelated fermionic systems.

In Chapter 3, a detailed derivation of the equations of motion for the scheme based on nonequilibrium Green’s functions [82] using the Chebyshev expansion is presented. This includes the derivation of the relevant observable quantities, such as the reduced single particle density operator or the electronic current through the system. In the NEGF scheme employed here, a single particle basis introduced in Chapter 2 is utilized and thus one deals with matrices of the dimension \(N \times N\) where \(N\) denotes the number of sites in the system. A useful trick [129] that substitutes all auxiliary matrices by \(N\)-dimensional vectors or even scalars is incorporated in the scheme as well. The computational effort is significantly reduced as a consequence and the scheme becomes applicable to larger systems. The Chebyshev based NEGF transport approach may be numerically treated in a straightforward manner and we perform a comparison of the Chebyshev decomposition based TD-NEGF approach with the NEGF approach based on the exponential decomposition from a numerical perspective. Specifically, the validity of the theory is discussed and tested for the time-independent and time-dependent single resonant level model. For the latter case the resonant level may be driven by a monochromatic or a pulsed external (laser) field. Such configurations have been discussed in various works, e.g. [62,130], in the context of the coherent destruction of tunneling (CDT) effect. Thereafter a more realistic physical system is investigated, namely a DNA molecular junction attached to fermionic reservoirs placed in a
fluctuating environment at room temperature, such that the surrounding molecules are causing rapid fluctuations in the environment. Charge transport through this multi-site system with time-dependent site energies is studied. For this model site energy trajectories are utilized which represent a chain of molecules surrounded by a polarizing solvent in contact with metallic leads [131]. To this end, Gaussian distributed trajectories set around the center of the conduction window are used. The reservoir self energies are equipped with a gapped spectral density with sharp edges to mimic the main characteristics of the energy profile of gold electrodes. Simulations using this latter kind of band structures would be unfeasible using the exponential decomposed NEGF scheme, while the Chebyshev-NEGF scheme is able to handle such a molecule-lead coupling without any additional numerical effort as compared to the simulation of, for instance, broad Lorentzian molecule-lead coupling. The advantages and limitations of the Chebyshev-NEGF approach are summarized along with some concluding remarks.

In Chapter 4 propagation schemes for energy transfer systems are presented. A rigorous derivation of the propagation scheme for the reduced density matrix for the system of interest is given for the Hierarchical equations of motion (HEOM) [77,98] approach. The chapter also introduces QMEs that are derived in second-order with regards to the system-bath coupling using the Chebyshev expansion [95]. After a short introduction to the path integral approach based on the Feynman-Vernon influence functional, the hierarchical equations of motion are derived utilizing the Chebyshev decomposition, and their recursive definition is presented that enables one to calculate the $n^{th}$ tier of the HEOM. This hierarchy of auxiliary density matrices forms a structure which is highly similar to that of the well-known exponential decomposition based HEOM. The newly developed Chebyshev-HEOM formalism is presented explicitly till the fourth order in the system-bath coupling or the 2nd tier truncation, in both time local and time non-local formulations. The results are benchmarked against the pre-existing exponential decomposition based HEOM. Both QME and HEOM treat the system-bath interaction by means of the bath correlation function which contains the spectral density of the environment. For exciton energy transfer systems, the importance of the ability of the Chebyshev approach to incorporate numerical and experimental spectral densities or environmental effects without any approximations is discussed.

In Chapter 5 we compare two schemes that may be used to obtain the current dynamics through a molecular junction numerically. Both the formalisms are able to treat electronic currents through molecular junctions subject to fluctuating environments, but while one of them is a time-independent scheme, the other obtains a time-dependent view of the electronic current. Within such formalisms the effect of the thermal environment can be incorporated within the system in several different ways. The models we compare here include the vibronic dephasing model within a Green’s function approach (the time-independent scheme), and the time-dependent non-equilibrium Green’s function scheme (TD-NEGF), in which the effect of the thermal environment manifests as the fluctuation of the on-site energies. The steady state results are obtained by time-averaging the results of the TD-NEGF approach and agree nearly perfectly with the results from the vibronic model. This numerical comparison aids in the understanding of the connection between these different pure dephasing schemes which both have their advantages and specific applications.
Chapter 2

Theoretical background

2.1 Model and hamiltonian

2.1.1 Hamiltonian: charge transport system

In this chapter the Hamiltonians for charge transport systems, i.e., molecular junctions, and for energy transfer systems, i.e., molecular aggregates surrounded by fluctuating environment, are introduced. The basis sets utilized in the schemes, i.e. the multi-particle set for the bosonic system scenario and the single particle basis set for the charge transport using NEGF scheme are presented. The density operator is introduced and its factorization into the relevant system, the reservoirs and the system-reservoir coupling are shortly discussed. The influence of the reservoirs or baths is brought into the system via self-energies or the correlation functions of the reservoirs which are next introduced. These self-energies or correlations functions normally appear in the form of non-trivial integrals the solution of which requires transforming the former to sums of exponential functions. Whereas in this work we use the Chebyshev polynomials to put the self-energies or correlation functions in numerically tractable forms. Finally, we present some background information regarding the NEGF formalism which is one of the main topics presented in this thesis.

The type of molecular junction discussed in this work is composed of a molecule or a chain of molecules attached to two fermionic reservoirs. This chain of molecules or the molecular wire is modeled as a linear chain of N sites within a tight-binding description. Either ends of the wire are connected to each reservoir or lead via their respective molecule-reservoir coupling. The idea is to sandwich a conducting molecule between charge or electron reservoirs such that its coupled to the reservoirs via tunneling barriers. A molecular wire is depicted in Fig. 1. Electrons travel from the left lead through each of the sites or the wire and into the right lead.
Figure 2.1: Sketch of the tight-binding model for a molecular wire. The spheres represent the sites of the wire coupled to left and right leads.

The term tight-binding implies that the electronic structure of the molecular wire described by the Hamiltonian is given in terms of highly localized basis states. In other words, the electrons within individual molecules in the wire stay tightly bound to their respective orbitals or sites. The highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) are responsible for the charge transport and each such orbital refers to a site of the wire where an electron can reside. The total Hamiltonian of such a system, in second quantization, is given by

\[ H(t) = H_S(t) + H_R + H_{SR} . \] (2.1)

In the above equation, \( H_S(t) \) is the relevant system part, \( H_R \) denotes the electron reservoirs and \( H_{SR} \) the system-reservoir coupling. In second quantization, the Hamiltonian of the wire reads

\[ H_S(t) = \sum_i \epsilon_i(t)c_i^\dagger c_i + \Delta_{i,i+1}(t) \sum_i (c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i) . \] (2.2)

In the above equation, \( i \) and \( j \) are site-indices and run from 1 till \( N \), the total number of sites in the system. The \( \epsilon_i(t) \) refer to the time-dependent site energies which basically depict the energy level of the state or site \( i \), while \( \Delta_{i,i+1}(t) \) denotes the time-dependent couplings to the nearest neighbouring site and is also called the hopping element as it describes the hopping action of the electrons as they jump from site to site during the transport across the molecular wire. Thus we work under the assumption that when passing through the wire the electrons can move only to the nearest site relative to their current position. The \( c_i^\dagger (c_i) \) denotes the creation (annihilation) operator at site \( i \) and follow the anticommutation relations for fermionic operators: \( \{ c_i, c_j^\dagger \} = \delta_{ij} \) & \( \{ c_i, c_j \} = 0 \). The electron can thus be imagined to be disappearing from one position and appearing at the next, in a sort of jump, described by the creation and annihilation operators. The reservoirs are described by non-interacting fermions (electrons) with \( b_{\alpha k}^\dagger (b_{\alpha k}) \) being the reservoir operators, creating (annihilating) particles with energy \( \epsilon_{\alpha k} \) in reservoir state \( k \) in the left or right \( (\alpha = L/R) \) electrode

\[ H_R = \sum_{\alpha \in L,R} \sum_k \epsilon_{\alpha k} b_{\alpha k}^\dagger b_{\alpha k} . \] (2.3)

The molecule-electrode coupling Hamiltonian is composed of the the system and bath creation and
annihilation operators along with coupling strength terms and reads

\[ H_{SR} = \sum_{\alpha k} \sum_{i} T_{ki}^{\alpha} c_i b_{\alpha k}^\dagger + T_{ki}^{\alpha*} b_{\alpha k} c_i^\dagger. \]  

(2.4)

Figure 2.2: Sketch of the transport set-up. The molecular sites are coupled to the leads by tunnel barriers, with coupling constants \( \Gamma_L \) and \( \Gamma_R \), whereas the leads are characterized by electrochemical potentials \( \mu_L \) and \( \mu_R \). \( V_{LR} \) denotes the applied voltage.

where \( T_{ki}^{\alpha} \) stands for the elements representing the coupling strength between the system state \( i \) and the reservoir state \( k \). One can define reservoir stochastic operators \( B_{\alpha i} \) and its conjugate \( B_{\alpha i}^\dagger \) such that

\[ B_{\alpha i} = \sum_{k} T_{ki}^{\alpha*} b_{\alpha k}, \quad B_{\alpha i}^\dagger = \sum_{k} T_{ki}^{\alpha} b_{\alpha k}^\dagger. \]

These operators are composed of linear combinations of reservoir creation or annihilation operators weighted by linear coefficients representing coupling strengths. The quantum average or the expectation of the products of these reservoir stochastic operators specifies the averaged correlation between interactions existing at two distinct points of time and are thus termed two-time correlation functions or self-energies. The self-energy describes the connection between the molecular wire and the leads, or in other words it describes the tunneling of the electrons between the reservoir and the system. The reservoir correlation functions are defined as [132]

\[ C_{\alpha ij}^+(t, \tau) = \langle B_{\alpha i}^\dagger(t) B_{\alpha j}(\tau) \rangle, \quad C_{\alpha ij}^-(t, \tau) = \langle B_{\alpha i}(t) B_{\alpha j}^\dagger(\tau) \rangle. \]

The correlation functions are highly similar to the self-energies, \( \Sigma_{\alpha ij}^{\geq}(t) \), that are utilized within the TD-NEGF formalism and are related in the following manner

\[ \Sigma_{\alpha ij}^{\geq}(t, \tau) = -i C_{\alpha ij}^-(t, \tau), \quad \Sigma_{\alpha ij}^{\leq}(t, \tau) = i C_{\alpha ij}^+(t, \tau). \]

The self-energies and correlation functions will be further discussed in section 2.4. The + and − attached
to the correlation function depicts the movement of the electrons from and to the fermionic reservoirs respectively. The lesser and greater sign along the self-energies has a similar function and represents the motion of electrons into and out of the reservoirs, respectively.

The leads within this model are presumed to be ideal electron reservoirs in thermal equilibrium. Their description is given in the grand canonical ensemble and the respective partition function reads

\[
Z = \text{Tr}_R \{ e^{-\beta (H_R - \sum_\alpha \mu_\alpha N_\alpha)} \} = \sum_{\alpha,k} e^{-\beta \epsilon_{\alpha k}},
\]

where \( N_\alpha \) denotes the number operator, i.e., \( N_\alpha = \sum_k b^\dagger_{\alpha k} b_{\alpha k} \), and \( \beta = 1/(k_B T) \) with \( T \) being the temperature of the reservoirs. As the reservoirs are in thermal equilibrium, the electronic distribution is characterized by the Fermi-Dirac function

\[
f_\alpha(\epsilon) = \frac{1}{1 + e^{(\epsilon - \mu_\alpha)/\beta}}.
\]

2.1.2 Hamiltonian: energy transfer system

As mentioned previously, in the open quantum system theory, the Hamiltonian of a composite system is decomposed into three constituent parts given by Eq. (2.1). For the case of bosonic systems, the total system is similarly dissociated into the relevant system Hamiltonian, \( H_S(t) \), for the molecular aggregate or the pigments within light harvesting complexes, bosonic reservoir Hamiltonian, \( H_R \), representing the environmental effects incident on the system, e.g., the pigments, while \( H_{SR} \) represents the system-reservoir coupling Hamiltonian. Here we look at the transfer of a single electronic excitation, i.e., the basis states of the system \(|i\rangle\) assume a single exciton at site \( i \). The sites basically correspond to valance bands with electrons that can potentially be excited, via absorption of photons, to jump into the conduction bands. In this model we have only a single exciton occupying only one site, which implies that all other sites are presumed to be in their ground states. The system is assumed to be composed of \( N \) sites with site energies \( E_i \) at each site \( i \). Sites \( i \) and \( j \) interact via electronic couplings, \( V_{ij} \). Each site may thus be coupled to any other site. The Hamiltonian of the \( N \)-site system in tight-binding description is given as

\[
H_S = \sum_i^N E_i |i\rangle \langle i| + \sum_{i \neq j}^N V_{ij} |i\rangle \langle j|.
\]

For the case of exciton transfer it is possible to calculate the exciton energies and the electronic couplings using the electronic structure of the system’s constituents. The resulting information may then be added to the above-mentioned tight-binding model [133] for increased accuracy of the model. The bosonic reservoir is described by the Bose-Einstein statistics

\[
n_\alpha(\epsilon) = \frac{1}{e^{(\epsilon - \mu_\alpha)/\beta} - 1}.
\]
Figure 2.3: Sketch of the molecular aggregates or pigments surrounding the reaction centre within a photosynthetic light harvesting apparatus. The absorbed photons or energy by externally lying pigments is transferred to the reaction centre following an energy gradient.

and is given as an infinite sum of displaced harmonic oscillators, linearly coupled to the system degrees of freedom (DOF) that are acting as a phonon or heat bath.

\[ H_R = \sum_\xi \left( \frac{p_\xi^2}{2m_\xi} + \frac{m_\xi \omega_\xi^2 x_\xi^2}{2} \right). \]  

(2.9)

In the above, \( p_\xi, x_\xi, \omega_\xi \) and \( m_\xi \) represent the momenta, displacements around the equilibrium, frequencies, and masses of the bath oscillators, respectively. \( H_{SR} \) or the system-reservoir coupling Hamiltonian can be written as a sum of products of system and bath operators, \( \Phi_j \). The system operators herein are supposed to be site diagonal for excitonic systems \[ \sum_j \Phi_j K_j = \sum_j \sum_\xi c_{j\xi} x_\xi \left| j \right\rangle \left\langle j \right| . \]  

(2.10)

In the above equation, \( c_{j\xi} \) represent the system-reservoir coupling strengths, while the system part of the system-reservoir coupling is given by a projector onto site \( j \), i.e., \( K_j = \left| j \right\rangle \left\langle j \right| \). In this form an interaction between the bath and the system at site \( j \) exists only if an excitation is present. This description is limited to situations in which each site has its own thermal bath that is uncorrelated to the bath modes at any other site.


2.2 Basis sets

Many-particle physics such as the one discussed in this work regarding the molecular wire and molecular aggregates is simpler to formulate within the second quantization or the occupation number representation. In this representation one obtains the basis states for an N-particle system by listing the occupation numbers of each basis state. The occupation number basis thus reads \( |n_1, ..., n_i, ..., n_N \rangle \) with \( n_i \) being the occupation number for the orbital or site \( i \). In this basis one essentially counts the number of particles residing within each molecular orbital or site. Here \( \sum_j n_j = N \), where \( N \) is the number of sites in the system. For fermions \( n_i \) can be \((0, 1)\), while for bosons it can be any non-negative number, i.e., \((0, 1, 2, 3,...)\). The fermionic creation and annihilation operators in the occupation-number representation are given by

\[
\begin{align*}
\hat{c}_i^\dagger |n_1, ..., n_i, ..., n \rangle &= (-1)^{\Sigma_i} (1 - n_i) |n_1, ..., n_i + 1, ... \rangle, \\
\hat{c}_i |n_1, ..., n_i, ... \rangle &= (-1)^{\Sigma_i} n_i |n_1, ..., n_i - 1, ... \rangle,
\end{align*}
\]

where \( \Sigma_i = n_1 + n_2 + ... + n_i - 1 \) and \( i = 1, ..., N \). Whereas the bosonic creation and annihilation operators are given by

\[
\begin{align*}
\hat{b}_i^\dagger |n_1, ..., n_i, ... \rangle &= \sqrt{n + 1} |n_1, ..., n_i + 1, ... \rangle, \\
\hat{b}_i |n_1, ..., n_i, ... \rangle &= \sqrt{n} |n_1, ..., n_i - 1, ... \rangle.
\end{align*}
\]

For bosons, creation/annihilation operators belonging to different states commute with each other while fermionic creation/annihilation operators for different states anti-commute. From the above definition of bosonic creation/annihilation operators it follows that \( \hat{b}_i^\dagger \hat{b}_i \) counts the number of bosons in the state \( i \). \( \hat{b}_i^\dagger \hat{b}_i \) is thus termed the number operator and is given as

\[
\hat{b}_i^\dagger \hat{b}_i |n_1, ..., n_i, ... \rangle = \sqrt{n^2} |n_1, ..., n_i, ... \rangle.
\]

The number operator, \( K_j \), for case of two possible states of the system, is given in matrix form as

\[
\begin{align*}
K_1 = \hat{b}_1^\dagger \hat{b}_1 &= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \\
K_2 = \hat{b}_2^\dagger \hat{b}_2 &= \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.
\end{align*}
\]

For computational purposes, one only needs \( H_S \) and \( H_{SB} \), while \( H_B \) is treated inside the EOMs. Furthermore, a matrix representation of the mentioned operators is necessary for numerical implementation. Given a system with two possible states, e.g. 1 and 2, which are orthogonal, the state ket for an arbitrary state can be written in terms of \( |1 \rangle \) and \( |2 \rangle \): \( |\phi \rangle = \alpha |1 \rangle + \beta |2 \rangle \). Where the expansion coefficients must satisfy \( |\alpha|^2 + |\beta|^2 = 1 \) for normalization of the wave function.

Using the above, the system and interaction Hamiltonians are given as:

\[
H_S = \begin{pmatrix}
|1 \rangle H_S |1 \rangle & |1 \rangle H_S |2 \rangle \\
|2 \rangle H_S |1 \rangle & |2 \rangle H_S |2 \rangle
\end{pmatrix} = \begin{pmatrix}
\epsilon_1 & \Delta_{12} \\
\Delta_{21} & \epsilon_2
\end{pmatrix}
\]

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\[ H_{SB} = \sum_j \Phi_j \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} \sum_j \Phi_j & 0 \\ 0 & 0 \end{pmatrix} \]

where \( \phi_j \) represents the system-reservoir coupling strength.

For a two-level system with a total of four possible states, \(|0,0\), \(|1,0\), \(|0,1\), \(|1,1\), one gets the following matrix representation for the combination of creation and anihilation operators:

\[ b_{11}^\dagger b_1 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \]

\[ b_{22}^\dagger b_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \]

Although the multiparticle basis set is able to include terms in the Hamiltonian describing particle correlation effects and consequently account for physical properties like the electron spin and Coulomb interactions etc., the TD-NEGF scheme discussed in this work utilized the single-particle basis. In the case of the single-particle TD-NEGF scheme the correlations between particles, i.e. electron-electron interactions, are neglected completely, enabling the usage of a direct product of single particle states: \(|n_1\otimes|n_i\otimes|n_N\rangle\). As a consequence involved matrices scale as \(N \times N\) rather than as \(2^N \times 2^N\) with \(N\) being the number of sites. The scaling of single particle basis scheme is numerically more efficient than the multi-particle basis and renders the scheme applicable to larger systems. In this basis an N-site system Hamiltonian reads:

\[ H_S = \begin{pmatrix} \epsilon_1 & -\Delta & 0 & \ldots & 0 \\ -\Delta & \epsilon_2 & -\Delta & \ldots & 0 \\ 0 & -\Delta & \epsilon_3 & -\Delta & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \ldots & -\Delta & \epsilon_{N-1} & -\Delta \\ 0 & \ldots & 0 & -\Delta & \epsilon_N \end{pmatrix} \]

2.3 Density matrix approach

In quantum mechanics, the knowledge one has about the state of a mixed-state system at a specific time is incomplete. What one knows are just the probabilities \(p_k\) of finding the system in the state \(|\psi_k\rangle\), where \(0 \leq p_1,p_2,\ldots,p_k,\ldots \leq 1\) and \(\sum_k p_k = 1\). This statistical mixture represents the incomplete information one has of the system. Thus, complex quantum systems cannot be fully characterized by single state kets or vectors and can only be described by the density operator

\[ \rho(t) = \sum_i p_k |\psi_k(t)\rangle \langle \psi_k(t)| \]  \hspace{1cm} (2.14)
where \( p_k \) obviously give the probabilities of finding the system in the pure state \(|\psi_k\rangle\). Also, \( \text{tr}\rho(t) = 1 \) and \( \sum_k p_k^2 \leq 1 \). The matrix representation of the density operator is obtained by choosing a basis in the underlying space. One can expand the pure states in terms of an orthonormal basis \(|\phi_n\rangle\) i.e. \(|\psi_k\rangle = \sum_n \alpha_n^{(k)} |\phi_n\rangle \) where \( \alpha_n^{(k)} \) are linear coefficients. The density matrix then reads

\[
\rho_{nm} = \sum_k p_k \langle \phi_n | \psi_k \rangle \langle \psi_k | \phi_m \rangle = \langle \phi_n | \rho | \phi_m \rangle \tag{2.15}
\]

where \( n \) and \( m \) run over all basis states. The diagonal elements of the density matrix are

\[
\rho_{nn} = \sum_k p_k |\langle \phi_n | \psi_k \rangle|^2,
\]

where \( |\langle \phi_n | \psi_k \rangle|^2 \) is a real positive number and gives the probability of finding the system in the state \(|\phi_n\rangle\) given that it existed in the state \(|\psi_k\rangle\) before the measurement. Each diagonal element thus gives the average probability of finding the system in the state \(|\phi_n\rangle\) and thus \( \rho_{nn} \) also give the population of the state \(|\phi_n\rangle\). The off diagonal elements of the density matrix, \( \rho_{nm} \), are complex numbers and are termed coherences as they represent interference effects between \(|\phi_n\rangle\) and \(|\phi_m\rangle\). The time evolution of a statistical mixture represented by \( \rho(t) \) from an initial time \( t_0 \) a certain time \( t \) is given by

\[
\rho(t) = \mathcal{T} e^{-\frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau)} \rho(t_0) e^{\frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau)} = U(t, t_0) \rho(t) \tag{2.16}
\]

where the Liouville superoperator represents a commutator with the Hamiltonian, \( \mathcal{T} \) is the time ordering operator in the positive direction of time and the time evolution operator, \( U(t, t_0) \), is defined as

\[
U(t, t_0) = \mathcal{T} e^{-\frac{i}{\hbar} \int_{t_0}^t d\tau \mathcal{L}(\tau)} \tag{2.17}
\]

The time derivative of the density matrix gives the dynamics of a complex quantum system and is termed the Liouville-von Neumann equation and may be obtained by writing down Eq. (2.16) in its differential form

\[
\frac{\partial}{\partial t} \rho(t) = -\frac{i}{\hbar} \{H(t), \rho(t)\} = -\frac{i}{\hbar} \mathcal{L}\rho(t) \tag{2.18}
\]

The solution of this equation would give the time-evolution of all system as well as bath degrees of freedom. This is often unnecessary and leads to equations to be solved regarding unnecessary degrees of freedom. Therefore one normally introduces the reduced density matrix of the system degrees of freedom only.

### 2.4 Projection operator technique

The density operator of the total system introduced above may contain information about the environmental degrees of freedom not relevant to a possible system of interest residing within a potentially massive total system. The idea then is to formulate a reduced density operator that describes completely
the outcome of measurements of the relevant system, given that the environment is left unobserved. This reduced density matrix for the relevant or the reduced system is obtained by the dissociation or factorization of the total quantum system. The total system is decomposed into the relevant system, i.e., the molecular wire and the environment, i.e., the electron reservoirs. This factorization of the total density operator into the constituent $\rho_S$, the density operator of the reduced system, and $\rho_R$, the density operator belonging to the reservoirs is written as

$$\rho = \rho_S \otimes \rho_R .$$

This factorization operation is actually carried out by tracing out the degrees of freedom of the reservoirs from the total density operator to obtain the density operator of the reduced system and can be formally regarded as a projection. Mathematically it boils down to the introduction of a projection operator, $\mathcal{P}$, defined below

$$\mathcal{P}(\ldots) = \rho_R \otimes \text{Tr}_R\{\ldots\}.$$  

This projection operator acts within the total system state space and when applied to the density operator, selects the DOF associated with the reduced system by tracing out the degrees of freedom of the reservoirs while ignoring any initial correlations between the system and reservoirs:

$$\mathcal{P}\rho(t) = \rho_R \otimes \text{Tr}_R\{\rho(t)\} = \rho_R \otimes \rho_S(t) .$$

Thus, the trace of the total density operator over the reservoir subspace ($\text{Tr}_R\{\rho(t)\}$) gives the density operator of the reduced system, $\rho_S$. The $\rho_R$ may be termed as an equilibrium density operator as it is time independent while the reduced system retains the time-dependent effects or the time-varying parts of the total system. The equilibrium density operator, $\rho_R$, is assumed to be normalized, i.e., $\text{Tr}_R\{\rho_R\} = 1$. The projector operator, $\mathcal{P}$, has a complementary operator, $\mathcal{Q}$, such that $\mathcal{P} + \mathcal{Q} = \mathcal{I}$, where $\mathcal{I}$ is the identity operator.

Figure 2.4: Decomposition of the total system into the relevant system and bath connected by a coupling term.

This projection operator acts within the total system state space and when applied to the density operator, selects the DOF associated with the reduced system by tracing out the degrees of freedom of the reservoirs while ignoring any initial correlations between the system and reservoirs:
2.5 Reservoir correlation functions

2.5.1 Correlation functions and self energies

As previously mentioned, the expectation value or the quantum statistical average of the products of reservoir stochastic operators yield correlation functions or self-energies. The self-energies or the correlation functions are responsible for bringing the environmental effects into the system. Their physical interpretation is that of the tunneling process whereby electrons move between the reservoirs and the system. In this work, correlation function are used with regard to energy transfer in bosonic systems using the QME or HEOM formalisms while self-energies are used within the NEGF formalism with regards to charge transport in fermionic systems.

Since in the model utilized herein each lead, for the case of fermionic systems, is only coupled to the site nearest to it, the site indices \( i \) and \( j \) from the self energies may be dropped without any loss of information or accuracy. The self-energies thus couple only the first and the last site of the molecular wire with the left and the right leads, respectively, meaning that electrons may enter or leave the molecular wire only via the first and last sites.

Starting from the definition of reservoir correlation functions for charge transport within fermionic systems \([132]\) we have

\[
C^+_{\alpha}(t, \tau) = \langle B^\dagger_{\alpha}(t) B_{\alpha}(\tau) \rangle, \quad C^-_{\alpha}(t, \tau) = \langle B_{\alpha}(t) B^\dagger_{\alpha}(\tau) \rangle.
\]

(2.22)

The + and - superscript in the above refers to the motion of electrons into and out of the reservoirs as far the fermionic systems are concerned \([72]\). For bosonic systems there is only dissipation or transfer of energy, as compared to two-way transport of charge in the case of fermionic systems. Since there is only heat dissipation, the energy transfer is described by a single correlation function and the \( \mp \) index in the superscript is not needed for the case of energy transfer systems. Thus one only has the following correlation function

\[
C^-_{\alpha}(t, \tau) = \langle B_{\alpha}(t) B^\dagger_{\alpha}(\tau) \rangle.
\]

(2.23)

The self-energies that appear in the NEGF formalism, \( \Sigma_{\alpha ij}^{\mp}(t) \), are written below using the same operators as the correlation functions above. Since the NEGF scheme discussed in this work is only applicable to fermionic systems, there needs to be an index present, namely the superscript \( \geq \), which denotes the direction of transport of charge between the system and the baths.

\[
\Sigma^\geq_{\alpha i}(t) = -i \langle B_{\alpha}(t) B^\dagger_{\alpha}(\tau) \rangle, \quad \Sigma^\leq_{\alpha i}(t) = i \langle B_{\alpha}(t) B^\dagger_{\alpha}(\tau) \rangle^\dagger.
\]

(2.24)

Specifically, a term referred to as the spectral density function or just the spectral density is responsible for the incorporation of external or enviromental effects within the system. The environmental degrees of freedom are present within the spectral density which appears inside the self-energy functions or the correlation functions. The relationship of the spectral density and the self-energies or correlation func-
ions is described using the fluctuation-dissipation theorem (FDT) [77,134] (more on FDT in Appendix D). For bosonic systems the correlation function is written in terms of the spectral density function and the Bose-Einstein function. The index \( j \) in the subscript of the correlation function denotes the site index. The spectral density, \( J_j(\omega) \), is related to the bath correlation functions by [76]

\[
C_j(t - \tau) = \frac{\hbar}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega(t-\tau)}J_j(\omega)}{1 - e^{-\beta\hbar\omega}}[1 + n_j(\hbar\omega)]
\]

or in the energy domain as

\[
C_j(t - \tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\epsilon n_j(-\epsilon + \mu_j)e^{-i\epsilon(t-\tau)/\hbar}J_j(\epsilon) .
\]

where \( \beta = 1/(k_B T) \) denotes the inverse temperature and \( n_j(\hbar\omega) \) the Bose-Einstein distribution. The spectral density, \( J_j(\omega) \), for the case of bosonic systems is, just as in the case of fermionic spectral density, responsible for the incorporation of environmental effects in the system and consists of information regarding the energy spectrum of the environment as well as the system-bath coupling. In terms of the system-reservoir coupling strength, \( c_j\xi \), frequencies of the bath oscillators, \( \omega_{\xi} \), and their masses, \( m_{\xi} \), the spectral density can be written as

\[
J_j(\omega) = \sum_{\xi} \frac{c_j^2}{2m_{\xi}\omega_{\xi}}\delta(\omega - \omega_{\xi}) .
\]

For a set of bath oscillators the spectral density consists of a sequence of \( \delta \)-functions presumed to have a density sufficient enough to yield a continuous spectrum.

For the case of Fermionic systems, the self energies are related to the spectral density which incorporate the effects of the leads that are assumed to be in equilibrium. The lesser and greater self-energies are given in the energy representation by

\[
\Sigma_\alpha^<(\epsilon) = i f_\alpha(\epsilon - \mu_\alpha)J_j(\epsilon), \quad \Sigma_\alpha^>(\epsilon) = i(1 - f_\alpha(\epsilon - \mu_\alpha))J_j(\epsilon) .
\]

To obtain the self-energies in time domain, one needs to take the inverse Fourier transform of the above lesser and greater self-energies. In terms of the spectral density and the Fermi functions of the leads they are given as

\[
\Sigma_\alpha^<(t,\tau) = \frac{i}{2\pi} \int_{-\infty}^{\infty} de f_\alpha(\epsilon - \mu_\alpha)e^{-i\epsilon(t-\tau)/\hbar}J_\alpha(\epsilon) ,
\]

\[
\Sigma_\alpha^>(t,\tau) = -\frac{i}{2\pi} \int_{-\infty}^{\infty} de f_\alpha(-\epsilon - \mu_\alpha)e^{-i\epsilon(t-\tau)/\hbar}J_\alpha(\epsilon) .
\]

The spectral function of the reservoirs, \( J(\epsilon) \), refers to the means by which the external properties of the reservoirs are accounted for within the system. The spectral density is defined in terms of the
Chapter 2. Theoretical background

tunnel matrix elements

\[ J_\alpha(\epsilon) = 2\pi \sum_k T^\alpha_k T^{\alpha*}_k \delta(\epsilon - \epsilon_{ak}) \] \hspace{1cm} (2.31)

On the other hand the single-particle density of states of the reservoir \( \alpha \) is\(^{16} \)

\[ D_\alpha(\epsilon) = \sum_k \delta(\epsilon - \epsilon_{ak}) \] \hspace{1cm} (2.32)

The spectral density can be seen to be directly proportional to the density of states. The tunnel coupling elements appear as weights next to the density of states, and one can physically interpret coupling strengths as tunnel barriers. Note that in the literature the spectral density is often termed as lead spectral function or coupling-weighted density of states. The spectral density function is defined physically for positive \( \epsilon \), in other words \( \epsilon \geq \min(\epsilon_{ak}) \equiv 0 \). Nevertheless, in order for the definitions of the correlation functions or the self-energies to hold, one needs a function defined on the whole real axis. The definition (2.31) can thus be extended to the negative region \( (\epsilon < 0) \) by setting \( J_\alpha(\epsilon) \equiv J_\alpha(-\epsilon) \), which yields

\[ J_\alpha = 2\pi \sum_k \left[ T^\alpha_k T^{\alpha*}_k \delta(\epsilon - \epsilon_k) + T^{\alpha*}_k T^\alpha_k \delta(\epsilon + \epsilon_k) \right] \] \hspace{1cm} (2.33)

The spectral density may potentially be a time-dependent quantity, which actually stems from time-dependent coupling elements. In this work, however, the coupling elements, \( T^\alpha_k \) are assumed to be time independent. The \( T^\alpha_k \) represent the coupling of the wire level energy levels (namely the first and the last sites of the wire) to the reservoir state at energy \( k \).

2.5.2 Chebyshev decomposition

The integrals present within the equations of the correlation functions, Eq. (2.26), or within the equations for the self-energies, Eq. (2.29) and Eq. (2.30), cannot be solved in their present forms due to their composition. The usage of an exponential decomposition scheme enables the expansion of the correlation functions or self-energies of the reservoirs in terms of sums of weighted exponential functions providing a route of side-stepping the issue of directly solving the integrals. The main idea of this decomposition scheme involves the decomposition of spectral densities contained within the self-energies or correlation functions in terms of Lorentzian functions in conjunction with an expansion of the Fermi function in terms of poles using, for example, the Ozaki scheme [104–106]. This approach has been utilized extensively for building complete sets of ordinary differential equations: QME [75,102,103], HEOM [107] as well as NEGF-based equations of motion [82].

An alternate to the above is the approach based on the usage of Chebyshev polynomials. This approach has been utilized in, for example, the propagation of wave packets [109] and have been shown to lead to a high stability of the resultant propagation schemes. Other polynomials used to build propagation schemes include Newton [109] and Hermite polynomials [135], for example. This scheme

\(^{16}D(\epsilon) d\epsilon \) gives the number of single-particle states with energy between \( \epsilon \) and \( \epsilon + d\epsilon \).
has been employed in recent years by Tian and Chen [112,136] to construct a single-particle fermionic hierarchical EOM for molecular junctions. The main idea in the Chebyshev decomposition scheme is to expand the Fourier kernel in Eq. (2.29), (2.30), or (2.26) by means of the Jacobi-Anger identity [137] given by

\[ e^{-i\Omega xt} = J_0(\Omega t) + \sum_{n=1}^{\infty} 2(-i)^n J_n(\Omega t) T_n(x) , \quad \forall t \in \mathbb{R} , \forall x \in [-1,1] , \quad (2.34) \]

with the Chebyshev polynomials \( T_n \) and the Bessel functions of the first kind \( J_n \) shown below.

Figure 2.5: Chebyshev polynomials of the 1st kind.

In contrast to the exponential decomposition scheme, the Chebyshev approach does not involve a series expansion of the Fermi function or the Bose-Einstein function, and incorporates the Fermi/Bose-Einstein function and the spectral density without any approximations. Specifically, it is the exponential term in the definitions of the self-energies or the correlation functions which is expanded using the above-mentioned Jacobi-Anger identity. This enables the expression of the self-energies or the correlation functions in terms of Chebyshev polynomials and Bessel functions. The details of this expansion will be discussed in the following chapters.

2.6 Non-equilibrium Green’s functions formalism

In the next chapter the Chebyshev expansion is applied to the well established nonequilibrium Green’s functions formalism. Here some background information regarding Green’s functions technique that is addressed in this work is presented. The Green’s functions within the tight-binding model are defined using the creation and annihilation operators defined on the system subspace as [72,84]

\[
G_{ij}^r(t,\tau) = -\frac{i}{\hbar} \Theta(t-\tau) \langle \{c_i(t), c_j^\dagger(\tau)\} \rangle \\
G_{ij}^a(t,\tau) = \frac{i}{\hbar} \Theta(\tau-t) \langle \{c_i(t), c_j^\dagger(\tau)\} \rangle \\
G_{ij}^<(t,\tau) = \frac{i}{\hbar} \langle c_j^\dagger(\tau)c_i(t) \rangle \\
G_{ij}^>(t,\tau) = -\frac{i}{\hbar} \langle c_i(t)c_j^\dagger(\tau) \rangle .
\]
where the superscripts $<, >, r$ or $a$ denote the lesser, greater, retarded or advanced version of the Green’s function, respectively. The $c_i$ and $c_i^\dagger$ are the system annihilation and creation operators and the function $\Theta(t)$ denotes the Heaviside or step function. Furthermore, the retarded and advanced versions and the lesser and the greater versions of the Green’s functions as well as the self energies are related by the following

\[
X_r^\alpha(t, \tau) = \pm \Theta(\pm t \mp \tau)[X^\alpha_r(t, \tau) - X^\alpha_s(t, \tau)] \tag{2.36}
\]

\[
\Sigma^\alpha_r(t, \tau) = \Theta(t - \tau)[\Sigma^\alpha_r(t, \tau) - \Sigma^\alpha_s(t, \tau)] \tag{2.37}
\]

The Green’s functions here are given as matrices since we are working with a discrete basis set of dimension $N$. The reduced-system density operator in the single particle basis employed here is termed as the single-particle reduced density operator. The relation between the single-particle and the multi-particle density matrix is as follows

\[
\rho_{S,i,j}^{s.p.}(t) = \text{Tr}_S\{c_i^\dagger c_j \rho_S(t)\} . \tag{2.38}
\]

Thus $\rho_{S,i,j}^{s.p.}(t)$ is a matrix of dimension $N \times N$. Moreover, the index $S$ shall now denote the respective quantities belonging to the system density matrix, Green’s functions or self-energies. The diagonal elements of $\rho_{S,i,i}^{s.p.}(t)$ represent the occupation numbers of the sites

\[
\rho_{S,i,i}^{s.p.}(t) = n_i(t) = \langle c_i^\dagger c_i \rangle . \tag{2.39}
\]

From the Green’s functions one is able to obtain the single-particle density matrix using

\[
\rho_{S,i,j}^{s.p.}(t) = \text{Im}\{G_S^{i,j}(t, t)\} . \tag{2.40}
\]

\[
\rho_{S,i,i}^{s.p.}(t) - 1 = \text{Im}\{G_S^{i,i}(t, t)\} . \tag{2.41}
\]

In general, the Green’s functions account for the response of the system to an external perturbation, which in our case is represented by the coupling Hamiltonian. The current through the wire consists of the current moving from the left lead to the wire and then from the wire to the right lead. At steady state these currents are equal. The time evolution of the occupation number operator of the reservoirs or leads gives the current flowing between that lead and the relevant system, i.e.,

\[
I_\alpha(t) = -\frac{ie}{\hbar} \langle [H, N_{\alpha}] \rangle . \tag{2.42}
\]

where $N_{\alpha} = \sum_{\alpha,k} b_{\alpha,k}^\dagger b_{\alpha,k}, \alpha = L/R$ and $H$ is the total hamiltonian defined earlier in this section. The system and reservoir hamiltonians, $H_S$ and $H_R$, respectively, commute with the number operator $N_{\alpha}$. The current from the left lead into the relevant system can then be written as

\[
I_\alpha(t) = -\frac{ie}{\hbar} \sum_{ik} \left( T_{k,i}^\alpha (c_i^\dagger b_{ak}) - T_{k,i}^{\alpha*} (b_{ak}^\dagger c_i) \right) . \tag{2.43}
\]
Defining the lesser (system-reservoirs) Green’s functions as
\[ G^<_\alpha,ki(t-\tau) = \frac{i}{\hbar}\langle c^\dagger_i(t) b_{\alpha k}(t) \rangle, \]
\[ G^<_\alpha,ik(t-\tau) = \frac{i}{\hbar}\langle b^\dagger_{\alpha k}(\tau)c_i(t) \rangle, \]
the current given above can be readily expressed in terms of these system-reservoirs Green’s functions
\[ I_\alpha(t) = -e \sum_{ik} \left( T_{ki}^\alpha G^<_\alpha,ki(t-\tau) - T_{ki}^{\alpha*} G^<_\alpha,ik(t-\tau) \right). \] (2.45)

The time-diagonal elements of the above defined system-reservoir Green’s functions contain information about the current [72] and have the property that
\[ G^<_\alpha,ki(t,t) = -[G^<_\alpha,ik(t,t)]^*. \]

The expression for the lesser system-reservoirs Green’s function can be calculated using analytic continuation rules given in Ref. 72, and the equations of motion of the contour-ordered and the time-ordered Green’s functions
\[ G^<_\alpha,ik(t-\tau) = \sum_j \int dt_1 T_{kj}^{\alpha*}[G^<_ij(t-t_1)g^<_k\alpha(t_1-\tau) + G^<_ij(t-t_1)g^a_k\alpha(t_1-\tau)], \] (2.47)
where \( i \neq j \) and \( g^<_\alpha \) are the Green’s functions for the leads defined as
\[ g^<_k\alpha(t-\tau) = \frac{i}{\hbar}\langle c^\dagger_{k,\alpha}(\tau)c_{k,\alpha}(t) \rangle = \frac{i}{\hbar} f(\epsilon_{\alpha k}) exp[-i\epsilon_{\alpha k}(t-\tau)], \] (2.48)
\[ g^{a \alpha}_k(t-\tau) = \mp \frac{i}{\hbar}\theta(\mp t \mp \tau)\langle c_{k,\alpha}(t), c^\dagger_{k,\alpha}(\tau) \rangle = \mp \frac{i}{\hbar}\theta(\mp t \mp \tau) exp[-i\epsilon_{\alpha k}(t-\tau)], \] (2.49)
where \( \theta \) is the step function and the Fermi function, \( f(\epsilon_{\alpha k}) \), gives the equilibrium distribution in a given lead. By taking the Fourier transform of Eq. 2.47, one obtains the lesser system-reservoir Green’s function in the energy domain
\[ G^<_\alpha,ik(\epsilon) = \sum_j T_{kj}^{\alpha*}[G^<_ij(\epsilon)g^<_k\alpha(\epsilon) + G^<_ij(\epsilon)g^a_k\alpha(\epsilon)]. \] (2.50)

Inserting the above in the expression of the current given in Eq. 2.46
\[ I_L = \frac{2e}{\hbar} \int \frac{d\epsilon}{2\pi} \text{Re} \left\{ \sum_{ijk} T_{ki}^{\alpha} T_{kj}^{\alpha*} \left[ G^<_ij(\epsilon)g^<_k\alpha(\epsilon) + G^<_ij(\epsilon)g^a_k\alpha(\epsilon) \right] \right\}, \] (2.51)
and identifying in the above expression the spectral density (level-width function), here denoted by \( \Gamma(\epsilon) \), defined earlier in Eq. 2.31, one can write the above after analytic manipulations \[72\] as

\[
I_L^{(R)} = \frac{ie}{2\hbar} \int \frac{d\epsilon}{2\pi} \text{Tr} \left\{ \Gamma^{L(R)}(\epsilon)(G^<(\epsilon) + f_L(\epsilon)[G^< + G^a] - G^a) \right\} .
\] (2.52)

Eq. 2.52 yields the general expression for the direct or steady state current (known as the Meir-Wingreen formula)

\[
I = \frac{ie}{\hbar} \int \frac{d\epsilon}{2\pi} \text{Tr} \left\{ \left[ \Gamma^L(\epsilon) - \Gamma^R(\epsilon) \right] G^<(\epsilon) + \left[ f_L(\epsilon)\Gamma^L(\epsilon) - f_R(\epsilon)\Gamma^R(\epsilon) \right] \left[ G^\sigma - G^a(\epsilon) \right] \right\} .
\] (2.53)

where \( \Gamma^{L(R)} \) is the level width function or the spectral density, and \( f(\epsilon) \) is the fermi function. In the steady state, \( I = I_L = -I_R \). Moreover, using the general relationship \( G^\sigma - G^a = G^< - G^> \), which is valid for both the reservoir as well as the system Green’s functions, one can express Eq. 2.51 as

\[
I_L = \frac{e}{\hbar} \int \frac{d\epsilon}{2\pi} \sum_{ijk} T_{ki}^{\alpha} T_{kj}^{\alpha} \left[ G_{ij}^<(\epsilon)g_{k\alpha}^<(\epsilon) + G_{ij}^< T_{kj}^{\alpha} \right] + \left[ f_L(\epsilon)\Gamma^L(\epsilon) - f_R(\epsilon)\Gamma^R(\epsilon) \right] \left[ G^\sigma - G^a(\epsilon) \right] .
\] (2.54)

Finally, in the energy domain, the current expression can be written as

\[
I_\alpha = \frac{e}{\hbar} \int \frac{d\epsilon}{2\pi} \text{Tr} \left\{ G^\sigma \Sigma^<_\alpha + G^< \Sigma^>_\alpha \right\} .
\] (2.57)

In the above expression, the Green’s functions, \( G^\xi \), provide information about the number of available states in the relevant system, while the self-energy terms, \( \Sigma^\xi \), provide information about the current flow rate into and out of each of the leads.

In the non-interacting case considered in this work, the Dyson equation reads \[71\],

\[
G_r^S = G_{0,r}^0 + G_{0,r}^0 \Sigma^r G_r^S ,
\] (2.58)

which can used to obtain the retarded Green’s function for the reduced system and is usually used to
Chapter 2. Theoretical background

derive the system dynamics. Here $G_{0,S}^r$ is the Green’s function of the isolated system,

$$
G_{0,S}^r = \frac{1}{(\epsilon + i\eta)I - H_S} \quad (\eta \to 0^+) ,
$$

(2.59)

and $\Sigma^r$ is the retarded self-energy of the leads. Inserting Eq. 2.59 into Eq. 2.58 one gets

$$
G_S^r = \frac{1}{(\epsilon + i\eta)I - H_S} (1 + \Sigma^r G_S^r) = \frac{1}{(\epsilon + i\eta)I - H_S - \Sigma^r} .
$$

(2.60)

where $I$ is the identity matrix and $\eta$ is an infinitely small, positive quantity. Moreover, the advanced version of Green’s function or the self-energy is the complex conjugate of the retarded version $G_S^a = [G_S^r]^\dagger$, $\Sigma^a = [\Sigma^r]^\dagger$. From Eq. 2.60 it can be seen that the inversion of a finite matrix of given quantities yields the Green’s function of the system.

The Keldysh equation for the non-interacting case is given as [72]

$$
G^\approx(\epsilon) = G^r(\epsilon)\Sigma^\approx_{\text{tot}}(\epsilon)G^a(\epsilon) .
$$

(2.61)

where $\Sigma^\approx_{\text{tot}}(\epsilon) = \Sigma^\approx_L(\epsilon) + \Sigma^\approx_R(\epsilon)$. The $\Sigma$ represents the tunneling self-energy introduced in Eq. 2.55 and 2.56. Substituting the above two equations in the expression for the current between the leads given in Eq. 2.57 can be written as

$$
I_\alpha = \frac{e}{h} \int \frac{d\epsilon}{2\pi} T(\epsilon)[f_L(\epsilon) - f_R(\epsilon)] ,
$$

(2.62)

with $T(\epsilon)$ denoting the transmission probability

$$
T(\epsilon) = \text{Tr}\{\Gamma_L^L(\epsilon)G^r(\epsilon)\Gamma_R^R(\epsilon)G^a(\epsilon)\} .
$$

(2.63)
2.7 Summary

In summary, we have discussed two different types of dynamics occurring in Quantum scale systems, namely charge transport in fermionic systems and energy transfer in bosonic systems. For the former we use in this work the NEGF formalism introduced briefly in the current chapter in Section 2.6 and will be discussed in detail in Chapter 3. For the latter we utilize the hierarchical equations of motion approach and the QME formalism that is presented in Chapter 4. The common mark of these approaches is that they all may be formulated by utilizing the exponential decomposition scheme as well as the Chebyshev decomposition scheme, discussed in Section 2.5.2. The Chebyshev decomposition in particular allows for truly arbitrary forms of couplings between device and leads and all temperatures.

![Diagram](image)

Figure 2.7: Sketch showing the decomposition of the correlation functions using different schemes as common element of the theories discussed in this thesis.

In the above, the exponential decomposition (ED) decomposes the self-energy or the correlation function into sums of weighted exponentials. The weights $\alpha$ and factors $\gamma$ are complex numbers resulting from the exponential expansion scheme. While in the Chebyshev decomposition (CD) scheme one obtains a sum of products of two terms, out of which the $I_n$’s are the time independent quantities and are in essence just complex numbers, while the operators $C_n$ retain the time-dependence.
Chapter 3

Chebyshev expansion applied to charge transport using NEGF

This chapter deals with the non-equilibrium Green’s function (NEGF) formalism which is extensively utilized to calculate charge transport through nano-scale junctions. The Green’s function approach to study nanosystems was developed by Keldysh, Kadanoff and Baym and is adopted for the study of realistic systems as well as used in conjunction with density functional theory to study time-dependent transport. Here we use the time-dependent TD-NEGF formalism developed by Croy and Saalmann [82]. Since the NEGF formalism can deal with any magnitude of the device-reservoir coupling, unlike QMEs which are confined to lower coupling strengths, it can be used to study quantum phenomena that occur in the strong coupling regime like the Coulomb blockade, negative differential resistance, current hysteresis, and chemical reactions [88]. Moreover, we utilize the single-particle NEGF scheme, which implies that the basis is composed of a direct product of single-particle functions, leading to the involved matrices having dimension $N\times N$ where $N$ denotes the number of sites in the system whereas the multi-particle basis requires matrices that scale as $N^2$. To further enhance the speed and efficiency of the NEGF scheme and to study larger systems we adopt a mathematical trick from Ref. 129 and replace all auxiliary matrices by $N$-dimensional vectors and scalars.

The main idea of this work is the utilization of the Chebyshev decomposition scheme to develop NEGF-based EOMs for the propagation of the single particle reduced density matrix (RDM). To this end, the Jacobi-Anger identity is utilized, which is composed of sums of products of Chebyhev polynomials of the first kind and the Bessel functions of the first kind, to decompose the self-energies of the reservoirs. Specifically the self-energies of the reservoirs are dissociated into a time independent and time-dependent parts. The time independent part, which carries all the information regarding the reservoir degree of freedom, can be computed separately from the equations of motion and allows the incorporation of any kind of spectral densities of the reservoirs. This idea presents an alternative scheme to decomposing the self-energies of the reservoirs in terms of weighted exponential functions, developed in earlier works [90, 131] and used to study, e.g., the effect of laser pulses on molecular junctions [62, 75, 138]. The idea of the Chebyshev decomposition adopted here is similar to works of Tian and Chen [112, 136], but the equations of motion developed here are completely different, in essence as
we used derivatives of Bessel functions, which can incidentally be written in terms of Bessel functions of different orders, to derive a set of coupled differential equations for the RDM and the corresponding auxiliaries as well current expression. The main advantage of using the Chebyshev decomposition is that systems at arbitrarily low temperatures can be simulated at no additional numerical cost as compared to systems at high temperatures. More importantly, the spectral densities no longer have to be in the form of sums of Lorentzian functions and can assume any analytic or numerical form, which allows the Chebyshev based NEGF scheme to study realistic systems. The main drawback of the Chebyshev based approach is that the computational effort scales linearly with the time to be simulated, thus the scheme may be limited to time-scales of the order of 1ps, unless the scheme is implemented on parallel computers. Specifically, the decomposition of the self-energy functionals is composed of a sum that need to be truncated at a certain number $N_{\text{cheb}}$ of Chebyshev polynomials which in terms the $N_{\text{cheb}}$ dependent simulation time.

To test the newly developed set of equations we utilize the typical setup of a molecular junction sandwiched between two conducting electrodes. The molecular junction is modelled as chain of $N$ sites representing a single molecule or a chain or atoms of molecules, which is attached to fermionic reservoirs within a tightbinding description. The hamiltonian of the complete system is composed of the relevant system part, the electron reservoirs, and the system-reservoir coupling parts. The Chebyshev expanded self-energies of the reservoirs are used to derive a complete set of equations of motion within the NEGF formalism. These equations are tested against the NEGF scheme based on the exponential decomposition of the self energies [82]. To this end we utilize a single-resonant level system as well as a two-site setup to compare the two schemes. The sites are coupled to fermionic reservoirs via self-energy functionals composed of spectral densities constructed out of a single Lorentzian function. This allows us to perform a fair comparison between the exponential and the Chebyshev versions of the NEGF EOMs. We show comparisons of current dynamics calculated using both of the above schemes, which show excellent agreement. We show results for room temperature as well as for the zero temperature case, for the which the Chebyshev NEGF scheme presents a considerable advantage. We also use the Chebyshev based scheme to study time-dependent scenarios, specifically the phenomenon of coherent destruction of tunneling (CDT) [62, 75, 139–141], where a gaussian laser pulse is used to quench the current passing through a single-site wire. The test of calculation of current dynamics across a two-site system with oscillating site energies further validates the Chebyshev scheme when it’s results match perfectly with the exponential NEGF scheme.

Next we apply the Chebyshev based scheme to a scenario which cannot be handled with the exponential scheme. We calculate and show current dynamics for a single site system, as well as a five-site non-trivial system akin to having site energies obtained by combining molecular dynamics (MD) and quantum chemistry calculations for, e.g., a DNA system in water. We use a super gaussian profile of a high order to obtain a flat energy profile with sharp edges, creating an energy profile with a steep gap in it, mimicking the energy band structure of Gold. This super gaussian spectral density, which may only be constructed out of several hundred Lorentzian functions, can be incorporated directly within the Chebyshev based NEGF scheme. We show current dynamics for this five-site system with time-dependent Gaussian distributed, exponentially correlated in time trajectories for site energies. Using this example
we show that highly complex and/or realistic band structures can be simulated at the computational cost of trivial band structures using the Chebyshev approach. The excellent agreement between the Chebyshev NEGF and the exponential NEGF schemes for all scenarios, as well as the applicability of the Chebyshev NEGF scheme to a wider range of system parameters at little to no extra numerical penalty makes it a promising approach.

Throughout the study, no assumptions were made concerning the time dependence of the system Hamiltonian and time dependencies in the leads can also be dealt with the scheme effectively. As it can handle time-dependent site and Fermi energies, the approach is also applicable to the strong external field limit. Moreover, since the Fermi function is not expanded using, e.g., the Matsubara, Ozaki or Padé schemes, the numerical performance of the approach remains independent of the temperature of the system. Finally, although the present scheme is restricted to non-interacting fermionic systems, an extension of the Chebyshev approach to the HEOM scheme for fermionic systems would enable the treatment of electron-electron interaction [142–144].

Chapter 3. Chebyshev expansion applied to charge transport using NEGF

3.1 NEGF technique for quantum transport

While QMEs derived in perturbation theory are limited to weak coupling regimes, in the NEGF formalism no restrictions on the magnitude of the device-reservoir coupling apply. Interesting quantum phenomena that occur in the strong coupling regime include Coulomb blockade, negative differential resistance, dynamical switching and switching noise, current hysteresis, heating, and chemical reactions [88]. Moreover, as a result of using the Chebyshev decomposition, there is no numerical penalty for simulating systems at arbitrarily low temperatures. In addition the spectral densities no longer have to be in the form of sums of Lorentzian functions. The main drawback of the Chebyshev approaches is that the computational effort scales linearly with the time to be simulated. Due to the usage of a single-particle basis for the NEGF scheme, one has to deal with matrices of the dimension $N \times N$ where $N$ denotes the number of sites in the system. A trick developed earlier [129] enables the replacement of all auxiliary matrices by $N$-dimensional vectors or even scalars. As a consequence, the computational effort is significantly reduced and studying larger systems using this approach becomes feasible.

Starting from the application of the Keldysh formalism to the non-equilibrium Green’s functions, differential equations can be derived for the density operator $\rho(t)$ as well as a general formula for the time-dependent current through a molecular junction. In the present context, the Green’s functions are defined in terms of the system creation and annihilation operators as

$$G_{ij}^{<}(t,\tau) = \frac{i}{\hbar}\langle c_j^\dagger(\tau) c_i(t) \rangle,$$

$$G_{ij}^{>}(t,\tau) = -\frac{i}{\hbar}\langle c_i(t), c_j^\dagger(\tau) \rangle. \quad (3.1)$$

In terms of these functions and the reservoir self-energies, $\Sigma$, the time-dependent current flowing between lead $\alpha$ and the wire is given by [72, 81, 145]

$$I_\alpha(t) = \frac{2e}{\hbar} \text{Re} \text{Tr} \left\{ \int_{-\infty}^{\infty} dt \left[ G^{<}(t, t_1) \Sigma^a(t_1, t) + G^{>}(t, t_1) \Sigma^{<}(t_1, t) \right] \right\}. \quad (3.3)$$

The superscripts < and > refer to lesser and greater as well as $r$ and $a$ to the retarded and advanced versions of the Green’s function or the self-energy, respectively. In the present study, the time-dependent TD-NEGF formalism developed by Croy and Saalmann [82] has been adopted. The lesser and greater self-energies in terms of the spectral density and the Fermi functions of the leads are given by

$$\Sigma_{ij}^{<}(t, \tau) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\epsilon f_\alpha(\epsilon - \mu_\alpha) e^{-i(\epsilon - \mu_\alpha)(t-\tau)/\hbar} J_\alpha(\epsilon),$$

$$\Sigma_{ij}^{>}(t, \tau) = -\frac{i}{2\pi} \int_{-\infty}^{\infty} d\epsilon f_\alpha(-\epsilon - \mu_\alpha) e^{-i(\epsilon + \mu_\alpha)(t-\tau)/\hbar} J_\alpha(\epsilon). \quad (3.4)$$

In this expression, the temperature-dependent Fermi distribution $f_\alpha$ characterizes the equilibrium state of reservoir $\alpha$ with chemical potential $\mu_\alpha$. To this end, the above expressions may be solved using the theorem of residues in conjunction with Jordan’s lemma as in the exponential decomposition scheme [82] or by using the Chebyshev decomposition.
As mentioned previously, the TD-NEGF formalism is derived with the assumption of non-interacting particles and consequently a direct product of single-particle functions can be employed as basis. This single-particle basis leads to much smaller matrices than a multi-particle basis. The use of the single-particle functions is possible since the equations do not explicitly include creation and annihilation operators on the wire which otherwise would have to be constructed in a multi-particle basis.

By employing a relation between two-time functions, a lesser (greater) Green’s function or self-energy may be found from a retarded (advanced) one or vice versa

\[ X^{r,a}(t, \tau) = \pm \Theta(\pm t \mp \tau)[X^>(t, \tau) - X^<(t, \tau)] \]  

with \( X = G \) or \( X = \Sigma \). Moreover, the expression for the current

\[ I_\alpha(t) = \frac{2e}{\hbar} \text{Re} \text{Tr} \{ \Pi_\alpha(t) \} \]  

is given in terms of the auxiliary quantities \( \Pi_\alpha(t) \)

\[ \Pi_\alpha(t) = \int_{t_0}^{t} dt_2 \left( G^>(t, t_2) \Sigma^<_\alpha(t_2, t) - G^<(t, t_2) \Sigma^>_\alpha(t_2, t) \right) . \]  

In the latter expression, the first and the second term on the right hand side describe electron tunneling into and out of the device, respectively. The derivation of the above expression starting from Eq. 3.3 is given in Appendix A1. It is important to note that the auxiliary matrices \( \Pi_\alpha(t) \) can be considered as an independent entities with a separate EOMs [82]. For utilizing the Chebyshev expansion, however, we need to split the \( \Pi_\alpha(t) \) and consider the tunnel in and out terms as independent quantities and develop their respective EOMs.

In order to calculate the expectation value of a system observable \( A_S \) it is convenient to use the reduced single-particle density matrix RSDM, \( \rho^{S,P.}(t) = \text{Im}G^<(t, t) = \text{Im}G^>(t, t) + 1 \). The expectation value of \( A_S \) is then given by

\[ \langle A_S(t) \rangle = \text{Tr}_S \{ A_S \rho_S \} . \]  

The time-evolution of the RSDM describing the dynamics of the molecule coupled to the electron reservoirs is found using \( G^<(\tau, t) = -[G^<(t, \tau)]^\dagger \) and the EOM for the lesser and greater Green’s functions

\[ \frac{\partial}{\partial t} G^\pm(t, \tau) = -i H_S(t) G^\pm(t, \tau) \]
\[ -i \int dt_2 \Sigma^\pm_{tot}(t, t_2) G^\pm(t_2, \tau) \]
\[ -i \int dt_2 \Sigma^\pm_{tot}(t, t_2) G^a(t_2, \tau) . \]  

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Putting these equations together, one obtains (details in Appendix A.)

\[
\frac{\partial}{\partial t} \rho_{s.p.}^S(t) = -\frac{i}{\hbar} [H_S(t), \rho_{s.p.}^S(t)] + \frac{i}{\hbar} \sum_\alpha \left( \Pi_\alpha(t) + \Pi_\alpha^\dagger(t) \right) .
\]  

(3.11)

The total self-energies are sums of the tunneling self-energies for each reservoir \( \alpha \). For future use within this study, the above equation is recast into the following form

\[
\frac{\partial}{\partial t} \rho_{s.p.}^S(t) = -\frac{i}{\hbar} [H_S(t), \rho_{s.p.}^S(t)] + \frac{i}{\hbar} \sum_\alpha \left( \Pi_\alpha(t) - \Pi_\alpha^>(t) + \Pi_\alpha^<\dagger(t) - \Pi_\alpha^>\dagger(t) \right)
\]  

(3.12)

where

\[
\Pi_\alpha^<(t) = \int_{t_0}^t dt_2 \left( G_\alpha^>(t,t_2) \Sigma_\alpha^<(t_2) \right) ,
\]

(3.13)

\[
\Pi_\alpha^>(t) = \int_{t_0}^t dt_2 \left( G_\alpha^<(t,t_2) \Sigma_\alpha^>(t_2) \right) .
\]

(3.14)

In the above relations, the \( \Sigma_\alpha^< \) denote the self-energies defined in Eqs. 3.4 and 3.5.

## 3.2 Vector-based method

The spectral density which is sometimes also called level-width function describes the coupling between the molecule and the reservoirs. In principle, non-vanishing coupling amplitudes \( T_{k,i}^\alpha \) can exist between any site \( i \) of the molecule with any state \( k \) of any reservoir \( \alpha \). Thus, the spectral density can be written as

\[
J_{\alpha,ij}(\epsilon) = 2\pi \sum_k T_{k,i}^\alpha(\epsilon) T_{k,j}^{\alpha*}(\epsilon) \delta(\epsilon - \epsilon_{ak}) .
\]

(3.15)

This function has a close relation to the single-particle density of states of the respective reservoir \( \alpha \), \( D_\alpha(\epsilon) = \sum_k \delta(\epsilon - \epsilon_{ak}) \) since gaps in the density of states of the reservoirs lead to gaps in the spectral density as well. The spectral densities have subscripts describing the sites to which they belong. Alternatively, one can write the spectral densities in a matrix form with respect to the site indices, i.e., \( J_\alpha(\epsilon) \). It is interesting to note, that the spectral density \( J_\alpha(\epsilon) \), can be expressed in terms of the imaginary part of the retarded self-energy \([72]\), while the real part of the retarded self-energy is related to \( J_\alpha(\epsilon) \) by the Kramers-Kronig relation

\[
J_\alpha(\epsilon) = -2\text{Im} \Sigma_\alpha^R(\epsilon), \quad \text{Re} \Sigma_\alpha^R(\epsilon) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} d\epsilon' \frac{J_\alpha(\epsilon')}{\epsilon' - \epsilon} .
\]

(3.16)

In this expression \( \mathcal{P} \) denotes the Cauchy principle value of the respective integral.

Following a recent work \([129]\), the symmetric matrix of level-width functions may be diagonalized.
In the above equation, \( \mathbf{v}_{\alpha c}(\epsilon) \) are energy-dependent vectors of dimension \( N \). The parameter \( N_{c,\alpha} \) denotes the number of open channels between the molecule and reservoir \( \alpha \). In the simple model considered in this paper, only the nearest site is connected to the respective reservoir \( \alpha \) and then \( N_{c,\alpha} \) is equal to one. In this case, the spectral density has only one non-zero element, given by \( j_{\alpha}(\epsilon) \). Furthermore, here we are dealing with energy-independent vectors and Eq. 3.17 becomes

\[
\mathcal{J}_{\alpha}(\epsilon) = \mathbf{v}_{\alpha} j_{\alpha}(\epsilon) \mathbf{v}_{\alpha}^\dagger.
\]  

(3.18)

In general, however, the number of open channels depends on the specific setup. As was detailed in Ref. [129], this diagonalization of the spectral density matrix leads to a large numerical advantage. One can replace all auxiliary matrices by vectors or even scalars. Depending on the size of the system, the computational effort and memory requirements of the method are thus significantly reduced [129].

Inserting the diagonalized spectral density in Eq. 3.18 into the original definitions of the self-energies, Eqs. 3.4 and 3.5, one gets,

\[
\Sigma^{<}_{\alpha}(t, \tau) = + \frac{i}{2\pi} \int_{-\infty}^{\infty} d\epsilon \ f_{\alpha}(\epsilon - \mu_{\alpha}) e^{-i(t-\tau)/\hbar} \mathbf{v}_{\alpha} j_{\alpha}(\epsilon) \mathbf{v}_{\alpha}^\dagger, \tag{3.19}
\]

\[
\Sigma^{>}_{\alpha}(t, \tau) = - \frac{i}{2\pi} \int_{-\infty}^{\infty} d\epsilon \ f_{\alpha}(\epsilon - \mu_{\alpha}) e^{-i(t-\tau)/\hbar} \mathbf{v}_{\alpha} j_{\alpha}(\epsilon) \mathbf{v}_{\alpha}^\dagger. \tag{3.20}
\]

As mentioned above, although the system example employed in this work implies that the spectral density is a diagonal matrix, the procedure in this section helps to write the self-energies as given in Eqs. 3.19 and 3.20, i.e., with vectors placed alongside the spectral density. This form enables the construction of the set of EOMs in the following section with vector and scalar quantities rather than matrices. Before this step, however, we continue in the next section with the Chebyshev expansion of the exponential terms found inside the above equations.

### 3.3 Chebyshev decomposition of self-energies

Tian and Chen [112, 136] utilized the Chebyshev spectral method [148] and employed it to construct a single-particle fermionic hierarchical EOM for molecular junctions. Moreover, these authors showed that this RSDM-HEOM for non-interacting systems has a direct correspondence to the single-particle NEGF formalism for quantum transport. This mapping is true for all RSDMs in which the total system exists in an equilibrium state at \( t = t_0 \) [149]. In a previous study [113] we detailed the use of a Chebyshev polynomial- and Bessel function-based decomposition to develop a different kind of differential equations based on the properties of the derivatives of the Bessel functions of the first kind.

On the level of a perturbative treatment, we have already employed the Chebyshev decomposition
for correlation functions \([95, 113]\). Here it will be applied to self energies. The spectral range of the Hamiltonian first needs to be mapped to the definition range of the Chebyshev polynomials, i.e., to the interval \([-1, 1]\). To be able to perform such a mapping, one has to define a lower and an upper bound of the energy integration \([\epsilon_{\text{min}}, \epsilon_{\text{max}}] = [h\omega_{\text{min}}, h\omega_{\text{max}}]\) in the expressions for the self energies, Eqs. 3.19 and 3.20. The width of this interval, i.e., the spectral range, is system specific and depending on the molecule-lead coupling strength the interval needs to be large enough in order to converge all quantities with respect to these limits. For the sake of simplicity and without loss of generality we assume \(\tau = 0\). Moreover, we perform a variable substitution of the form \(\omega = \Omega x + \bar{\omega}\), i.e., the interval \([\omega_{\text{min}}, \omega_{\text{max}}]\) is mapped onto \([-1, 1]\) via
\[
\bar{\omega} = \frac{\omega_{\text{max}} + \omega_{\text{min}}}{2}, \quad \Omega = \frac{\omega_{\text{max}} - \omega_{\text{min}}}{2}.
\]
These transformations then lead to
\[
\Sigma^\leq_\alpha(t) = \pm \frac{i\hbar \Omega}{2\pi} \int_{-1}^{1} dx \, f_\alpha(h\Omega x + h\bar{\omega} - \mu_\alpha) e^{-i\Omega x t} e^{-i\bar{\omega} t} v_\alpha j_\alpha(h\Omega x + h\bar{\omega}) v_\alpha^\dagger, \quad (3.21)
\]
\[
\Sigma^\geq_\alpha(t) = \mp \frac{i\hbar \Omega}{2\pi} \int_{-1}^{1} dx \, f_\alpha(-h\Omega x + h\bar{\omega} - \mu_\alpha) e^{-i\Omega x t} e^{-i\bar{\omega} t} v_\alpha j_\alpha(h\Omega x + h\bar{\omega}) v_\alpha^\dagger. \quad (3.22)
\]
In a next step, we employ the Jacobi-Anger identity which is given by \([150]\)
\[
e^{-i\Omega x t} = J_0(\Omega t) + \sum_{n=1}^{\infty} 2(-i)^n J_n(\Omega t) T_n(x), \quad \forall t \in \mathbb{R}, \forall x \in [-1, 1] \quad (3.23)
\]
where \(J_n\) denotes the Bessel function of the first kind and \(T_n\) the Chebyshev polynomial of the first kind. The infinite sum in Eq. 3.23 will later on be approximated by a finite one with cutoff parameter \(N_{\text{cheb}}\) denoting the number of polynomials used in the decomposition. Employing the Jacobi-Anger identity, the time-dependent part in the expressions for the self-energies can be separated from the time-independent integral yielding
\[
\Sigma^\leq_\alpha(t) = \frac{J_0(\Omega t)}{\Sigma_0^\leq(t)} \frac{i\hbar \Omega}{2\pi} \int_{-1}^{1} dx \, f_\alpha(h\Omega x + h\bar{\omega} - \mu_\alpha) j_\alpha(h\Omega x + h\bar{\omega}) v_\alpha^\dagger, \quad (3.24)
\]
\[
\quad + \sum_{n=1}^{\infty} \frac{J_n(\Omega t)}{\Sigma_0^\leq(t)} \frac{i\hbar \Omega}{2\pi} \int_{-1}^{1} dx \, 2(-i)^n T_n(x) f_\alpha(h\Omega x + h\bar{\omega} - \mu_\alpha) j_\alpha(h\Omega x + h\bar{\omega}) v_\alpha^\dagger, \quad (3.25)
\]
\[ \Sigma_\alpha^\leq(t) = \frac{J_0(\Omega t)e^{-i\varphi t}}{\Sigma_\alpha^0(t)} v_\alpha \left( -i \frac{\hbar \Omega}{2\pi} \int_{-1}^{1} dx \, f_\alpha \left( -(\hbar \Omega x + \hbar \bar{\omega} - \mu_\alpha) \right) j_\alpha(\hbar \Omega x + \hbar \bar{\omega}) \, v_\alpha^\dagger \right) \]
\[ + \sum_{n=1}^{\infty} \frac{J_n(\Omega t)e^{-i\varphi t}}{\Sigma_\alpha^0(t)} v_\alpha \left( -i \frac{\hbar \Omega}{2\pi} \int_{-1}^{1} dx \, 2(-i)^n T_n(x) f_\alpha \left( -(\hbar \Omega x + \hbar \bar{\omega} - \mu_\alpha) \right) j_\alpha(\hbar \Omega x + \hbar \bar{\omega}) \, v_\alpha^\dagger . \right) \]

In the above equations we identify the time-dependent quantities \( \Sigma_\alpha^\leq(t) \) and the time-independent integrals \( I_{\alpha,n}^\leq \). Thus, the self-energies can be written in a compact form as

\[ \Sigma_\alpha^\leq(t) = \sum_{n=0}^{\infty} v_\alpha I_{\alpha,n}^\leq \Sigma_n^\leq(t) v_\alpha^\dagger \]
\[ \Sigma_\alpha^\geq(t) = \sum_{n=0}^{\infty} v_\alpha I_{\alpha,n}^\geq \Sigma_n^\geq(t) v_\alpha^\dagger . \]

The time-independent integrals \( I_{\alpha,n}^\leq \) need to be calculated only once during a simulation and do not form an explicit part of the equations that are propagated. As the integrand is quite complex, it is usually solved numerically. The Chebyshev polynomials \( T_n(x) \) cause the integrands to strongly oscillate, especially for larger \( n \). Moreover, these oscillations are not periodic, so one needs to perform the variable substitution \( x = \cos(\Theta) \) and to utilize the relation \( T_n(\cos(\Theta)) = \cos(n \Theta) \) to obtain integrands within the \( I_{\alpha,n}^\leq \) of the form \( f(x) \cdot \cos(\omega x) \). Integrals with this kind of integrand can efficiently be computed using the appropriate subroutines for highly oscillating integrands, e.g., from the QUADPACK library [151].

The representation of the self-energies as a weighted sum over exponential functions, as in the exponential decomposition of correlation functions or self-energies, results in the fact that time derivatives of partial self-energies can be expressed in terms of themselves [75,82]. This property is then employed to derive coupled differential equations. Similarly, the derivatives of Bessel functions of the first kind are simply Bessel functions of the same kind [150], leading to a similar set of coupled differential equations

\[ \frac{d}{dt} J_n(\Omega t) = \frac{\Omega}{2} \left( J_{n-1}(\Omega t) + J_{n+1}(\Omega t) \right) . \]

With the help of the above relation, the time derivatives of \( \Sigma_n^\leq(t) \) can be cast in terms of themselves and their neighboring terms

\[ \frac{d}{dt} \Sigma_n^\leq(t) = -i \bar{\omega} \Sigma_n^\leq(t) + \frac{\Omega}{2} \Sigma_{n-1}^\leq(t) - \frac{\Omega}{2} \Sigma_{n+1}^\leq(t) = \frac{d}{dt} \Sigma_n^\geq(t) . \]

Next we insert the definition of the auxiliary operators in Eqs. 3.26 and 3.27 into Eqs. 3.13 and 3.14 and define the auxiliary vectors \( \pi_{\alpha,n} \) leading to

\[ \Pi_n^\leq(t) = \frac{1}{\hbar} \sum_n \int_{t_0}^{t} dt_2 G_n^\geq(t, t_2) v_\alpha \Sigma_n^\leq(t) v_\alpha^\dagger , \quad \Pi_n^\geq(t) = \frac{1}{\hbar} \sum_n \int_{t_0}^{t} dt_2 G_n^\leq(t, t_2) v_\alpha \Sigma_n^\geq(t) v_\alpha^\dagger \]
where the vectors $\pi_{a,n}(t)$ with dimension $N$ are given by

$$
\pi_{a,n}^{<}(t) = \int_{t_0}^{t} dt_2 G^{>}(t, t_2) \, v_{a} \Sigma_{n}^{<}, \quad \pi_{a,n}^{>}(t) = \int_{t_0}^{t} dt_2 G^{<}(t, t_2) \, v_{a} \Sigma_{n}^{>}. \tag{3.32}
$$

The equations of motion of these vectors is found using Eqs. 3.10 and 3.29. The resulting differential equations for the general case and for the limiting cases, $n = 0$ and $n = N$, are given below

$$
\frac{\partial}{\partial t} \pi_{a,0}^{<}(t) = i(\rho^{<p}(t)v_{a'}) - 1 - i\omega \pi_{a,0}^{<}(t) - \Omega \pi_{a,1}^{<}(t) - \frac{i}{\hbar} H_{S}(t) \pi_{a,0}^{<}(t) - \frac{i}{\hbar}(\chi_{a,0}^{<}(t) - \gamma_{a,0}^{<}(t)) v_{a'}, \tag{3.33}
$$

$$
\frac{\partial}{\partial t} \pi_{a,N}^{<}(t) = -i\omega \pi_{a,N}^{<}(t) + \frac{\Omega}{2} \pi_{a,N-1}^{<}(t) - \frac{i}{\hbar} H_{S}(t) \pi_{a,N}^{<}(t) - \frac{i}{\hbar}(\chi_{a,0}^{<}(t) - \gamma_{a,0}^{<}(t)) v_{a'}, \tag{3.34}
$$

$$
\frac{\partial}{\partial t} \pi_{a,n}^{<}(t) = -i\omega \pi_{a,n}^{<}(t) + \frac{\Omega}{2} \pi_{a,n-1}^{<}(t) - \frac{\Omega}{2} \pi_{a,n+1}^{<}(t) - \frac{i}{\hbar} H_{S}(t) \pi_{a,n}^{<}(t) - \frac{i}{\hbar}(\chi_{a,0}^{<}(t) - \gamma_{a,0}^{<}(t)) v_{a'}, \tag{3.35}
$$

$$
\frac{\partial}{\partial t} \pi_{a,n}^{>}(t) = -i\omega \pi_{a,n}^{>}(t) + \frac{\Omega}{2} \pi_{a,n-1}^{>}(t) - \frac{\Omega}{2} \pi_{a,n+1}^{>}(t) - \frac{i}{\hbar} H_{S}(t) \pi_{a,n}^{>}(t) - \frac{i}{\hbar}(\chi_{a,0}^{>}(t) - \gamma_{a,0}^{>}(t)) v_{a'}. \tag{3.36}
$$

In the above equations, $\chi_{a,0}^{<}(t) = \sum_{n'=0}^{N} t_{a,n'}^{<} \chi_{a,n'a'}^{<}$ and $\gamma_{a,0}^{<}(t) = \sum_{n'=0}^{N} t_{a,n'}^{<} \gamma_{a,n'a'}^{<}$ are terms resulting from the derivatives of the Green’s functions which contain double integrals. These equations form the second-tier of the NEGF equations. A derivation is given in appendix A. The EOMs of the quantities $X_{an,a'n'}^{<}, Y_{an,a'n'}^{<}$ for the general case, $[n, n'] = [1, 2, ..., N - 1; 1, 2, ..., N - 1]$, are as follows

$$
\frac{\partial}{\partial t} X_{an,a'n'}^{<} = \frac{\Omega}{2} X_{an,a'n'-1}^{<} - \frac{\Omega}{2} X_{an-1,a'n'}^{<} - \frac{\Omega}{2} X_{an,a'n'+1}^{<} - \frac{\Omega}{2} X_{an+1,a'n'}^{<}, \tag{3.37}
$$

$$
\frac{\partial}{\partial t} Y_{an,a'n'}^{<} = \frac{\Omega}{2} Y_{an,a'n'-1}^{<} - \frac{\Omega}{2} Y_{an-1,a'n'}^{<} - \frac{\Omega}{2} Y_{an,a'n'+1}^{<} - \frac{\Omega}{2} Y_{an+1,a'n'}^{<}. \tag{3.38}
$$

The two indices $n$ and $n'$ are running from 0 to $N$. Thus, there are combinations of these indices which form the boundaries enabling the construction of a closed set of EOMs. The equations for the boundary cases are given in appendix B.
Furthermore, the quantities $\varphi_\alpha(t)$ and $\varphi_{\alpha,\alpha'}(t)$ involved in the HEOM approach [77] are related to the NEGF entities developed in this article as follows

$$\varphi_\alpha(t) = -i(\Pi^\leq_\alpha(t) - \Pi^\geq_\alpha(t)),$$

(3.39)

$$\varphi_{\alpha,\alpha'}(t) = -i(X^\leq_{\alpha,\alpha'}(t) - Y^\leq_{\alpha,\alpha'}(t) - X^\geq_{\alpha,\alpha'}(t) + Y^\geq_{\alpha,\alpha'}(t))$$

(3.40)

The above relations are in agreement with the one-to-one correspondence shown previously between the HEOM theory and the single-particle NEGF theory [82].

From the construction of the above equations for the second-tier quantities $X^\leq_{\alpha,n,\alpha'}_{n'}$ and $Y^\leq_{\alpha,n,\alpha'}_{n'}$ it is easy to see that they are, for a 1d molecular junction, scalars rather than matrices. This renders the method efficient in terms of computational time and memory consumption. The scaling with the number of sites should be very similar to that of the vector version of the exponential decomposition [129]. Thus, for systems of less than 100 sites the computation time scales approximately linearly with the size of the system. In the limit of extremely large systems [129], however, the method would eventually scale as $O(N^3)$. If more than next-neighbor interactions are taken into account, also the computation of the commutator of the RSDM with the Hamiltonian matrix, Eq. 3.12, can become numerically expensive as it involves matrix-matrix multiplications.

Equation 3.11, together with Eqs. 3.33 to 3.36 and Eq.3.37-3.38 along with their boundary cases in appendix B constitute a closed system of ODEs solvable by standard methods such as the Runge-Kutta scheme to obtain the non-equilibrium dynamics of the system density matrix. The time-dependent current through the molecular junction can subsequently be computed using Eq. 3.3. For calculations of 1d molecular junctions and using the Chebyshev-NEGF scheme developed here, $N\cdot(4N_{cheb})$ auxiliary vectors of length $N$ and $16N_{cheb}$ scalars need to be propagated. As mentioned already above, $N_{cheb}$ denotes the number of Chebyshev polynomials used to reconstruct the self-energies. Without the vector decomposition of the spectral density as introduced in Ref. [129], the number of first tier auxiliary matrices of dimension $(N\times N)$ would be $N^2\cdot(4N_{cheb})$ while there would be $N^2\cdot(16N_{cheb})$ second-tier matrices $(N\times N)$. The substitution of many matrix-matrix multiplications by matrix-vector operations results in the above described speed-up and reduced memory requirement.

As for the case of the second-order perturbation theory [113], a clear advantage of the present Chebyshev decomposition over the exponential decomposition scheme [82] is the fact that the time-independent integrals $I^\leq_{\alpha,n}$ need only be integrated once and can be done numerically. Thus, no restrictions to the form of the spectral density apply and the Fermi function does not need to be expanded. Therefore, the scheme can be applied to any form of spectral density and to arbitrarily low temperatures. These advantages do not come for free and as discussed earlier [112, 113], truncating at a certain number $N_{cheb}$ of Chebyshev terms limits this approach to a certain simulation time that depends on $N_{cheb}$. This truncation is necessary due to the nature of the sum in Eq. 3.22 and has no adverse effects on the results as long as one stays within the convergence regime of the expansion. The number of terms needed to obtain converged results is given by [113, 152, 153]

$$N_{cheb} = \Omega T_{sim} + 10 \ln(\Omega T_{sim}).$$

(3.41)
In other words, the number of terms needed to approximate the sum in Eq. 3.22 depends on the maximum simulation time $T_{\text{sim}}$ as well as on the spectral range of the Hamiltonian, i.e., the integration limits $\epsilon_{\text{min}}$ and $\epsilon_{\text{max}}$. As long as the relation in Eq. 3.41 is fulfilled, the Chebyshev based scheme converges exponentially and yields very accurate results [109,112].

### 3.4 Chebyshev-decomposed NEGF method: Results

In order to validate the new NEGF scheme developed using the Chebyshev decomposition we compare the results to the ones obtained using the NEGF scheme based on the exponential decomposition of the self energies [82]. Below, we abbreviate the NEGF approach based on the exponential decomposition as E-NEGF and the Chebyshev-based NEGF approach as C-NEGF. In order to compare the two schemes, we use a single-resonant level system as well as a two-site setup with equal couplings to both leads in each of the systems. The site energies are located in the middle of the conduction window with a voltage drop of 2 V across the leads (unless otherwise stated). The coupling to the leads is described by spectral densities of the leads introduced in section IV, in particular the non-zero element $j_{\alpha}(\epsilon)$. If one is working within the Chebyshev decomposed NEGF framework, this non-zero element may be incorporated into the integrands (Eq. 3.25, 3.26) in any analytical or numerical form.

Since we are benchmarking against the exponential decomposition based NEGF scheme, $j_{\alpha}(\epsilon)$ is expanded using Lorentzian functions

$$j_{\alpha}(\epsilon) = \sum_{l=1}^{N_l} \frac{A_{\alpha l} W_{\alpha l}^2}{(\epsilon - \epsilon_{\alpha l})^2 + W_{\alpha l}^2}. \quad (3.42)$$

In this equation, $N_l$ denotes the number of Lorentzian functions used for fitting the respective density of states. Each Lorentzian function is characterized by three (scalar) parameters, namely the width $W_{\alpha l}$, the height (system-reservoir coupling strength) $A_{\alpha l}$, and the position of the center of the Lorentzian, $\epsilon_{\alpha l}$. A partitioned nonlinear regression [154] may be employed to calculate these parameters in general.

In the present case we only have to expand $j_{\alpha}(\epsilon)$ for one channel ($N_c = 1$), while in general, multiple Lorentzian functions may be used to approximate the spectral density for each channel $c$. While in general the non-zero elements may be obtained by fitting any spectral density by a sum of Lorentzian functions [75, 102], in the numerical examples below, we assume a single non-zero Lorentzian function, i.e., $N_l=1$, and thus

$$j_{\alpha}(\epsilon) = \frac{A_{\alpha} W_{\alpha}^2}{(\epsilon - \epsilon_{\alpha})^2 + W_{\alpha}^2}. \quad (3.43)$$

The diagonalization for a given geometry only needs to be done once for a given simulation setup. The spectral density matrix now reads

$$\mathcal{J}_{\alpha}(\epsilon) = \mathfrak{v}_{\alpha}(\epsilon) \frac{A_{\alpha} W_{\alpha}^2}{(\epsilon - \epsilon_{\alpha})^2 + W_{\alpha}^2} \mathfrak{v}_{\alpha}^\dagger(\epsilon). \quad (3.44)$$

In the following, we adopt a broad Lorentzian form with a width $W_{\alpha} = 10$ eV making the coupling approximately constant across the conduction window. Thus, this case is very close to the wide-band
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Figure 3.1: Comparison of simulated current dynamics using different numbers of Chebyshev polynomials showing accurate results of the scheme as long as Eq. 3.41 is fulfilled. The data are compared to the exponential decomposition E-NEGF theory (black curve) which is used as a benchmark. The inset shows results at 0 K temperature compared to those at 300 K.

The current dynamics for a single resonant level model with an initial site population of 0.5 is depicted in Fig. 3.1. The current shows a typical transient behavior occurring only for very short times due to the strength of the system-lead coupling followed by a steady state behavior. Moreover, the figure shows the time domain validity range of the C-NEGF scheme given by Eq. 3.41. At times larger than the time determined by the number of the Chebyshev polynomials utilized in the expansion of the self energies, the results of the C-NEGF very quickly diverge from the correct results. This behavior is as expected from the limited validity range given by Eq. 3.41. To this end, we see that it is a useful property of the present scheme that the necessary number of Chebyshev terms can be determined a priori. Furthermore, as predicted by Eq. 3.41, the validity range of the Chebyshev decomposition-based approach increases quasi-linearly with simulation time.

In addition, the inset of Fig. 3.1 shows results at a temperature of 0 K. For the E-NEGF scheme
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Figure 3.2: Coherent destruction of tunneling using a Gaussian laser pulse in a single site system. The top panel shows the laser field, the middle one the current through the wire, and the lowest panel the averaged current. The current has been determined by the E-NEGF and the C-NEGF approaches.

Next, we analyze the behavior of the Chebyshev scheme for time-dependent scenarios. In Fig. 3.2, the effect of a specific short laser pulse centered at $t = 400$ fs on the single resonant level is shown. This model mimics physical situations in which a pulsed laser field is focused on a molecular junction. The laser pulse used here has a Gaussian envelope and a rather fast oscillating driving field $E(t) = A \exp\left(-\frac{(t - T)^2}{2\sigma^2}\right) \sin(\omega t)$ with $\sigma = 80$ fs, $T = 400$ fs and a maximum amplitude $A = 2.405$ eV. For these parameters, the ratio of the maximum amplitude and driving frequency $\hbar \omega = 1$ eV fulfills the condition for a coherent destruction of tunneling (CDT) [62, 75, 139–141]. The determined current and the averaged current obtained using a running average together with the laser field are shown in Fig. 3.2. In this calculation, the coupling strength between system and leads is set to 1 meV. Moreover, the voltage drop across the molecular junction is set at 0.4 eV, i.e., $E_R - E_L = 0.4$ eV. As the total current across a driven molecular junction consists of several partial currents, additional channels might...
be opened by an external field. Therefore, a small bias voltage is needed to observe a complete CDT in a molecular junction [62]. Otherwise, only a partial CDT can be observed [62].

Figure 3.3: A two-site system with a site energy oscillation period of 40 fs. The occupation number of both sites as a function of time calculated using the C-NEGF scheme is shown in red and blue, compared to the E-NEGF scheme, shown in black and green. The inset shows the site energy of the first site as a function of time.

In a next step, we consider a two-site system. The parameters employed closely mimic the situation for a DNA system in a fluctuating environment [90]. The system-lead coupling strength is set to 1 meV while the intersite coupling is set to 0.01 eV. In the present simulation, the occupation probabilities of both sites are initially set to 0.5. The population dynamics is depicted in Fig. 3.3, where larger transient oscillations in the initial part can be observed to decay over time to steady state values. The site energies $E_1$ and $E_2$ oscillate sinusoidally with the same phase between the two values $E_{\text{min}}$ and $E_{\text{max}}$ due to the switching of the external field. Moreover, the frequency of the oscillation depends on that of the driving fields. This effect may be interpreted as charging or discharging of the molecular sites. The charging and discharging of the corresponding site gives rise to a current through the molecular junction.

No difference between the E-NEGF and the C-NEGF schemes is visible for any of the obtained results. As mentioned before, the exponential decomposition-based schemes, e.g., using perturbative [75] or E-NEGF [82] approaches have the limitation that the spectral density, i.e., the level-width function, needs to be decomposed into a sum of Lorentzian functions. This restriction, along with the need for a large number of Matsubara terms (or equivalent) at lower temperatures restricts the E-NEGF
scheme considerably for many applications. These two restrictions are not present in the case of the Chebyshev-decomposed versions of the above mentioned schemes.

Figure 3.4: Left: Schematic of the molecular junction with a sharply changing spectral density depicted as black lines. The site energy is initially located in the middle of the gap and oscillates in a sinusoidal manner. Upper right panel: Current dynamics for a site with a sinusoidally oscillating energy shown in blue and its running average in red. In black, the results for a constant site energy are depicted. Lower right panel: Coherent destruction of tunneling using a specific ratio of laser amplitude and frequency. The current through the wire is shown in black while its average is shown in red.

In the following we would like to apply the C-NEGF scheme to a scenario in which the E-NEGF approach cannot be used easily. In Fig. 3.4 we show the current dynamics for a single site system with spectral densities that may only be constructed out of several hundred Lorentzian functions, while the Chebyshev scheme is able to incorporate directly any form for the spectral density. In the present example, we used a super-Gaussian profile of high order to construct a flat profile with steep edges for creating an energy profile including a sharp gap. Such a gap in the band structure and thus in the molecule-lead coupling, i.e., the band structure weighted with the respective coupling parameters, can be used to mimic, for example, semiconductor or gold leads. The function that described the spectral density in this example is \( j_\alpha(\epsilon) = A_\alpha \exp((\epsilon - \epsilon_\alpha)/B)^n \), where \( W \) determines the width of the gap and is set to \( B=0.1 \text{ eV} \) and \( n \), set to \( n=50 \) here, determines the sharpness of the edges. When the site energy is placed such that it falls within that gap, no current through the junction can be observed. If the site energy is varied in a sinusoidal manner, i.e., \( \epsilon(t) = \epsilon_0 + A \sin(\omega t) \) with \( A=2.405 \text{ eV} \) and \( \hbar \omega = 0.1 \text{ eV} \), the site energy crosses past the gap in the molecule-lead coupling and a non-zero average current is found as shown in Fig. 3.4. It is interesting to see that by tuning the frequency such that the CDT conditions are fulfilled, i.e., \( \hbar \omega = 1 \text{ eV} \), the current can again be suppressed on average even in this non-trivial scenario (see Fig. 3.4).
Next we consider a multi-site system with time-dependent site energies and determine the current dynamics. The results for a five-site arrangement are shown in Fig. 3.5. This more complex situation is akin to the site energies obtained by combining molecular dynamics (MD) and quantum chemical simulations for, e.g., a DNA system in water [90]. Here we utilize model site energy trajectories that mimic, e.g., a chain of molecules surrounded by a solvent in contact with metallic leads [131]. To this end, we obtain Gaussian distributed trajectories with variance $\sigma^2 = 0.1 \text{ eV}^2$ around a mean value set to the center of the conduction window. These site energies are also exponentially correlated in time with a correlation time of $t_c = 100 \text{ fs}$. The couplings to the leads have been chosen to be $\Gamma_\alpha = 10^{-3} \text{ eV}$ and two types of spectral densities have been employed. For one calculation, the wide-band limit has been used, i.e., a energy-independent spectral density which can also be studied using the E-NEGF scheme employing a very broad Lorentzian function. In the second calculation, we again used the spectral density discussed in the previous example, i.e., a spectral density with a gap and sharp edges. Simulations using this latter kind of band structures would be unfeasible using the E-NEGF scheme, while the C-NEGF scheme is able to handle such a molecule-lead coupling without any additional numerical effort as compared to the simulation of a trivial energy-independent molecule-lead coupling. Thus, highly complex and/or more realistic band structures can be simulated at the computational cost.
Chapter 3. Chebyshev expansion applied to charge transport using NEGF

of trivial band structures using the Chebyshev approach even at low temperatures.

3.5 Summary

A Chebyshev decomposition was used to develop NEGF-based EOMs for the propagation of the single particle reduced density matrix. This method is presented as an alternative to the earlier developed formalisms [90,131] which have been utilized to study the effect of laser pulses on molecular junctions [62, 75,138]. These earlier theories were based on the assumption that the time correlation functions or the self energies of the leads can be written as a weighted set of exponentials. Similar to earlier work of Tian and Chen [112, 136] we employed a Chebyshev decomposition but, in a stark difference from the EOMs developed by these authors, we used the fact that a derivative of a Bessel function can be written in terms of two Bessel functions to derive a set of coupled differential equations for the reduced density matrix and the corresponding auxiliary quantities. The foundation of this scheme is a reformulation of the well-known expression for the current, Eq. 3.3, by means of the reduced density matrix and newly introduced auxiliary quantities.

Although the present NEGF scheme is restricted to a non-interacting electron system, an extension to a quite similar HEOM scheme for fermionic systems can be envisioned which then would be able to treat electron-electron interaction [142–144]. Due to the inherent multi-particle basis in the HEOM scheme, such an approach would be computationally already more expensive at the second tier which for a non-interacting electron system is equivalent to the present NEGF scheme. At the same time, a HEOM scheme could be extended to higher tiers to include correlation effects. Furthermore, one could think about including electron-phonon effects in the present scheme. Here we showed how to include such effects in a time-dependent manner. The correspondence between including a time-independent electron-phonon term or using explicit fluctuations has been shown earlier, e.g., in Ref. 156.

No assumptions were made concerning the time dependence of the system Hamiltonian and the scheme is also able to incorporate time dependencies in the leads similar to the exponential scheme [82], while the treatment of time dependencies in the molecule-lead Hamiltonian would require a non-trivial extension of the present scheme. For the exponential HEOM formalism such an add-on has recently been proposed by Erpenbeck et al. [157]. Due to the ability to include time-dependent site and Fermi energies, the approach can also be employed in the strong external field limit. Furthermore, expansions such as Matsubara, Ozaki or Padé are not necessary for the Fermi function resulting in the fact that the numerical performance of the approach is completely independent of the temperature of the molecular junction. The Fermi function and the spectral density appears only in the integrals $I_n^\infty$, which can be evaluated once at the beginning of any simulation. The scheme thus works for any form of the spectral density of the leads whether given analytically or numerically. A limitation for this approach is that it breaks down after a certain simulation time as given by Eq. 3.41 depending on the number of Chebyshev polynomials. In most applications one deals with a steady state following a perturbation of the system. Thus, a finite amount of simulation time after the perturbation usually suffices. Before this maximal simulation time is reached, the Chebyshev expansion is stable and numerically accurate as known, e.g., from wave packet propagation schemes [109]. The new scheme was tested for some examples with and
without time-dependent fields incident on the molecular junction. An excellent agreement was observed between the C-NEGF and E-NEGF schemes for all scenarios, making C-NEGF a promising alternative with fewer parametric restrictions.
Chapter 4

Chebyshev expansion applied to dissipative systems

In this chapter the Chebyshev expansion scheme is utilized to develop equations of motion within the Quantum master equation (QME) framework as well as the Hierarchical equations of motion (HEOM) scheme. Both schemes are derived for Bosonic systems. The line of reasoning utilized herein was originally presented in Ref. 113 for quantum transport in Fermionic systems and consisted of expanding the correlation function of the bath in terms of Chebyshev polynomials. Here the scheme is adopted for bosonic environments. We use the Chebyshev expansion to derive QME in perturbation theory up to the second order in the first part of this chapter and extend the scheme to arbitrary orders in perturbation theory by deriving hierarchically linked equations using the derivatives of Bessel functions in the second part of the chapter. The schemes are used to obtain the dissipation dynamics in Bosonic systems. We employ a two-level model system in contact with bosonic reservoirs to test our schemes and compare them to other well established methods. In the model considered here one looks at the transfer of energy from the relevant, smaller system to the large environment, leading to decoherence. The dissipation of energy into the environment is irreversible within a physically relevant time-frame. The reduced density matrix (RDM) based schemes present one way to account for external effects onto a relevant system. The RDM may be determined by, e.g., QMEs or HEOM. While the former is limited to low orders in perturbation theory, the latter extends to higher orders with ease using iterative, linked equations. Both of these schemes generally rely on decomposing the bath correlation function in terms of sums of weighted exponential functions. This feature has the limitation that when spectral densities of the environment show highly fluctuating or nonlinear behaviour, such as for the case of light-absorbing aggregates, the energy profiles cannot be reconstructed efficiently or completely using Lorentzian functions.

The Chebyshev expansion scheme employed in this work allows the bath correlation to be written in terms of Chebyshev polynomials and Bessel functions, rather than in terms of weighted exponential functions. The advantages are two-fold. First, the numerical or computational effort now has no relationship with the temperature of the system. In contrast, for the exponential functions based schemes, lower temperatures become extremely inefficient to simulation. Secondly, any kind of spectral
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densities, including experimental or numerical, strongly oscillating profiles, can be dealt with at the same numerical effort as highly trivial energy profiles such as single Lorentzian forms. This is again in stark contrast to exponential functions based schemes, where, in general, sharp oscillations translate to high computational load. However, these advantages come at the cost of the fact the simulation time becomes dependent on the number of Chebyshev polynomials used in the expansion of the correlation functions. The main idea in performing this expansion is the utilization of the Jacobi-Anger indentity to expand the bath correlation function. This applies to the application of the Chebyshev expansion to QMEs as well as HEOM. Although the two schemes are derived in different formalisms, the method of incorporating the Chebyhev expansion in either of them is exactly the same. The main components of the Jacobi-Anger indentity are Chebyshev polynomials and Bessel functions. The latter have the property that their derivatives can be written out in terms of Bessel functions of different orders, allowing for a recursive structure of the equations which are composed using this property. We build hierarchical linkages between equations and complete sets of differential equations using this property of the Bessel function. A function with a similar property is, of course, the exponential function. In the end the bath correlation function is split into a time independent part, calculated just once at runtime, and a time-dependent part, which is evaluated by propagating the equations using a scheme such as the Runge Kutta solver.

We use the tight-binding description of the Hamiltonian, which is composed of the usual three parts, namely the system, reservoir and system-reservoir coupling parts. The bosonic or heat bath here is taken as an infinite collection of displaced harmonic oscillators, linearly coupled to the system. As already mentioned, we use a two-level model system to test our new Chebyshev decomposed QMEs and HEOM. To validate and test the QMEs, which are derived up to the second order in perturbation theory, we use a Drude form of the spectral density of the bath and compare it, for different values of reorganization energy, to converged results obtained using the exponential decomposed HEOM, the ensemble averaged wave-packed scheme, as well as the Markov limit of the QMEs. We use two different configurations of the site energies, one where the site energies are set equal to each other and another where one site is set at a higher energy level. The population of the excited site is recorded and compared with the above-mentioned schemes. Throughout the simulations using QMEs the temperature is set at 300K. It is found and reported that for small values of the reorganization energy, the second order QMEs predict population dynamics that are very close to the converged dynamics. As the value of the reorganization energy is raised, however, the discrepancy between the converged and second order results keeps on increasing, indicating that the scheme is only valid for small reorganization energies. To showcase the capabilities of the Chebyshev based scheme, we utilize a spectral density which falls sharply to zero after a linear increase, the kind of spectral density which cannot handled accurately using schemes that are based on the exponential decomposition. To be able to treat spectral densities with realistic features like this the Chebyshev based schemes are ideal, however to treat such features at high reorganization energy, which correspond more with realistic scenarios, one needs to use higher orders in perturbation theory. These can be generated in a systematic fashion using the HEOM scheme, which is the topic of the next part of this chapter.

The HEOM scheme presented in the second part of this chapter is derived within the Path integral...
formalism. The general formula for the HEOM is derived starting from the Feynman-Vernon influence functional. This allows the calculation of arbitrary tiers of the hierarchy that correspond to orders in the perturbation theory. We write out specifically the HEOM up till the second tier, truncated using the time local as well as the the time non-local truncation schemes. We then show results for the population dynamics obtained using these first and the second tier, time non-local as well as the time-local truncations of the Chebyshev decomposed HEOM. We note that the second tier of the HEOM corresponds to the fourth order in perturbation theory. As comparative benchmarks we use the converged exponentially decomposed HEOM as well as the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) theory. The Chebyshev HEOM can handle all kinds of reservoir spectral densities but a Drude-Lorentz form is employed to to perform a basic first test against the exponential HEOM. Next we use an Ohmic spectral density to compare the Chebyshev HEOM results with the ML-MCTDH scheme, and finally a super-Ohmic spectral density is utilized to show the capabilities of the Chebyshev HEOM. We note in the results that improving the tier by one order does not always directly increase the results and that the fourth order in perturbation theory does not always perform better than the second order in perturbation theory for all parameter sets. We show that for low to intermediate coupling strengths or reorganization energies the fourth order in perturbation theory is in general sufficient to produce converged results, while for higher reorganization energies higher tiers of the hierarchy are needed to obtain converged population dynamics. We note also some limitations of the Chebyshev HEOM scheme, namely that the sizes of the involved matrices becomes very large. If $n$ represents the tier of the Chebyshev or the exponential HEOM, then the sizes of auxiliaries scales as $O^n$. While for the exponential HEOM, where the simulation time does not depend on the number of poles used in the expansion of the bath correlation function, this causes no drawbacks. Whereas for the Chebyshev decomposition, where the simulation time is related to the number of polynomials used in the expansion of the correlation function, one sees a large increase in the size of the matrices involved.


4.1 Chebyshev Expansion Applied to QME

In this work the Chebyshev expansion scheme is adapted to QME in perturbation theory up to the second order and used to obtain the dissipation dynamics in Bosonic systems. Previously the same QME was developed for quantum transport in Fermionic systems [113]. Here the system of interest, specifically a two-level system, is modelled to be in contact with bosonic reservoirs. Within this model, one is interested in the transfer of energy from the small system to the large environment, where the latter imposes friction onto the former leading to decoherence. The transferred energy dissipates into the environment and does not return to the system within a time frame which is physically relevant.

4.1.1 Chebyshev Decomposition of the Correlation Functions

In this section, we follow the line of reasoning presented in Ref. 113 and Ref. 95 to expand the bath correlation function in terms of Chebyshev polynomials. However, here only the scheme for the bosonic environments is presented. To make use of this type of orthogonal polynomials, a mapping of the spectral range of the Hamiltonian to their interval of definition is required, i.e., to the interval \([-1, 1]\).

To this end, one first needs to restrict the infinite integration range present in correlation functions to a finite range \([\omega_{\text{min}}, \omega_{\text{max}}]\). Then, by introducing the dimensionless variable \(x = (\omega - \bar{\omega})/\Omega\), where \(\bar{\omega} = (\omega_{\text{max}} + \omega_{\text{min}})/2\) and \(\Omega = (\omega_{\text{max}} - \omega_{\text{min}})/2\), the integral expression for the correlation function turns into

\[
C_j(t) = \frac{\hbar \Omega}{\pi} \int_{-1}^{1} dx \frac{e^{-i(\Omega x + \bar{\omega})t} J_j(\Omega x + \bar{\omega})}{1 - e^{-\beta \hbar (\Omega x + \bar{\omega})}}. \tag{4.1}
\]

Next, we expand the Fourier kernel in by means of the Jacobi-Anger identity [137] given by

\[
e^{-i\Omega xt} = J_0(\Omega t) + \sum_{n=1}^{\infty} 2(-i)^n J_n(\Omega t) T_n(x), \quad \forall t \in \mathbb{R}, \quad \forall x \in [-1, 1], \tag{4.2}
\]

with the Chebyshev polynomials \(T_n\) and the Bessel functions of the first kind \(J_n\). Subsequently, the BCF can be written as

\[
C_j(t) = \sum_{n=0}^{\infty} J_n(\Omega t)e^{-i\bar{\omega}t} \frac{\hbar \Omega}{\pi} \int_{-1}^{1} dx \frac{(2 - \delta_{0,n})(-i)^n T_n(x) J_j(\Omega x + \bar{\omega})}{1 - e^{-\beta \hbar (\Omega x + \bar{\omega})}} = \sum_{n=0}^{\infty} C_n(t) I_{j,n}, \tag{4.3}
\]

where \(\delta_{0,n}\) denotes the Kronecker delta. In Eq. (4.22) the time-dependent quantities \(C_n(t)\) as well as the time-independent integrals \(I_{j,n}\) were defined. It is crucial to note that the quantities \(I_{j,n}\) need to be computed only once at runtime, whereas the time-dependence of the BCF is encapsulated in the simpler expressions \(C_n(t)\). Moreover, up to this point there where no assumptions on the form of spectral densities nor on the Bose-Einstein distribution, hence on the involved temperature. This suggests that such an expansion might be advantageous for embedding complex spectral densities and low temperatures. This fact is in quite some contrast to the exponential decomposition of the BCF.
which becomes very demanding for complex spectral densities and/or low temperatures. We like to note that the numerical evaluation of the integrals $I_{j,n}$ by standard techniques turns out to be non-trivial due to the strongly oscillating Chebyshev polynomials for larger values of $n$. However, this can be circumvented by the substitution $x = \cos(\theta)$ and the subsequent use of the property $T_n(\cos(\theta)) = \cos(n\theta)$, which renders the integrands to the general form $f(x) \cdot \cos(\omega x)$, thus amenable to specifically designed integration subroutines, e.g., from the QUADPACK library [151]. The key point in deriving a QME in the exponential decomposition of the correlation function [103] combined with a complex-pole expansion of the Bose-Einstein distribution is to be able to write the BCF to a weighted sum over exponentials. This decomposition guarantees that time derivatives of partial BCFs can be expressed in terms of themselves. However, to achieve the latter goal one can instead benefit from the Bessel functions of the first kind entering the time-dependent part of the BCF in Eq. (4.22) since these have a similar property [137]

$$\frac{d}{dt} J_n(\Omega t) = \Omega^2 \left( J_{n-1}(\Omega t) - J_{n+1}(\Omega t) \right).$$

Consequently, the time derivative of $C_n(t) = J_n(\Omega t)e^{-i\omega t}$ can be given by

$$\frac{d}{dt} C_n(t) = -i\omega J_n(\Omega t)e^{-i\omega t} + e^{-i\omega t} \frac{d}{dt} J_n(\Omega t) = -i\omega C_n(t) + \frac{\Omega}{2}(C_{n-1}(t) - C_{n+1}(t)),$$

which connects the derivative of $C_n(t)$ to itself and its nearest-rank neighbours. This expression is the key point in deriving a QME in the next section.

### 4.1.2 Quantum Master Equations

The time-local approach is based on the Hashitsume-Shibata-Takahashi identity and is also denoted as time-convolutionless formalism [43], partial time ordering prescription (POP) [40-42], or Tokuyama-Mori approach [46]. This can be derived formally from a second-order cumulant expansion of the time-ordered exponential function and yields a resummation of the COP expression [40, 42]. Sometimes the approach is also called the time-dependent Redfield theory [47]. As was shown by Gzyl [48] the time-convolutionless formulation of Shibata et al. [10, 11] is equivalent to the antecedent version by Fulinski and Kramarczyk [49, 50]. Using the Hashitsume-Shibata-Takahashi identity whose derivation is reviewed in the appendix, one yields in secondorder in the system-bath coupling [51]

$$\frac{\partial}{\partial t}\rho(t) = -iL\rho(t) + \int_0^t dt' K(t')\rho(t).$$

As discussed in previous studies [76, 103, 158] the second-order time-local quantum master equation can be written as

$$\frac{d}{dt} \rho_S(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \operatorname{Tr}_R \{ [\tilde{H}_{SR}(t), [\tilde{H}_{SR}(\tau), \tilde{\rho}_S(t)\rho_R^{eq}]] \},$$

where $\rho_R^{eq}$ denotes the equilibrium density operator of the reservoir, $\rho_S(t)$ the system reduced density operator and the tilde on top of the operator symbols marks the interaction picture. Eq. (4.7) can be
given in a more convenient form by inserting the expression of the coupling Hamiltonian, Eq. (4.18), and subsequently changing to the Schrödinger picture

$$\frac{d}{dt} \rho_S(t) = -\frac{i}{\hbar} \mathcal{L}_S(t) \rho_S(t) - \frac{1}{\hbar} \sum_j [K_j, A_j(t) \rho_S(t) - \rho_s(t) A^\dagger_j(t)] .$$  \hspace{1cm} (4.8)

Here $\mathcal{L}_S = [H_S(t), \cdot]$ denotes the Liouville operator and the $A_j(t)$ are auxiliary density operators (ADOs) defined as [103]

$$A_j(t) = \int_0^t d\tau \, C_j(t - \tau) U_S(t, \tau) K_j U_S^\dagger(t, \tau) ,$$  \hspace{1cm} (4.9)

where $U_S(t, \tau)$ stands for the time-evolution operator of the system. The QME given in Eq. (4.7) is given in the so-called time-local (TL) form [103] rather than in its time-nonlocal form [102]. In Ref. 103 this TL form has been combined with the exponential decomposition of the BCF leading to the exponential decomposition time-local (EDTL) formalism. Alternatively we now make use of the Chebyshev decomposition of the BCF detailed in the previous section. This leads than to the Chebyshev decomposition time-local (CDTL) formalism, a notation introduced previously [113]. When the respective decomposition is converged, the EDTL and CDTL approaches do yield of course the same results since they are based on the same time-local QME.

Using the Chebyshev expansion turns Eq. (4.20) into

$$A_j(t) = \sum_{n=0}^\infty I_{j,n} \int_0^t d\tau \, C_n(t - \tau) U_S(t, \tau) K_j U_S^\dagger(t, \tau) = \sum_{n=0}^\infty I_{j,n} A_{j,n}(t) .$$  \hspace{1cm} (4.10)

This result consists of a time-dependent part of the ADO encapsulated in the new quantities $A_{j,n}(t)$ which we term partial ADOs. For later usage, one can derive simple master equations for these partial ADOs by directly differentiating their defining expression, Eq. 4.25, and by using the relation, Eq. (4.24). In addition, the infinite sum over the partial ADOs is truncated at a finite order $N_C$. As detailed in Ref. 113 and similar to the method of Ref. 112, truncating at a certain $N_C$ limits the approach to a $N_C$-dependent simulation time. The uniform Chebyshev approximation shows an exponential convergence leading to very accurate results if the above relation is fulfilled [109]. An estimate for terms needed to obtain converged results can be given by [113,152,153]

$$N = \Omega T + 10 \ln(\Omega T) .$$  \hspace{1cm} (4.11)

Summarizing the final set of QMEs for the quantities $A_{j,n}(t)$ together with the boundary cases that for the zeroth and $N_C$-th order these QMEs assume modified forms one obtains

$$\frac{d}{dt} A_{j,n}(t) = \begin{cases} 
K_j - \frac{i}{\hbar} \mathcal{L}_S(t) A_{j,0}(t) - i\bar{\omega} A_{j,0}(t) - \Omega A_{j,1}(t) , & \text{if } n = 0 , \\
-\frac{i}{\hbar} \mathcal{L}_S(t) A_{j,n}(t) - i\bar{\omega} A_{j,n}(t) + \frac{\Omega}{2} [A_{j,n-1}(t) - A_{j,n+1}(t)] , & \text{if } 0 > n > N_C , \\
-\frac{i}{\hbar} \mathcal{L}_S(t) A_{j,N_C}(t) - i\bar{\omega} A_{j,N_C}(t) + \frac{\Omega}{2} A_{j,N_C-1}(t) , & \text{if } n = N_C .
\end{cases}$$  \hspace{1cm} (4.12)
The above system along with the summation rule (4.25) and the equation of motion for the RDO, Eq. (4.8), forms a complete set of coupled differential equations, amenable to numerical treatment.

Concerning the Markovian limit of the obtained set of QMEs. This limit is not simply obtained analytically but rather needs to be generated numerically for a time-independent Hamiltonian. For this one first propagates the above detailed set of QMEs until reaching equilibrium in which the ADOs become time-independent. These time-independent ADOs are then propagated together with Eq. (4.8) for $\rho_S$ to get the Markovian limit of the present theory. The non-Markovian results together with this Markovian limit are tested below for a simple model, i.e., a two-level dissipative system, showing its performance, in comparison to the well-established HEOM theory.

The advantage of this method, as mentioned earlier, over other similar approaches [75] is that the Bose-Einstein distribution and the bath spectral densities only enter the time-independent quantities $I_{j,n}$, which need to be computed only once at the beginning of a simulation. The Chebyshev scheme thus does not present a limitation, neither on the form of the respective spectral density nor on the system temperature, and therefore is able to cope with numerically or experimentally obtained spectral densities as well as an arbitrary range temperatures.
4.1.3 Hierarchy equations of motion and ensemble-averaged wave packet dynamics

The HEOM scheme can only be employed in cases in which the correlation function can be written as a weighted sum of exponentials, i.e., it uses the exponential decomposition [101, 107, 159]. The EDTL scheme [103] is actually equivalent to the first tier of the HEOM formalism. This restriction implies that the spectral density can be written as a sum of Lorentzian functions and that the Fermi function is written in a series expansion such as the Matsubara series. To this end, auxiliary density matrices take into account the non-Markovian dynamics induced by the environment. The exponential decomposition together with the hierarchical scheme leads, in principle, to an infinite number of terms which can be truncated at a finite level, however, depending on the required accuracy. Appropriate approximations can, for example, be employed in the case of low temperatures [155, 160]. In the present case the obtained results are converged with respect to the number of auxiliary terms and coincided with those results already presented in Ref. 156.

The other method to which we compare the present CDTL results is the ensemble-averaged wave packet dynamics in its classical-path based version. In this approach, other than in the standard Ehrenfest dynamics as, for example, employed in Ref. 161, the effect of the system on the bath is neglected. In other words, the bath always stays in equilibrium if initially in equilibrium. This assumption is common in perturbative density matrix schemes [76]. At the same time, this assumption clearly indicates that the approach will not be able to handle strongly coupled system-bath configurations. In the ensemble-averaged wave packet dynamics, the effect of the environment is given in terms of fluctuations in the site energies $\Delta E_m(t)$ which are determined as specific matrix elements of bath operators. As a starting point one determines time-dependent trajectories of site energies including the $\Delta E_m(t)$ and couplings. Subsequently, the time-dependent Schrödinger equation is solved for state vector $|\Psi^S_\alpha(t)\rangle$ of ensemble member $\alpha$ long $N$ pieces of the trajectory or an ensemble of trajectories. Finally, an ensemble average over the different pieces of the trajectory has to be performed to obtain the expectation value of an observable $A$ leading to

$$
\langle A(t) \rangle = \frac{1}{N_\alpha} \sum_{\alpha=1}^{N_\alpha} \langle \Psi^S_\alpha(t)|A|\Psi^S_\alpha(t)\rangle = \langle \Psi^S(t)|A|\Psi^S(t)\rangle .
$$

(4.13)

A comparison of the HEOM and ensemble-averaged wave packet has been reported earlier [156] though not with a second-order perturbative treatment.

4.1.4 Results and Discussion

In this section we employ a simple model system, i.e., a dissipative two-site system, to validate the Chebyshev QME and to compare the results to the aforementioned established methods. To this end, we consider the system Hamiltonian of form discussed before, Eq. (4.16), with site energies $E_1$ and $E_2$ and coupling elements $V_{12} = V_{21} = V$. Each site is coupled independently to its own thermal bath,
where the coupling is governed by Drude-Lorentz spectral densities defined as

$$J_i(\omega) = 2\pi \lambda_i \gamma_i \frac{\omega}{\omega^2 + \gamma_i^2},$$  \hspace{1cm} (4.14)

with the real parameters $\gamma_i$ and $\lambda_i$. Specifically, $\gamma_i$ affects the width of the function and represents the inverse correlation time, whereas the reorganization energy $\lambda_i$ influences its amplitude. For the sake of simplicity, however, we chose the same spectral density for both sites. This system has been used in several benchmark studies in literature [156, 162, 163] in which the simulation parameters were chosen to be $V = 100 \text{ cm}^{-1}$ for the electronic coupling, $T = 300 \text{ K}$ for the temperature, and $1/\gamma_i = 100 \text{ fs}$ for the correlation time. Moreover, we distinguish two cases, i.e., in Fig. 4.4 equal site energies $E_1 = E_2$ are considered, whereas Fig. 4.2 shows the case of unequal site energies, i.e., a energy splitting of $\Delta E = E_2 - E_1 = 100 \text{ cm}^{-1}$.

For both cases, i.e., Figs. 1 and 2, the reorganization energy, $\lambda_i$ assumes four different values, indicated in each panel spanning the system-bath coupling regime from low to high values. The plots show the population dynamics of the first site, i.e., element $(1,1)$ of the density operator, given by the present Chebyshev QME as compared to its counterparts computed by the HEOM scheme. The HEOM
Figure 4.2: Same as in Fig. 1 but for unequal site energies $\Delta E = E_2 - E_1 = 100 \text{ cm}^{-1}$.

results including details of their calculation have been reported in Ref. 156 already. The important point for the present study is that these can serve as benchmark results since these are converged in the system-bath coupling.

In Fig. 4.1 the results for the case of equal site energies are shown. For the lowest reorganization energy (i.e. $\lambda = 2 \text{ cm}^{-1}$) the agreement with the HEOM results is good which points out that the present scheme correctly describes the underlying dynamics. Moving on to intermediate values of $\lambda$, i.e. Figs. 1b and 1c the damped oscillations in the Chebyshev dynamics start to differ from those of the HEOM results mainly in amplitude. Moreover, a slight shift in frequency can be observed as well. This finding indicates that this medium magnitude range of the system-bath coupling already shows already the start of the break-down of second-order perturbation theory which is the basis of the CDTL QME. However, it is interesting to note that the scheme still correctly describes the long-time limit which corresponds to equal population of both sites for equal site energies. For the largest reorganization energy in Fig. 1 quite some difference in the dyensemble-average wave packet dynamics towards the equilibrium is observed for the CDTL scheme and the higher-order HEOM approach. The case of uneven site energies is shown in Fig. 2. The agreement between the two approaches is quite similar to that for even site energies. Again, the CDTL scheme almost reaches the same equilibrium value.
as the converged results. Small deviations can be explained by the second-order nature of the present approach [164].

In addition, the Markovian limit of the present scheme is shown in Figs. 4.1 and 4.2. The procedure how this limit has been obtained, was detailed in the methods section. For the case of even site energies, the Markovian limit actually shows larger oscillations than the non-Markovian results and are less accurate at the same time. This behavior is different for the case of unequal site energies. Not many differences are visible for the smallest reorganisation energy. For the reorganisation energy of $\lambda = 20$ cm$^{-1}$ the agreement with the HEOM result is better for the Markovian than for the non-Markovian dynamics. For even larger reorganisation energies, the reminiscents of oscillations which are present in the non-Markovian case do vanish completely in the Markovian limit. The behavior of the Markovian case is very similar to that of the Redfield dynamics in Ref. 162.

Moreover, shown in Figs. 4.1 and 4.2 are the results for the classical path-based ensemble-average wave packet dynamics outline in the previous section. It is interesting to see how different this approximation behaves compared to a perturbative treatment. For the case of equal site energies in Fig. 4.1, the wave packet dynamics nicely agrees with the HEOM results even for reorganisation energies up to $\lambda = 100$ cm$^{-1}$. Only for the largest reorganisation energy quantitative differences are visible though qualitatively the behavior is similar again. So for equal site energies, the ensemble-average wave packet dynamics outperforms the present Chebyshev scheme which is based on a second-order treatment. In the wave-packet dynamics the dephasing is actually included properly in the theory by the ensemble average. This theory is missing an relaxation term, however. A fact which is invisible for equal site energies. Moving on to a bias between the site energies this deficiency of the wave packet dynamics becomes obvious since the long term limit is not properly reproduced, a fact which is well known [156]. Nevertheless, it is clearly visible that the dephasing part of the dynamics is still quite accurately reproduced though the dynamics leads to the wrong thermal state.

Finally, in Fig. 4.3 we deal with a non-smooth spectral density as depicted in the inset of Fig. 4.3. The spectral density is linearly increasing with frequency and then suddenly dropping to zero. Such a spectral density is practically not reproducible by a sum of Lorentzian functions, i.e., cannot be handled properly by the EDLT or standard HEOM approaches.

Note that the spectral density is extended to negative frequencies by $J_i(-\omega) = -J_i(\omega)$ before being inserted into Eq. (2.25). The thermal equilibria are the same as in Fig. 1 and 2, respectively, since these do not depend on the spectral density when neglecting higher-order corrections [164]. This example clearly shows the advantage of the present scheme in being able to use any form of spectral density or temperature. As in earlier approaches [75, 102, 107] including the EDTL one [103], the present scheme does not make any additional assumptions and approximations in the time-dependence of the system Hamiltonian. So the approach is able to treat systems with rapidly fluctuating and/or strong external or internal perturbations. In the fermionic case, this has, for example, be employed in studying the coherent destruction of tunneling in molecular wire systems [62,141]. In these investigations we did use the EDTL scheme which is only efficiently usable when the spectral density can be decomposed in terms of a few Lorentzian functions and if the temperature is not too low since otherwise too many terms are needed in the decomposition of the Fermi function. The CDTL approach does lift the restriction on
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Figure 4.3: Population dynamics of the first site determined by the CDTL scheme, for both configurations, i.e., $\Delta E = 0$ and $\Delta E = 100 \text{ cm}^{-1}$. The employed spectral density is shown in the inset. It consists a linearly increasing function which drops to zero at half the maximum frequency. The maximum of the spectral density $J_{\text{max}}$ is chosen such that it should lie within the validity range of perturbation theory.

simple forms of spectral densities and not too low temperatures. However we note the drawback that the simulation time is limited by the number of terms used in the Chebyshev expansion.

In recent years complex spectral densities have been extracted from experiments [165,166] or from a combination of classical molecular dynamics simulations and quantum chemical calculations [167–171]. These spectral densities do show a very complex structure which can only approximately be reproduced by sum of Lorentzian functions [172]. To be able to treat systems with these spectral densities one probably first has to extend the present scheme to higher orders or to the hierarchical scheme. To this end, in the following section we extend the Chebyshev scheme to the HEOM formalism.
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4.2 Chebyshev Expansion Applied to HEOM

Chebyshev Hierarchical Equations of Motion for Systems with Arbitrary Spectral Densities and Temperatures.

An accurate description of quantum dissipation continues to be formidable challenge. While various reduced density matrix (RDM) based schemes [76,134,158] can account for the external influences, e.g., from a protein environment, on the excitation energy transfer in systems such as pigment-protein complexes, there exist only a few methods that can tackle arbitrary intra-system and system-environment couplings [97,98,173–176]. One way to determine the RDM dynamics is via quantum master equations (QMEs). The latter methods, however, can usually only account for the lowest orders in the system-bath interaction due to their complex and very tedious extension to higher orders. This limitation is not present in the well-known hierarchical equations of motion (HEOM) approach [98,107,177–180] first formulated by Tanimura and Kubo [98] for bosonic environments. The HEOM scheme employs a possibly infinite hierarchy of auxiliary density operators (ADO) to generate arbitrary orders of system-bath coupling in a systematic and iterative fashion. Thus, in principle the HEOM approach allows for an exact treatment of the system-bath interaction and can be used to obtain exact solutions for the energy transfer in systems such as light-harvesting complexes for arbitrary exciton-phonon coupling strengths. The hierarchy has theoretically an infinite number of terms and may be truncated at a finite level depending on the strength of the system-environment coupling. For the case of low temperatures [155,160], certain approximations can render the HEOM computationally highly efficient [181]. Although the HEOM scheme remains one of the most powerful and well-known approaches, it is computationally expensive for larger systems, and depending on the chosen parameters, may require tens of gigabytes of computer memory and large amounts of computation time. GPU implementations [182] of the HEOM provide a considerable improvement in computation time, but due to GPU memory limitations the approach is usually constricted to systems composed of only a few chromophores. HEOM implementations on parallel computers [101] and/or in a distributed memory fashion might render the scheme applicable to larger systems [183]. Furthermore, the HEOM may be reformulated in terms of a linear transformation to gain considerable computational advantage [184].

The standard HEOM equations can only be constructed for specific forms of the environment correlation functions. Typically the hierarchical linkages are built using an exponential form of the correlation function, i.e., the correlation functions are represented as weighted sums of exponential functions. This scheme is also termed exponential decomposition approach [101,107,159]. However, using the exponential decomposition implies that the corresponding spectral densities of the environment are generally constricted to certain specific forms such as the one composed of Lorentzian functions and the Bose-Einstein function is approximated by a series expansion such as the Matsubara series. This fitting procedure of a given spectral density in terms of Lorentzian functions can be complicated in practice [185] while numerical techniques such as least-squares solver may be employed to minimize the error of the Lorentzian reconstruction. The Ohmic spectral density, for instance, can be decomposed into a sum of Lorentzian functions [102]. For realistic spectral densities such as those extracted from atomistic simulations, the spectral density can exhibit a highly nonlinear behavior and cannot be
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represented accurately using a finite sum Lorentzian functions. To overcome this obstacle, schemes to fit certain classes of functions better suited to mimic super-Ohmic behavior do exist [186]. However, the complications regarding the fitting procedures only escalate especially when reconstructing experimentally or numerically obtained spectral densities, which, at least for certain systems, show sharply varying energy profiles [171, 187]. Nonetheless, a wide variety of spectral densities may be dealt with using the scheme presented in Ref. ?.

As an alternative to the regular exponential decomposition method and the corresponding Lorentzian expansion of the spectral density, an extended version of the HEOM scheme was presented by Tang and co-workers [135] where a complete set of orthonormal functions is introduced to expand the bath correlation function. The HEOM is then constructed using auxiliary fields composed of these orthonormal functions. This expansion of the correlation function allows the extended HEOM to be usable for the zero-temperature case where the original exponential HEOM version faces an extreme numerical inefficiency. It is also possible, however, as we show in this work, that a hierarchically linked set of equations be built using the Chebyshev decomposition scheme [95, 113, 188]. If the bath correlation function is expanded in terms of Chebyshev polynomials and Bessel functions instead of exponentially decaying functions, the derivatives of Bessel functions allow the construction of a set of hierarchical equations which are similar in structure to the exponential decomposition based HEOM. This Chebyshev decomposed HEOM scheme (C-HEOM) has the clear advantage that no expansion of the spectral density of the environment is necessary and any kind of environmental spectral density can be incorporated into the scheme in an exact manner. Furthermore, all temperatures can be simulated at the exact same numerical cost. The Chebyshev decomposition has been previously applied to the second- tier truncation of the HEOM [136] for Fermionic systems to simulate arbitrary temperatures. These equations correspond to the Keldysh nonequilibrium Green’s functions scheme [82], an approach that is exact for noninteracting particles. The HEOM itself have been applied to a range of Fermionic systems. An extension of the HEOM approach (RSHEOM) [157], which uses an analytic re-summation over poles, also shows similar advantages and drawbacks as the scheme presented in this work. In earlier studies [113, 188], we have reported Chebyshev decomposed QMEs as well as a nonequilibrium Green’s function scheme for Fermionic systems, which present the advantage of not being limited to simple forms of spectral densities or being inefficient for low temperatures.

Polynomial expansions such as the Chebyshev expansion employed in the present study have been applied previously in the context of wave packet propagation [109], for inhomogeneous [189] as well as for explicitly time-dependent cases [190]. For open quantum systems polynomial-based schemes such as those based on Chebyshev polynomials [191] as well as on Faber and Newton polynomials [192] have been studied. Furthermore, a time-evolving density with orthogonal polynomials algorithm (TEDOPA) has been reported in the literature that is able to treat dissipative systems with arbitrary spectral densities [193]. Ensemble average methods such as the hierarchy of pure states HOPS [?] scheme is also able to deal with sharply oscillating spectral densities at stronger coupling strengths. Another efficient method for the time propagation of the total wave function is the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) theory [?, 194]. The quantities of the system of interest, e.g., the reduced density matrix (RDM) of the system can be estimated by the partial trace over the bath
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degrees of freedom. Alternatively using path integral-based methods [195], the time evolution of the
RDM can then be calculated by, e.g., the quasi-adiabatic propagator path integral (QUAPI) [196] or
the stochastic path integral [197].

The HEOM formalism may be derived using the path integral approach utilizing the Feynman-Vernon influence functional formalism [98,107,177,178], or alternatively, by separating the system and bath degrees of freedom via stochastic fields as shown by Shao et al. [179,180], leading to the same
equations of motion in both cases. While the latter approach dissociates the system and bath degrees
of freedom using stochastic fields in this work we utilize the former. In the present study the HEOM
approach based on the the Chebyshev decomposition is derived from scratch utilizing the path integral
formalism and then applied to some test cases. To this end, the article is organized as follows. In
the subsequent section the typical tight-binding model for open quantum systems is presented, while in
section III the Chebyshev expansion is summarized. In section IV we employ the Chebyshev expansion to
derive hierarchically linked equations of motion and present their general formulas. Numerical results for
test examples are shown and discussed in section V followed by a final conclusions. More specifically, we
apply the newly developed C-HEOM to a two-level model and compare the results with other standard
methods such as the exponential HEOM and ML-MCTDH.

4.2.1 Model Hamiltonian

In the theory of open quantum systems, the Hamiltonian of a composite system is usually considered
to be composed of three constituent parts,

\[ H(t) = H_S + H_R + H_{SR}(t), \]

i.e., the total Hamiltonian \( H(t) \) is split into the relevant system Hamiltonian, \( H_S(t) \), for the molecular
aggregate, and the thermal bath Hamiltonian, \( H_R \), while \( H_{SR} \) represents the system-reservoir coupling
Hamiltonian. The system Hamiltonian is assumed to be of the tight-binding type and, for example,
for light-harvesting complexes one usually restricts oneself to the single-exciton manifold. In this case,
the basis states of the system \( |i⟩ \) mimic potential states of single excitons. The ground state without
any excitation, \( |0⟩ \), is usually not considered in these models. In general, the system is assumed to be
composed of \( N \) sites with site energies \( E_i \) at site \( i \). Sites \( i \) and \( j \) interact via electronic couplings, \( V_{ij} \).
Each site may thus be coupled to any other site. The Hamiltonian of the \( N \)-site system in tight-binding
description can be written as

\[ H_S = \sum_{i}^{N} E_i |i⟩⟨i| + \sum_{i \neq j}^{N} V_{ij} |i⟩⟨j|. \]

For the case of exciton transfer it is possible to calculate the exciton energies and the electronic couplings
using the electronic structure of the system constituents. The resulting information may then be used
to parameterize the above mentioned tight-binding model [171,187]. Each thermal reservoir \( \alpha \) with
chemical potential $\mu_\alpha$ is described by the Bose-Einstein statistics

$$n_\alpha(\epsilon) = \frac{1}{e^{(\epsilon-\mu_\alpha)/\beta} - 1} .$$  \hspace{1cm} (4.17)$$

and is given as a sum of displaced harmonic oscillators. The system-reservoir coupling Hamiltonian $H_{SR}$ can be written as a sum of products of system, $K_j$, and bath operators, $\Phi_j$. As for the application have excitonic systems in mind, the system operators are assumed to be site diagonal for excitonic systems $[76]$

$$H_{SR} = \sum_j \Phi_j K_j = \sum_j \sum_\xi c_\xi x_\xi |j\rangle \langle j| .$$  \hspace{1cm} (4.18)$$

In the above equation, $x_\xi$ denotes the displacements of the harmonic bath coordinates $\xi$ and $c_\xi$ the system-reservoir coupling strengths. The operator $K_j = |j\rangle \langle j|$, i.e., the projector onto site $j$, described the system part of the system-reservoir coupling. This choice insures that an interaction between the system and the environment at site $j$ exists only if the site hosts an excitation. This description is limited to situations in which each site has an independent thermal bath that is uncorrelated to the bath modes from other sites. The Chebyshev approach outlined below can be extended to other types of system-bath interactions in a straightforward manner.

### 4.2.2 Chebyshev Decomposition of the Correlation Functions

In this section, we follow the line of reasoning presented in our studies $[95, 113, 188]$ to expand the bath correlation functions in terms of Chebyshev polynomials. To make use of Chebyshev polynomials, a mapping of the spectral range of the Hamiltonian to their interval of definition, $[-1,1]$, is required. In a first step, the infinite integration range usually present in correlation functions is restricted to a finite range $[\omega_{\text{min}}, \omega_{\text{max}}]$. Subsequently, by introducing the dimensionless variable $x = (\omega - \bar{\omega})/\Omega$, where $\bar{\omega} = (\omega_{\text{max}} + \omega_{\text{min}})/2$ and $\Omega = (\omega_{\text{max}} - \omega_{\text{min}})/2$, the integral expression for the correlation function can be written as

$$C_j(t) = \frac{\hbar \Omega}{\pi} \int_{-1}^{1} dx \frac{e^{-i(\Omega x + \bar{\omega})t} J_j(\Omega x + \bar{\omega})}{1 - e^{-\beta \hbar (\Omega x + \bar{\omega})}} .$$  \hspace{1cm} (4.19)$$

with $J_j$ denoting the spectral density of the environment or reservoirs, which for this scheme can assume any form. The correlation functions play a major role inside the auxiliary density operators (ADOs), $A_j(t)$, which appear inside the definition of the influence functional given in below Eq. 4.30 below and are defined as $[103]$

$$A_j(t) = \int_0^t d\tau C_j(t-\tau) U_S(t,\tau) K_j U_S^\dagger(t,\tau) ,$$  \hspace{1cm} (4.20)$$

where $U_S(t,\tau)$ denotes the time-evolution operator of the system. The next step is to expand the exponential term inside the Fourier kernel in Eq. 4.19 by using the Jacobi-Anger identity $[137]$ given by

$$e^{-i\Omega_xt} = J_0(\Omega t) + \sum_{k=1}^{\infty} 2(-i)^k J_k(\Omega t) T_k(x) , \quad \forall t \in \mathbb{R} , \forall x \in [-1,1] ,$$  \hspace{1cm} (4.21)$$

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where $T_k$ and $J_k$ denote the Chebyshev polynomials and the Bessel functions of the first kind, respectively. Consequently, the correlation functions can be written as

$$C_j(t) = \sum_{k=0}^{\infty} J_k(\Omega t) e^{-i\omega t} \frac{\hbar \Omega}{\pi} \int_{-1}^{1} dx \left( 2 - \delta_{0,k} \right) (-i)^k T_k(x) \frac{J_j(\Omega x + \bar{\omega})}{1 - e^{-\beta h(\Omega x + \bar{\omega})}} = \sum_{k=0}^{\infty} C_k(t) I_{j,k} , \quad (4.22)$$

where $\delta_{0,k}$ denotes the Kronecker delta function. Moreover, in Eq. (4.22) the time-dependent quantities $C_k(t)$ as well as the time-independent integrals $I_{j,k}$ are defined and grouped separately. The time-independent quantities $I_{j,k}$ need to be calculated once at the start of a simulation, while the time-dependent part of the correlation functions resides in the expression for $C_k(t)$. Moreover, it is clear that no assumptions were made regarding the form of spectral densities or on the Bose-Einstein distribution, hence on the involved temperature. Thus, such an expansion is able to embed complex spectral densities and handle low temperatures. The Chebyshev polynomials of higher orders, i.e., larger values of $k$, show a strongly oscillating behavior not amenable to standard techniques of numerical integration. To this end, the use of a property of the Chebyshev polynomials, $T_k(\cos(\Theta)) = \cos(k\Theta)$, renders the integrals, $I_{j,k}$, to the general form $f(x) \cdot \cos(\omega x)$, a form that can easily be dealt with using specifically designed integration subroutines from the QUADPACK library [151].

The central idea of the exponential decomposition used in formulating the QME or the HEOM is to decompose the correlation functions into a sum of exponential functions [103], typically formulated in conjunction with a complex-pole expansion of the Bose-Einstein distribution. This allows for writing the time derivatives of the partial correlation functions in terms of themselves, enabling the formation of closed forms of equations. To achieve the latter goal one can avail an interesting, comparable property [137] of the derivatives of the Bessel functions of the first kind that appear inside the time-dependent part of the bath correlation function in Eq. (4.22):

$$\frac{d}{dt} J_k(\Omega t) = \frac{\Omega}{2} \left( J_{k-1}(\Omega t) - J_{k+1}(\Omega t) \right) . \quad (4.23)$$

Since the derivatives of a certain order of Bessel functions can be written as a sum of Bessel functions of its nearest-order neighbours, the time derivative of $C_k(t) = J_k(\Omega t)e^{-i\omega t}$ can be written as

$$\frac{d}{dt} C_k(t) = -i\omega J_k(\Omega t)e^{-i\omega t} + e^{-i\omega t} \frac{d}{dt} J_k(\Omega t) = -i\omega C_k(t) + \frac{\Omega}{2} \left( C_{k-1}(t) - C_{k+1}(t) \right) , \quad (4.24)$$

where the derivative of $C_k(t)$ can be seen to be related to itself and its nearest-order neighbours. This expression is the key point utilized in the derivation of the C-HEOM. Using the Chebyshev expansion one can rewrite Eq. (4.20) as

$$\Lambda_j(t) = \sum_{k=0}^{\infty} I_{j,k} \int_{0}^{t} d\tau \, C_k(t - \tau) U_s(t, \tau) K_j U_s^\dagger(t, \tau) = \sum_{k=0}^{\infty} I_{j,k} \Lambda_{j,k}(t) . \quad (4.25)$$

Thus, the $\Lambda_j(t)$ are dissociated into time-independent and time-dependent parts, and the quantities

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\[ A_{j,k}(t) \] now carry the time-dependence. Their defining expression, Eq. 4.25, can be differentiated in a straightforward manner and used together with the relation in Eq. (4.24) to construct a hierarchically linked set of equations. For practical purposes, the infinite sum over the partial ADOs, \( A_{j,k}(t) \), needs to be truncated at a finite order \( K_{ch} \). As detailed in Ref. 113 and similar to the method of Ref. 112, truncating at a certain \( K_{ch} \) limits the approach to a simulation time dependent on the truncation order \( K_{ch} \). The uniform Chebyshev decomposition scheme shows an exponential convergence, generating extremely accurate results given the criteria for convergence are fulfilled [109].

### 4.2.3 Chebyshev Expansion Applied to HEOM

In order to derive a HEOM version based on the Chebyshev decomposition, we start, in analogy to the derivation of the exponential HEOM [198] with the time evolution of the reduced density matrix, \( \rho_S(t) \), obtained by applying the time evolution operator to the density matrix at \( t_0 \),

\[
\rho_S(t) = \text{tr}_{\text{bath}} \{ U(t, t_0) \rho(0) U^\dagger(t, t_0) \} = \tilde{U}(t, t_0) \rho_S(t_0). \tag{4.26}
\]

The Liouville space propagator, \( \tilde{U}(t, t_0) \), depends on the system part as well as the system-bath interaction part of the total system. To factorize the total system or to separate the system and bath DOFs, the Feynman-Vernon influence functional formalism [199] needs to be utilized by rewriting \( \tilde{U}(t, t_0) \) in the path integral formalism. The time evolution operator \( U(t, t_0) \) in path integral representation is given by [76]

\[
U(t, t_0) = \int_{\alpha_0}^{\alpha_t} D\alpha \ e^{i\int S_{\text{total}}[\alpha]}, \tag{4.27}
\]

where \( \alpha \) denotes arbitrary paths in phase space with the respective fixed starting and ending points \( \alpha_0 \) and \( \alpha_t \). The action functional \( S_{\text{total}}[\alpha] \) describes the evolution of the total system but can be decomposed into system, bath, and system-bath interaction parts. The time evolution of the full density matrix in path integral formalism therefore reads [177]

\[
\rho_{\alpha,\alpha',t} = \int_{\alpha_0}^{\alpha_t} D\alpha \int_{\alpha_0'}^{\alpha'_t} D\alpha' \ e^{i\int (S_S[\alpha]+S_B[\alpha]+S_{SB}[\alpha])} \rho_{\alpha_0,\alpha'_0,t_0} e^{-i\int (S_S[\alpha']+S_B[\alpha']+S_{SB}[\alpha'])} \tag{4.28}
\]

By tracing over the bath DOFs one gets [178]

\[
\mathcal{U}(\alpha, \alpha', t; \alpha_0, \alpha'_0, t_0) = \int_{\alpha_0}^{\alpha_t} D\alpha \int_{\alpha_0'}^{\alpha'_t} D\alpha' \ e^{i(S_S[\alpha])} \mathcal{F}(\alpha, \alpha') e^{S_B[\alpha']}. \tag{4.29}
\]

In this expression the Feynman-Vernon influence functional \( \mathcal{F}(\alpha, \alpha') \) represents the system-bath interaction [199]. We note in passing that it is of course important to maintain the order of the terms in Liouville space as, for instance, the time evolution operator and the density operator do not commute.
Employing the Caldeira-Leggett model for the system-bath interaction and using a single system operator $K$, the influence functional can be written as (adopting an arbitrary Liouville space representation $\alpha = (\alpha, \alpha')$)

$$F[\alpha(t)] = \exp\left\{ -\int_{t_i}^{t} d\tau K^\times[\alpha(\tau)] \Lambda^\times[\alpha(\tau)] \right\}.$$  \hspace{1cm} (4.30)

In the above, the symbol $\times$ denotes a commutator, i.e.,

$$F[\alpha(t)] = \exp\left\{ -\sum_j \int_{t_i}^{t} d\tau (K_j[\alpha(\tau)] - K^\dagger_j[\alpha(\tau)]) (A_j[\alpha(\tau)] - A^\dagger_j[\alpha(\tau)]) \right\}.$$  \hspace{1cm} (4.31)

Taking the time derivative of $\rho_S(t)$ leads to an equation of motion describing the time evolution of the system in connection with the external bath. Therefore, the derivative of the time evolution operator defined earlier, $\mathcal{U}(\alpha_t, \alpha'_t; t; \alpha_0, \alpha'_0, t_0)$, needs to be evaluated. This operator $\mathcal{U}(\alpha_t, \alpha'_t; t; \alpha_0, \alpha'_0, t_0)$ basically contains the influence functional $F(\alpha, \alpha')$ and the time derivatives of the action term describing the evolution of the unperturbed system, given by

$$\frac{\partial}{\partial t} e^{iS_\alpha} = -iH_S e^{iS_\alpha},$$  \hspace{1cm} (4.32)

while the time derivative of influence functional, containing the influence of the system-bath interaction, is given by

$$\frac{\partial}{\partial t} F[\alpha(t)] = -K^\times[\alpha(t)] \Lambda^\times[\alpha(t)] F[\alpha(t)].$$  \hspace{1cm} (4.33)

To evaluate the above expression further, one needs to introduce the so-called auxiliary influence functional (AIF) $F_1$ so that

$$\frac{\partial}{\partial t} F[\alpha(t)] = -K^\times[\alpha(t)] F_1[\alpha(t)]$$  \hspace{1cm} (4.34)

A solution in a closed form, i.e., an exact solution can only be obtained by taking the derivatives of $F$ up to $n^{th}$ order. This approach leads to an infinite number of equations of motion for a hierarchical set of auxiliary influence functionals $F_n$.

The time derivatives of $\Lambda^\times[\alpha(\tau)]$ in general may yield terms that are non-hierarchical and thus not all forms of the bath correlation function may be employed to obtain hierarchically linked EOMs. The form of the bath correlation functions such as the one based on the exponential decomposition scheme or the Chebyshev decomposition scheme ensures the hierarchical form of the derivatives of $F$. The leading order of the system-bath coupling of the auxiliary influence functional $F_n$ is $2n$. Thus memory effects as well as the influence of higher orders of the system-bath coupling are included in each tiers of the HEOM scheme.

In the present study, the Chebyshev decomposition scheme is utilized to find a closed solution to the above problem by deriving hierarchically linked equations of motion of the auxiliary density matrices. As mentioned earlier, the starting point in the Chebyshev decomposition is the utilization of the Chebyshev
polynomials and Bessel functions to express the bath correlation function in terms of a time dependent and independent part: \( C_j(t) = I_{j,n}C_{j,n}(t) \). Feynman showed [199] that by employing stochastic bath variables that obey Gaussian statistics, the bath averaged influence functional can be written in terms of the bath correlation function, \( C_j(t - \tau) \):

\[
F[\alpha(t)] = \exp \left\{ - \sum_j \int_{t_0}^{t} d\tau K_j^\alpha[\alpha(\tau)] \Lambda_j^\alpha[\alpha(\tau)] \right\}.
\]

(4.35)

where

\[
\Lambda_j[\alpha(\tau)] = \int_{t_0}^{t} d\tau C_j(t - \tau)K_j[\alpha(\tau)].
\]

(4.36)

Taking the time derivative of the Influence functional, Eq. 4.35, one gets

\[
\partial_t F[\alpha(t)] = - \sum_j K_j^\alpha[\alpha(t)] \Lambda_j^\alpha[\alpha(t)] F[\alpha(t)] .
\]

(4.37)

Finally, using the Chebyshev form of the bath correlation functions, i.e., \( C_j(t) = \sum_k I_{j,k}C_{j,k}(t) \), results in

\[
\partial_t F[\alpha(t)] = - \sum_j K_j^\alpha[\alpha(t)]
\]

\[
\times \left( \int_{t_0}^{t} d\tau \sum_k I_{j,k}C_{j,k}(t - \tau)K_j[\alpha(t)]F[\alpha(t)] - F[\alpha(t)] \int_{t_0}^{t} d\tau K_j[\alpha(t)]C_j(t - \tau) \right) .
\]

(4.39)

At this point we introduce auxiliary influence functionals \( F_{j_1}[\alpha(t)] \), such that

\[
F_{j_1}[\alpha(t)] = \Lambda_{j_1}[\alpha(t)]F[\alpha(t)] .
\]

Using these auxiliaries, the time derivative of the influence functional can be rewritten as

\[
\partial_t F[\alpha(t)] = - \sum_j K_j^\alpha[\alpha(t)] \left[ F_{j_1}[\alpha(t)] - F[\alpha(t)] \Lambda_{j_1}[\alpha(t)] \right] ,
\]

(4.40)

where

\[
F_{j_1}[\alpha(t)] = \int_{t_0}^{t} d\tau \ C_{j_1}(t - \tau) \ F[\alpha(t)]K_{j_1}[\alpha(t)] .
\]

(4.41)
are now written also as decomposed into time-independent and time-dependent parts

\[ F_{j_1}[\alpha(t)] = \sum_k I_{j_1,k} F_{j_1,k}[\alpha(t)] \].

(4.42)

Subsequently, one employs the time derivatives of \( F_{j_1,k}[\alpha(t)] \) given by

\[
\partial_t F_{j_1,k}[\alpha(t)] = \partial_t (A_{j_1,k}[\alpha(t)] F[\alpha(t)])
\]

\[
= \partial_t (A_{j_1,k}[\alpha(t)]) F[\alpha(t)] + A_{j_1,k}[\alpha(t)] \partial_t F[\alpha(t)]
\]

(4.43)

Thus, the derivative of \( F_{j_1}[\alpha(t)] \) can be written as

\[
\partial_t F_{j_1}[\alpha(t)] = \partial_t (A_{j_1}[\alpha(t)] F[\alpha(t)])
\]

\[
= \partial_t (\sum_k I_{j_1,k} A_{j_1,k}[\alpha(t)] F[\alpha(t)]) = \sum_k I_{j_1,k} \partial_t (A_{j_1,k}[\alpha(t)] F[\alpha(t)])
\]

(4.44)

To proceed further, one needs the derivatives of the time dependent quantities in Eq. 30, i.e., \( A_{j_1,k}[\alpha(t)] \) and \( F[\alpha(t)] \). The time derivative of the term \( A_{j_1,k}[\alpha(t)] \) is obtained using the time derivatives of the respective Bessel functions. The time derivative of \( F[\alpha(t)] \) is given in Eq. 4.40. Plugging it into Eq. 4.44 above, one gets the following expression

\[
\partial_t F_{j_1,k}[\alpha(t)] = \partial_t (A_{j_1,k}[\alpha(t)] F[\alpha(t)]) + A_{j_1,k}[\alpha(t)] \left( - \sum_{j_2} K_{j_2}^\alpha[\alpha(t)] A_{j_2}[\alpha(t)] F[\alpha(t)] - F[\alpha(t)] A_{j_2}^\dagger[\alpha(t)] \right)
\]

(4.45)

Moving \( A_{j_1,k}[\alpha(t)] \) inside the sum and identifying already defined operators in the resulting equations, one gets

\[
\partial_t F_{j_1,k}[\alpha(t)] = (\partial_t A_{j_1,k}[\alpha(t)]) F[\alpha(t)]
\]

\[
- \sum_{j_2} K_{j_2}^\alpha[\alpha(t)] A_{j_1,k}[\alpha(t)] A_{j_2}[\alpha(t)] F[\alpha(t)] - A_{j_1,k}[\alpha(t)] F[\alpha(t)] A_{j_2}^\dagger[\alpha(t)]
\]

\[
= (\partial_t A_{j_1,k}[\alpha(t)]) F[\alpha(t)]
\]

\[
- \sum_{j_2} K_{j_2}^\alpha[\alpha(t)] \left( \sum_{k'} I_{j_2,k'} A_{j_1,k}[\alpha(t)] A_{j_2,k'}[\alpha(t)] F[\alpha(t)] - A_{j_1,k}[\alpha(t)] F[\alpha(t)] A_{j_2}^\dagger[\alpha(t)] \right)
\]

\[
= (\partial_t A_{j_1,k}[\alpha(t)]) F[\alpha(t)]
\]

\[
- \sum_{j_2} K_{j_2}^\alpha[\alpha(t)] \left( \sum_{k'} I_{j_2,k'} F_{j_1,j_2,k,k'}[\alpha(t)] - A_{j_1,k}[\alpha(t)] F[\alpha(t)] A_{j_2}^\dagger[\alpha(t)] \right)
\]

(4.46)

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The obtained infinite hierarchy of influence functionals leads to an infinite hierarchy of auxiliary reduced density matrices. The final form of the first-tier ADM is therefore given by

$$\partial_t F_{j1,k}^{(n)}[\alpha(t)] = (\partial_t A_{j1,k}^{\dagger}[\alpha(t)]) F[\alpha(t)] \tag{4.47}$$

$$- \sum_{j2} K_{j2}^{\infty} [\alpha(t)] \left( \sum_{k'} I_{j2,k'} F_{j3,j2,k,k'}^{(n)}[\alpha(t)] - F_{j1,k}^{(n)} A_{j2}^{\dagger}[\alpha(t)] \right).$$

Time derivatives of the second-tier AIF which can be found in the above derivative of the first-tier AIF and are defined is as follows

$$\partial_t F_{j1,j2,k,k'}^{(n)}[\alpha(t)] = (\partial_t A_{j1,k}^{\dagger}[\alpha(t)]) A_{j2,k'}^{\dagger}[\alpha(t)] F[\alpha(t)]$$

$$+ A_{j1,k}^{\dagger}[\alpha(t)] (\partial_t A_{j2,k'}^{\dagger}[\alpha(t)]) F[\alpha(t)]$$

$$- \sum_{j3} K_{j3}^{\infty} \left( \sum_{k''} I_{j3,k''} F_{j3,j2,j3,k,k',k''}^{(n)}[\alpha(t)] - F_{j1,j2,k,k'}^{(n)} A_{j3}^{\dagger}[\alpha(t)] \right).$$

Using the simplified notation $F^{(n)}[\alpha(t)] = F(t)$ and noting that the $(n)$ in the superscript denotes the level of the hierarchy while the $k$ in the subscript denotes the Chebyshev polynomials, the general form of the AIF is given by

$$F_{jm,k}^{(n)}(t) = \prod_{j,m,k} (A_{jm,k}(t)) F(t). \tag{4.49}$$

Here $m$ denotes the site index, and $A_{jm}(t)$ is given as

$$A_{jm}(t) = \sum_n I_{jm,k} A_{jm,k}(t). \tag{4.50}$$

The time derivative of the general form, or the $n^{th}$ tier of the AIF, can be calculated to yield

$$\partial_t F_{jm,k}^{(n)} = - \sum_j K_j^{\infty} [\alpha(t)] \left( \sum_k^n I_{jm,k} F_{jm,k}^{(n+)} - F_{jm,k}^{(n)} A_{jm,k}^{\dagger}[\alpha(t)] \right)$$

$$- i \sum_{r=1}^n (\bar{\omega} F_{jm,k}^{(n)}$$

$$+ \begin{cases} \theta \sum_{r=1}^n (F_{jm,k}^{(n)} - F_{jm,k}^{(n-1)} & \text{if } k = 0 \\
 \frac{\phi}{2} \sum_{r=1}^n (F_{jm,k}^{(n)} - F_{jm,k+1}^{(n)}) & \text{if } 0 < k < K_{ch} \\
 \frac{\phi}{2} \sum_{r=1}^n (F_{jm,k}^{(n)} - F_{jm,k-1}^{(n)}) & \text{if } n = K_{ch} \end{cases}.$$}

The obtained infinite hierarchy of influence functionals leads to an infinite hierarchy of auxiliary reduced density matrices

$$\rho^{(n)}(t) = U_n(\alpha, \alpha', t; \alpha_0, \alpha'_0, t_0) \rho^{(n)}(t_0), \tag{4.52}$$

where the auxiliary time evolution operator $U_n$ is obtained by replacing the influence functional $F$ in Eq. 4.29 by the corresponding auxiliary influence functional $F_n$. The time evolution of the RDM and
the ADMs can thus be expressed in terms of a system of coupled differential equations

\[ \partial_t \rho_{jm,k}^{(n)} = -i L_S(t) \rho_{jm,k}^{(n)} \]  

\[ - \sum_j K_j^x \left( \sum_n I_{jm,k}^{(n+)} \rho_{jm,k}^{(n)} - \rho_{jm,k}^{(n)} \Lambda_{jm}^\dagger \right) \]

\[ - i \sum_{r=1}^n (\tilde{\omega} \rho_{jm,k}^{(n)}) \]

\[ + \begin{cases} \Omega \sum_{r=1}^n ( - \rho_{jm,k}^{(n)}) + \sum_{r=1}^n (K_j \rho_{jm,k}^{(n-1)}) & \text{if } n = 0 \\ \frac{\Omega}{2} \sum_{r=1}^n (\rho_{jm,k-1}^{(n)} - \rho_{jm,k+1}^{(n)}) & \text{if } 0 < k < K_{ch} \\ \frac{\Omega}{2} \sum_{r=1}^n (\rho_{jm,k-1}^{(n)}) & \text{if } k = K_{ch} \end{cases} \]

where \( L_S = [H_S, \cdot] \) denotes the Liouville superoperator.

Since the above HEOM has potentially infinite orders, it needs to be truncated at a certain level of hierarchy. Different truncation schemes [103, 200–202] exist that cut the HEOM at a specific level of hierarchy with the resulting equations corresponding to different orders of perturbative QMEs. Truncating the HEOM equations at a given level \( n \) results in the perturbation order \( N = 2n \). If the ADOs whose level is higher than \( n \) are simply discarded, one obtains the so-called time-nonlocal truncation. For \( n = 1 \) one gets the second-order TNL QME [201]. This truncation scheme has been shown for several test cases to lead to spurious oscillations in the population dynamics. Another scheme developed by Xu and Yan yields the time-local approximation [200] for the leading tier of the HEOM. With regard to truncating the Chebyshev HEOM, this amounts to approximating the term of the leading tier using the following equation

\[ \sum_k \rho_{jm,k}^{(n+)} = -i[A_{jm} \rho_{jm,k}^{(n)}] \]  

where

\[ A_{jm} = \int_{t_0}^t d\tau C_{jm} (t - \tau) e^{-iH_S\tau}K_j e^{iH_S\tau}. \]

Below we will denote the first-tier HEOM which is second order in the system-bath coupling as TL2 and TNL2 for the time-local and the time-nonlocal truncation schemes, respectively. The second-tier variants which are fourth order in system-bath coupling will be denoted as TL4 and TNL4. In an earlier study [95], the C-HEOM TL2 has also been termed CDTL, i.e., Chebyshev decomposition time-local (second-order in system-bath coupling).

### 4.2.4 Results and Discussion

In the following we apply the Chebyshev-HEOM to calculate the dynamics of a dissipative two-level model system. This arrangement has been extensively studied as a benchmark system [156, 162, 163]. At
higher temperatures, the dephasing in this model and similar models can even reasonably be described by classical noise [2, 156]. In the following, we show and discuss results for the population dynamics obtained using the first and the second tier of the time-non-local (TNL2 and TNL4) as well as the time-local truncation (TL2 and TL4) of the C-HEOM together with converged results calculated using the exponentially decomposed HEOM as well as the ML-MCTDH [?, 194] schemes. Some calculations using the Chebyshev decomposition in a 2nd-order scheme that have been presented in a previous study [95] are also included. In the model considered, each of the two sites, with site energies $E_1$ and $E_2$ and coupling elements $V_{12} = V_{21}$, is coupled to its own independent phonon bath, each of which is assumed to have the same spectral density. While the C-HEOM can handle any kind of an energy distribution or spectral density of the bath, as a first test case we employ a Drude-Lorentz form of the system-bath coupling so that the scheme can be tested against the exponential HEOM. Thereafter, we employ an Ohmic spectral density and compare C-HEOM results with the ML-MCTDH scheme, followed by a super-Ohmic spectral density that we employ to show the capabilities of the C-HEOM.

**Drude-Lorentz Spectral Density**

The Drude-Lorentz form of the spectral density is given by

$$\mathcal{J}(\omega) = 2\pi \lambda \gamma \frac{\omega}{\omega^2 + \gamma^2},$$

with the real parameters $\gamma$ and $\lambda$. Since each bath is connected to its own thermal bath, the spectral densities could vary but for simplicity we assume that the system-bath coupling is the same for all sites. The parameter $\gamma$ denotes the inverse correlation time and determines the width of the function, while the parameter $\lambda$ denotes the reorganization energy and determines the amplitude of the function. For the simulations shown in this section the correlation time is chosen to be $1/\gamma = 100$ fs, the electronic coupling $V_{12} = V_{21} = 100$ cm$^{-1}$ while the temperature $T$ is set to 300 K. Two different configurations of the site energies are chosen for the test below. Fig. 1 shows the case where the site energies are equal, i.e., $E_1 = E_2$, while Fig. 2 shows a biased case where the energy of the one site is higher than that of the other one, i.e., $E_1 - E_2 = 100$ cm$^{-1}$. For the above scenarios we show results for four different values of the reorganization energy, which represents the strength of the electronic coupling, ranging from low to high values. Each of the panels for the different values of $\lambda$ shows the population dynamics of the first site given by the first element (1, 1) of the density matrix. The converged exponential HEOM results mentioned earlier are obtained from Ref. 156 while the C-HEOM TL2 results have been discussed already in Ref. 95. The population dynamics that are converged in the system-bath coupling are obtained by increasing the number of tiers utilized in the HEOM scheme until no change in the dynamics is visible anymore. The larger the reorganization energy, the higher the number of tiers in the HEOM scheme required to achieve convergence.

For the case of equal site energies, i.e., $E_1 = E_2$, one can see that for the lowest reorganization energy, the agreement between all approaches and tiers is good. Since the influence of the bath on the system is very low, even the second-order perturbative treatment of the system-bath coupling can account for the effects of the environment correctly. For $\lambda = 20$ cm$^{-1}$ the level of damping in the oscillations shown
Figure 4.4: Time evolution of the population on the first site which is initially populated for different reorganization energies. The site energies are set to equal values for this case.

by C-HEOM TL2, TNL2 and TNL4 starts to differ from the converged results that are most closely obtained by TL4 C-HEOM. For the reorganization energy value set to 100 cm\(^{-1}\), the TL4 C-HEOM deviates from the converged results and remains close to the TL2 C-HEOM, while the TNL4 and TNL2 C-HEOM results shows higher oscillations which are a characteristic of the TNL approach, where the next tier of HEOM is simply put to zero. Thus, the second-order perturbation theory, i.e., TL2 and TNL2, as well as the fourth-order TNL4 and TL4 C-HEOM find their theoretical limits already in the intermediate coupling regime. For the highest coupling strength of 500 cm\(^{-1}\), the TNL4 as well as the TL4 versions of the C-HEOM seem to decay to erroneous values with the TNL version showing higher oscillations. As compared to the converged results, TL2 C-HEOM appears to be overdamped and decays to the thermal equilibrium quickly, while TNL2 C-HEOM predicts a dynamics that decays too slow.

For the case of unequal site energies shown in Fig. 2, the overall picture is somewhat different. Similar to the above case, the fourth and even the second-order perturbative approaches yield an accurate description of the level of damping when the reorganization energy is low, i.e., \(\lambda = 2\) cm\(^{-1}\). Already for intermediate coupling strengths, the TL4 C-HEOM can be seen to deviate from the equilibrium value of the converged results although it follows the dynamics of the converged E-HEOM closely for the initial part, at least for \(\lambda = 20\) cm\(^{-1}\). At the same time, the TNL4 C-HEOM results reach the equilibrium value of the converged results more closely, albeit showing a lower damping or higher oscil-
The second-order TL scheme is overdamped as compared to converged E-HEOM values, while the TNL version predicts higher oscillation amplitudes. For the highest reorganization energy shown (\(\lambda = 500 \text{ cm}^{-1}\)), the TL4 as well as TNL4 C-HEOM deviate strongly from the equilibrium populations at longer times, while the TL2 and TNL2 C-HEOM seem to decay to the correct equilibrium values. This indicates that using more tiers of the HEOM does not necessarily provide better results, i.e., results closer to the converged dynamics. As convergence is not achieved by neither the first nor the second-tier approaches, the accuracy of the results is difficult to assess. Before convergence is achieved, different tiers could behave differently, a higher one not necessarily being better than the lower ones, and each may show its own peculiar behavior. Successive tiers of the HEOM may show convergence to a particular converged value for a chosen, specific set of parameters, but might behave completely different in another parameter regime. Overall one can see that the TL4 or TNL4 C-HEOM, which represent the fourth order in perturbation theory, do perform better only for a small range of system-bath coupling strengths. For low to intermediate coupling strengths, the second tier or fourth order can be seen to perform better than the second order schemes, but for higher values of the reorganization energy one needs an enlarged number of tiers of the HEOM in order to achieve convergence. Moreover, the TNL2 as well as TNL4 results are obtained both from the Chebyshev version of the HEOM as well as the exponential scheme and are equal (data not shown). Thus, we can conclude that the presented C-HEOM approach
is a valid scheme and provides the same results as the E-HEOM for scenarios in which both of them can be applied without further approximations. In this work we conducted simulations only for the second tier truncation of the C-HEOM, which can in principle be extended to higher tiers. Memory constraints would not allow the extension of the scheme to a high number of tiers and thus the formalism may be inapplicable to strong coupling regimes unless the computational load is somehow reduced by, for example, implementing the C-HEOM scheme on parallel processing units.

**Ohmic Spectral Density**

Next we apply the time-local versions TL2 and TL4 as well as the time non-local version TNL2 of the C-HEOM approach to the dissipative dynamics in two level systems at zero temperature. In this case, the system is in contact with a bosonic bath that is described by an Ohmic spectral density given by

\[ J(\omega) = \frac{\pi \lambda \omega}{4 \omega_c} \exp\left(\frac{-\omega}{\omega_c}\right). \]  

(4.56)

As a benchmark we utilize the ML-MCTDH approach [7, 194] to provide converged results of quantum dissipative dynamics as reported in Ref. [135]. This test is carried out in order to further demonstrate the capability and reliability of the C-HEOM formalism. Specifically, it should be shown that the numerical cost of the C-HEOM remains constant at all temperatures, including \( T = 0 \) K, a property that sets the C-HEOM completely apart from the exponential HEOM. With decreasing temperature the exponential HEOM requires more terms from the Matsubara or Padé expansion to achieve convergence and to accurately obtain the dynamics. Thus, at low temperatures the application of the exponential HEOM is severely limited. While the extended HEOM [135] is expected to be available at an arbitrary temperature under the condition that a proper expansion set is applied, the C-HEOM is available at all temperatures without any accompanying restrictions.

As in the previous section, two different configurations of the site energies have been chosen. Figure 3 shows the equal site energy case, i.e., \( E_1 = E = 2 \), while Fig. 4 shows the biased case where the energy of the first site is higher, i.e., \( E_1 - E_2 = 100 \) cm\(^{-1}\). The initial population of site one is again set to one. The calculations have been performed using the C-HEOM approach for different sets of parameters \( \Delta \), i.e., the coupling strength between the sites, and \( \lambda \), the reorganization energy. The same parameters sets as in Ref. 135 were selected to be able to compare to the converged ML-MCTDH results.

For the cases with the largest inter-site coupling, i.e., \( \Delta = 100 \) cm\(^{-1}\), the C-HEOM results improve with the order of the hierarchy and gradually converge to the benchmark result obtained by the ML-MCTDH approach. These cases are depicted in panels c) and d) of Figs. 4 and 5. For \( \Delta E = E_1 - E_2 = 0, \Delta = 40 \) cm\(^{-1}\), and \( \lambda = 40 \) cm\(^{-1}\) shown in Fig. 4 a, the TL4 findings seem to follow the converged results the best, albeit being slightly overdamped. The TL2 findings, while retaining the correct damping strength, deviate slightly in phase. If one cranks up the reorganization energy \( \lambda \), as shown in Fig. 4 b, the TL4 results follow the converged results much better than the TL2 ones. For the biased site energy case shown in Fig. 5, with \( \Delta = 20 \) cm\(^{-1}\), and \( \lambda = 40 \) cm\(^{-1}\), the TNL2 scheme behaves most accurately, while for higher reorganization energy \( \lambda \) the TL2 findings mimic the converged results.
Figure 4.6: Population dynamics of the initially populate site. Quantum Ohmic noise ($\omega_c = 10$ ps$^{-1}$) is employed at zero temperature: (a) $\lambda = 40$ cm$^{-1}$ and (b) $\lambda = 120$ cm$^{-1}$ (both with $\Delta = 40$ cm$^{-1}$); (c) $\lambda = 80$ cm$^{-1}$ and (d) $\lambda = 200$ cm$^{-1}$ (both with $\Delta = 100$ cm$^{-1}$). The site energies are set to equal values.

closely. As already discussed above, improving the tier by one order does not always directly increase the results as can be seen for this case in the transition from TL2 to TL4.

Super-Ohmic Spectral Density

To obtain a spectral density with a super-Ohmic character, we utilize the following function, setting the value of $s$ to 4

$$J(\omega) = \frac{\pi \lambda s}{4\Gamma(1 + s)} \left(\frac{\omega}{\omega_c}\right)^s \exp\left(-\frac{\omega}{\omega_c}\right).$$  \hspace{1cm} (4.57)

According to the value of $s$, the spectral density given above can be classified into three categories

- $0 < s < 1$: sub-Ohmic;
- $s = 1$: Ohmic;
- $s > 1$: super-Ohmic;
While the Ohmic spectral density \((s = 1)\) has been thoroughly investigated by analytical and numerical approaches, the dynamics for the sub-Ohmic \((0 < s < 1)\) and especially for the super-Ohmic \((s > 1)\) cases are less thoroughly understood \([?, ?]\). Using the C-HEOM, the super-Ohmic case can be studied at the numerical cost of other simpler spectral densities, even at zero temperature. In Fig. 5 we show results using the TL2 and TL4 schemes as well as TNL2 using C-HEOM for a two-site system at zero temperature attached to a super-Ohmic environment. To this end, we study the above system for two different values of reorganization energy \(\lambda\). The parameter \(\omega_c\) is kept at 10 ps\(^{-1}\), while the electronic coupling is set at \(V_{12} = V_{21} = 100\) cm\(^{-1}\). For \(\lambda = 2\) cm\(^{-1}\) one obtains no difference between the aforementioned tiers tested here, thus for low reorganization energies one obtains converged results using even the second order in perturbation theory. This is shown in Fig. 5 by the curves showing low damping. Moreover, we tested the initial tiers of the C-HEOM for a reorganization energy \(\lambda = 30\) cm\(^{-1}\) shown in Fig. 5 by the lines that show a higher damping. As can be seen, TL2 slightly deviates from the TL4. As evident from the previous section, for larger \(\omega_c\), i.e., 100 cm\(^{-1}\), the second tier of the C-HEOM has more or less converged to the accurate results of the ML-MCTDH approach for \(\lambda = 80\) cm\(^{-1}\). It is therefore reasonable to assume that the results here for \(\lambda = 30\) cm\(^{-1}\) are not far from convergence.
Figure 4.8: Population dynamics of the site which is initially populated for a super-Ohmic spectral
density at zero temperature for two different values of $\lambda$. The site energies are assumed the same.

4.2.5 Conclusion

In this paper we have introduced a new hierarchical equation of motion by employing the Chebyshev
decomposition of the bath correlation functions. The C-HEOM approach presented forms an extension
of the already reported work for the second-order QME [95] which is identical to the first tier C-HEOM.
Here we have derived the general formula for calculating the C-HEOM to any number of tiers and
presented numerical results for the first and second tier truncation of the C-HEOM. We note that the
simulation time using the C-HEOM scales linearly with the number of Chebyshev polynomials utilized in
the expansion of the bath correlation functions. With regard to the second-order QME, this restriction
does not create any numerical hindrance since the sizes of the involved matrices are small. In fact, for
moderate simulation time the Chebyshev based QME, i.e., TL2 C-HEOM, approach in general takes up
to two orders of magnitude less time to generate the results compared to the exponential decomposed
QME. However, the story changes when one goes a higher number of tiers (or orders if one is talking
in terms of perturbation theory) in the EOMs. Already the second tier of the C-HEOM performs on a
similar level as compared to the E-HEOM as far as the time taken to simulate a certain simulation time
is concerned. In general for the Chebyshev based scheme, the higher the tier of the hierarchy, the larger
the size of the auxiliary matrices it is composed of. For example, while the size of the first tier auxiliary
operators depends linearly on the number of Chebyshev polynomials utilized, the size of the second-tier
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auxiliary operators scales with the square of the number of Chebyshev polynomials, i.e., one has a quadratic scaling. The situation worsens for three tiers, where the above mentioned scaling becomes cubic. Thus, in general, if \( n \) represents the tier of the C-HEOM, and in fact also of the E-HEOM, then the size of auxiliary operator scales as \( \mathcal{O}^n \). In the case of the E-HEOM, where the scaling behavior is the same, one does not see any practical hindrance as the simulated time does not depend on the number of poles utilized in the exponential decomposition scheme. The number of poles over which a sum is taken to reproduce the correlation functions in terms of a sum of weighted exponential functions, the number which is truncated at a certain point where one can observe converged results, is affected only by the shape of the Bose-Einstein or the Fermi function or the temperature of the bath(s), and the spectral density, i.e., the form or shape of the energy distribution of the particles in the bath. Thus, for a fixed number of poles one can obtain converged results for an arbitrary length of time. The case of the Chebyshev decomposition scheme is, in a certain way, opposite to the case of the exponential decomposition scheme. There is no effect of the shape of the energy distribution function or the spectral density of the baths on the number of Chebyshev polynomials needed to produce converged results. But while one gains the ability to simulate arbitrary temperatures and forms of the bath density of states, one can only obtain converged results up to a certain simulation time after which the scheme breaks down. An estimate for terms needed to obtain converged results can be given by [113, 152, 153]

\[
N = \omega T + 10 \ln(\omega T) .
\] (4.58)

The C-HEOM scheme has a bottleneck in the above mentioned scaling and is thus only suitable for shorter to moderate lengths of time if one needs to employ higher tiers of the C-HEOM. Nevertheless the crucial advantage of the C-HEOM, as mentioned earlier, over approaches that utilize exponential functions to represent the correlation functions, such as the original HEOM, is that there is no limitation on the form of the spectral density or on the system temperature. Sharply fluctuating, even step-like energy profiles of the environment at zero temperature can be dealt with using the C-HEOM at no additional numerical cost as compared to single Lorentzian forms at high temperatures. The advantage of the C-HEOM then is twofold. Firstly, that the scheme can directly incorporate numerically or experimentally obtained spectral densities as well as an arbitrary range of temperatures without any need of fitting procedures or numerically unfeasible expansions. Secondly that it does so at no numerical penalty. This unique set of properties of the C-HEOM approach renders it preferable to the original HEOM for systems with low to intermediate coupling strengths.

As the number of tiers needed to obtain converged exciton dynamics increases with the system-bath coupling strength, higher coupling strengths can only be dealt with using higher tiers of the hierarchy. It is possible, however, to implement the C-HEOM on highly parallel processing units. This would allow the C-HEOM to be used for higher coupling strengths and/or to obtain the dynamics for longer simulation times. Complex spectral densities obtained from experiments [165, 166] or from a combination of classical molecular dynamics simulations and quantum chemical calculations [171, 187] that show complex structures that cannot be reproduced by sum of Lorentzian functions [172] may be treated accurately using higher tiers of the C-HEOM approach. Work in this direction is in progress.
Chapter 5

Comparison of time dependent and independent models

The current through a molecular wire or junction can be modelled by a number of different theoretical approaches. The well-known scattering approach, the Landauer scheme, is applicable to regimes where coherent transport takes place, i.e., quantum coherence is preserved. If a molecular system is influenced by a fluctuating environment, e.g., a temperature dependent vibronic bath, time-dependent approaches, such as Quantum master equations, can be employed to determine the current dynamics. However, the effect of thermal environment can also be incorporated using time-independent methods. For instance, the Landauer-Büttiker approach can be modified to the Büttiker probe (BP) model [203–206] so that decoherence effects can be taken into account. Within a vibronic bath the coupling to phonons induces decoherence effects [207–210] (termed as vibronic dephasing), influencing the conduction of the molecular junction [211, 212]. Of the two kinds of probe models, “dephasing” and “voltage” probes, we consider here the former where the strength of the dephasing is empirically determined. The non-equilibrium Green’s function (NEGF) based schemes, such as the vibronic dephasing model [213–217] considered here, allow going beyond the coherent theory and can account for electron-phonon interactions directly. These interactions are incorporated as an additional self-energy term. On the other hand, time-dependent methods for incorporating environmental effects on molecular junction include also the time-dependent, TD-NEGF scheme, where the effect of the thermal environment is incorporated as the time-dependent fluctuations of site energies. The TD-NEGF scheme considered in this work includes the decomposition of the Fermi function and the spectral densities [82] and is exact for the non-interacting case. This TD-NEGF scheme is contrasted with the above-mentioned time-independent NEGF approach in this work. The time-averaged results of the TD-NEGF approach are found to agree with the results of the time-independent vibronic model in an excellent manner. The comparison aids in the understanding of the relationship between these pure dephasing schemes, which seem considerably different at the first glance. Both of these methods describe decoherence effects produced by phonons which effect conduction across the junction. However the way this influence is realized is different in each model. The idea of this work is to compare these both to evaluate and understand their similarities and differences. The time-independent vibronic dephasing, VD-NEGF scheme, uses the
Meir-Wingreen-Jauho formula to calculate the steady state current through the system. Whereas an efficient version [129] of the TD-NEGF scheme is used to calculate the time-dependent current across the junction.

The typical formulation of the molecular junction is considered here, where a chain of \( N \) sites is in contact with two fermionic reservoirs on either side. A tight binding description is considered here and the total Hamiltonian of the system is composed of the usual system, reservoir and tunnel-coupling parts, as well as terms describing the coupling of the electronic system to the phonon bath and the phonon bath itself. The present work considers a system of two sites attached to reservoirs on the left and right side, with each site being in contact with its individual vibronic bath as well. A Drude spectral density is employed to couple the sites with the above-mentioned bosonic baths. The Drude form is used since it’s possible to numerically generate the time-dependent noise equivalent to this spectral density. For the TD-NEGF case the bosonic bath is indirectly incorporated as fluctuating site energies, with fluctuations being modelled by a Gaussian distributed coloured noise. A wide-band limit is assumed and the temperature of the system is set to 300K. The comparison results are obtained for a range of values of reorganization energies for three values of the correlation times and two different setups of the averaged site energies. For the TD-NEGF scheme, the current is time-averaged from the point where the initial transient behavior vanishes. Without any noise present, the current assumes the highest value when the site energies are equal, thereafter with an increase in the noise, the current through the junction decreases. For the setup with unequal site energies, the current starts from a small non-zero value at zero noise and rises to a maximum value at a certain level of the noise or reorganization energy which can be considered to be the point when the transfer between the sites is resonant. For larger reorganization energies the current flow again decays to a smaller value. The results obtained by the TD-NEGF and the VD-NEGF approaches are almost identical, except at larger reorganization energies, where minute differences can be seen, which can be attributed to the averaging procedure of the time-dependent currents which is not extremely accurate when the noise causes large fluctuations in the current. To further test the two theories, we performed tests with setups of three and four sites as well. For these setups the two schemes once again showed excellent agreement. Thus, the two studied schemes yielded the same results when it comes to the (average) current through the device. If the average current is the required observable, the VD-NEGF scheme is more efficient to use, while the TD-NEGF can yield other observable quantities such as the population dynamics as well as the time dependencies in the current.

5.1 Dephasing from time-dependent and independent perspectives

In recent years the scientific interest in the charge transport characteristics of molecular junctions has grown enormously, both theoretically [53, 71, 218, 219] as well as experimentally [54, 55, 120, 220–222]. Molecular junctions form integral active elements in molecular electronics and their theoretical understanding is essential for the development of functional molecular systems such as nanoscale electronics [43, 223, 224]. The molecules utilized in such junctions for the formation of molecular wires often consist of conjugated structures [59, 225–227]. Another class of systems contains biological molecules like DNA due to their important role in the life sciences as well as in electronic applications [123, 228, 229]. Experimentally, molecular junctions may be realized, e.g., as mechanically controlled break junctions or as scanning tunneling microscopy break junctions allowing a direct current measurement [71].

To model the current flow through a single molecule, several theoretical approaches have been developed. The coherent time-independent charge transport can be calculated by means of the Landauer-Büttiker approach (also known as the scattering method), which is practically formulated in terms of the Green’s function technique [146, 230–232]. Apart from scattering approaches, nonequilibrium Green’s function (NEGF) based approaches and quantum master equations (QME) schemes [131] are among the alternative approaches which may be utilized for the determination of the charge dynamics through molecular junctions [233, 234].

When charge transport is influenced by environmental effects and temperature dependent vibrations, quantum coherence is not preserved and scattering approaches are not sufficient as they are often limited to coherent scenarios. To overcome this drawback, the Landauer-Büttiker method can be extended by the Büttiker probe (BP) model [203–206] which allows taking decoherence effects into account empirically. As phonons we denote here vibrational modes associated with any nuclear vibration [235]. The coupling to these phonons induces decoherence effects [207–210], influences conduction [211, 212] and also has functional applications, e.g., in molecular switches [236].

An efficient version [129] of the TD-NEGF formalism that builds upon the decomposition of the Fermi function and the spectral densities [82] is utilized in the present study. This TD-NEGF formalism is known to be exact for describing the non-interacting case, i.e., when electron interactions are neglected.

There are several options how to include decoherence effects in time-independent charge transport calculations. One way is to use the Büttiker probe model which relies on the idea of virtual probes coupled to the system. There are two main variants of this probe technique, the “dephasing” probes which allow only elastic scattering and the “voltage” probes only allowing for inelastic-dissipative scattering [206, 237]. Here we focus on the former variant in which the strength of the dephasing is chosen empirically. On the other hand, a more physical approach is to go beyond the coherent theory and to use an NEGF method which allows including electron-phonon interaction directly in the so-called vibronic dephasing model [213–217], which will be called VD-NEGF approach in the following. In the elastic approximation, the electron-phonon coupling can be taken into account by an additional self-energy, which depends on the Green’s function at the same energy. A comparison of the dephasing Büttiker
As mentioned already above, environmental effects on the charge transport through a molecular junction can also be treated in a time-dependent manner using, e.g., the TD-NEGF formalism. The vibrations of the environment but also of internal vibrations lead to time-dependent fluctuations of the site energies which in turn influence the conduction. The TD-NEGF scheme has been compared in detail to the Landauer approach [50, 90]. The latter scheme has been found to be reasonable when delocalization of the molecular eigenstates responsible for transport is not changed drastically and when the charge transfer between molecular wire and the respective contacts is fast with respect to the molecular correlation time [50].

The VD-NEGF scheme is an improvement of the original Landauer formalism and naturally the question arises how the VD-NEGF scheme compares to the TD-NEGF scheme. Although both methods describe physical decoherence phenomena induced by phonons the way it is realized is different. The aim of this paper is to compare both models and to understand the similarities as well as the differences. A schematic diagram of the two models is given in Fig. 1. In the next Section the two scheme are described in more detail while Section 3 describes how the two models can be compared. Thereafter, the results are shown and discussed. Finally, the results of the comparative study are summarized in the last Section.

### 5.1.1 Hamiltonian

As usual, the molecular junction is modeled as a chain of $N$ sites in contact with fermionic reservoirs. The total Hamiltonian of the molecular wire sandwiched between two electrodes, which are assumed to be in equilibrium, can be written as

$$\hat{H}(t) = \hat{H}_S(t) + \hat{H}_R + \hat{H}_{SR} + \hat{H}_B + \hat{H}_{SB} \quad (5.1)$$
where $\hat{H}_S(t)$ describes the time-dependent electronic properties of the relevant system part, namely the molecular wire which actually can consist of a single molecule only. It can be represented as a quantum wire by using a nearest-neighbor tight-binding model

$$\hat{H}_S(t) = \sum_{i=1}^{N} E_i(t) c_i^\dagger c_i - \Delta(t) \sum_{i=1}^{N} \left( c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i \right)$$

(5.2)

where $c_i^\dagger$ ($c_i$) denotes the creation (annihilation) operator at site $i$, $E_i(t)$ the time-dependent onsite energies and $\Delta(t)$ the possibly time-dependent charge transfer integral between to adjacent sites. The leads are defined as fermionic (electronic) baths

$$\hat{H}_R = \sum_{\alpha=L,R} \sum_k \varepsilon_{\alpha,k} b_{\alpha,k}^\dagger b_{\alpha,k}$$

(5.3)

where the operator $b_{\alpha,k}^\dagger$ ($b_{\alpha,k}$) creates (annihilates) a particle with energy $\varepsilon_{\alpha,k}$ in the reservoir state $k$ in lead $\alpha = L/R$. The wire-lead coupling is characterized by the tunneling Hamiltonian

$$\hat{H}_{SR} = \sum_{\alpha,k} \sum_i T_{\alpha,k,i}^\alpha b_{\alpha,k}^\dagger c_i + T_{\alpha,k,i}^{\alpha*} c_i^\dagger b_{\alpha k}$$

(5.4)

where $T_{\alpha,k,i}^\alpha$ describes the coupling between reservoir state $k$ and system state $i$. The details of the coupling between molecular wire and fermionic reservoirs can be assembled in the reservoir spectral density also termed broadening function. In general, non-vanishing coupling amplitudes $T_{\alpha,k,i}^\alpha$ can be present between any site $i$ of the wire and any state $k$ of each reservoir $\alpha$ leading to

$$\Gamma_{\alpha,ij}(\epsilon) = 2\pi \sum_k T_{\alpha,k,j}^\alpha(\epsilon) T_{\alpha,k,i}^{\alpha*}(\epsilon) \delta(\epsilon - \epsilon_{\alpha k}) .$$

(5.5)

This broadening function is often given in a matrix form with respect to the site indices, i.e., $\Gamma_{\alpha}(\epsilon)$. In the numerical examples below, we assume for simplicity that only the first (site 1) or left-most and the last (site $N$) or right-most site of the wire are coupled to the left and right electrode, respectively. Thus, only one element for each of the matrices $\Gamma_L(\epsilon)$ and $\Gamma_R(\epsilon)$ is non-zero in this case.

The main objective of this study is to investigate the effect of additional phonon baths on the conduction through a molecular junction. This is described by the last two terms in Eq. (5.1). The coupling of the phonon bath to the electronic system is described by

$$\hat{H}_{SB} = \sum_{i,j} \sum_q \xi_{ij,q} (d_q + d_q^\dagger) c_i^\dagger c_j$$

(5.6)

where $\xi_{ij,q}$ represents the coupling strength and the operator $d_q^\dagger$ ($d_q$) creates (annihilates) a phonon with the respective energy. In the applications below, we assume that the electron-phonon interaction
occurs just site-locally, i.e., $\xi_{ij,q} = \delta_{ij}\xi_{ii,q}$. Then the coupling Hamiltonian reads

$$\hat{H}_{SB} = \sum_i \sum_q \xi_{ii,q} (d_q + d_q^\dagger)c_i^\dagger c_i = \sum_i \Phi_i c_i^\dagger c_i , \quad (5.7)$$

where we have defined the bath part of the system-bath interaction as $\Phi_i$ for later reference. Thereby all information regarding the coupling between system and phonon bath are characterized by the so-called phonon spectral density $J_i(\omega)$ at site $i$

$$J_i(\omega) = \sum_q \frac{\xi_{ii,q}^2}{2m_q\omega_q} \delta(\omega - \omega_q) \quad (5.8)$$

with $m_q$ and $\omega_q$ denoting the mass and frequency of the bath oscillators, respectively. It can be determined as [169,238]

$$J_j(\omega) = \frac{\beta \omega}{\pi} \int_0^\infty dt \, C_j(t) \cos(\omega t) \quad (5.9)$$

where the inverse temperature is denoted by $\beta = 1/(k_B T)$. This expression shows that the spectral density can be given as a half-sided Fourier transform of the energy autocorrelation function by $C_i(t) = \langle \Delta E_i(t)\Delta E_i(0) \rangle$ with the energy fluctuations $\Delta E = E - \langle E \rangle$. At this point we need to state that for a consistent use of the high-temperature limit, the prefactor $\beta \omega/\pi$ is being employed instead of $2\tan(\beta \hbar \omega/2)/(\pi \hbar)$ as used earlier [133, 156]. Moreover, the spectral density of the present Holstein model is connected to that of the similar Caldeira-Leggett model $J_{CL,j}(\omega)$ by a factor, i.e., $J_{CL,j}(\omega) = \frac{\pi}{\hbar}J_j(\omega)$. To describe the coupling to the environment by a single number, one usually defines the reorganization energy of the bath $\lambda_i$ as

$$\lambda_i = \int_0^\infty \frac{J_i(\omega)}{\omega} d\omega . \quad (5.10)$$

The results below will also be discussed in terms of the reorganization energy.

### 5.1.2 Time-dependent Green’s function method

As mentioned earlier, the TD-NEGF formalism utilized herein is introduced in Ref. 82 where the authors combine the TD-NEGF formalism with a spectral decomposition of the spectral density of the electronic baths. This decomposition results in an expression of the self-energies composed of a weighted sum of exponentials, forming the basis of the derivation of differentials equations for reduced-system density operator in the single-particle basis $\rho_S^{s.p.}(t)$. This operator is related to the multi-particle operator of the density matrix by $\rho_S^{s.p.}(t) = Tr_S\{c_i^\dagger c_i \rho_S(t)\}$. 85
The self-energies of the leads are given by [82]

\[
\Sigma_\alpha^<(t_1,t_2) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\varepsilon \, f_\alpha(\varepsilon - \mu_\alpha) e^{-i(\varepsilon(t_1-t_2))/\hbar} \Gamma_\alpha(\varepsilon),
\]

(5.11)

\[
\Sigma_\alpha^>(t_1,t_2) = -\frac{i}{2\pi} \int_{-\infty}^{\infty} d\varepsilon \, f_\alpha(-(\varepsilon - \mu_\alpha)) e^{-i(\varepsilon(t_1-t_2))/\hbar} \Gamma_\alpha(\varepsilon),
\]

(5.12)

where \( f_\alpha(\varepsilon) \) denotes the Fermi distribution of lead \( \alpha \) and \( \mu_\alpha \) the corresponding chemical potential. Different decomposition schemes can be used for the Fermi function such as the partial fractional decomposition [7] or the Ozaki decomposition scheme [104]. The broadening function, \( \Gamma_\alpha(\varepsilon) \), for the coupling to the leads, i.e., the density of states of the leads weighted by coupling factors, needs to be given in terms of a sum of Lorentzian functions

\[
\Gamma_\alpha(\varepsilon) = \sum_{l=1}^{N_L} \frac{W_{\alpha l}^2 \Gamma_{\alpha l}}{(|\varepsilon - \varepsilon_{\alpha l}|^2 + W_{\alpha l}^2)}
\]

(5.13)

with the real parameters \( W_{\alpha l}, \Gamma_{\alpha l}, \) and \( \varepsilon_{\alpha l} \) determined, in general, during a fitting procedure [75].

In the TD-NEGF approach the coupling through the phonon bath is treated indirectly, i.e., through the fluctuation of the site energies induced by the environment. For a tight-binding system without leads this has been detailed in Ref. 156. Under the assumption that the phonon bath always stays in equilibrium if initially in equilibrium, the effect of the bosonic bath can be transformed into an additional time-dependent site energy term at site \( i \), namely \( \Delta E_i(t) = \langle \hat{\Phi}_i(t) | \hat{g}_B(t) | \hat{\Phi}_i(t) \rangle \) with the bath term of the system-bath coupling \( \Phi \) as defined in Eq. [7]. Therefore, the site energy at site \( i \), i.e., \( E_i(t) \), is replaced by \( E_i(t) + \Delta E_i(t) \) to account for the environmental effects. How these site energy fluctuations can be generated for a specific example is delineated below. Thus for the description of the TD-NEGF only the molecular wire and its coupling to the fermionic reservoirs needs to be taken into account.

The time evolution of the single particle reduced density matrix of the wire is given by [82,131]

\[
\frac{\partial \rho_{S}^{sp}(t)}{\partial t} = -\frac{i}{\hbar} [H_S(t), \rho_{S}^{sp}(t)] + \frac{1}{\hbar} \sum_{a,k} \{ \Pi_{ak}(t) + \Pi^\dagger_{ak}(t) \}
\]

(5.14)

\[
\frac{\partial \Pi_{ak}(t)}{\partial t} = -\frac{i}{\hbar} [H_S(t) - \chi_{ak}^+] \Pi_{ak}(t)
\]

(5.15)

\[
-\Gamma_{ak}^{<,+} - i(\Gamma_{ak}^{>,+} - \Gamma_{ak}^{<,+}) \rho_{S}^{sp}(t) - \frac{i}{\hbar} \sum_{\alpha',k'} \Omega_{ak,\alpha'k'}(t)
\]

\[
\frac{\partial \Omega_{ak,\alpha'k'}(t)}{\partial t} = -\frac{i}{\hbar} [\chi_{\alpha'k'}^-(t) - \chi_{ak}^+(t)] \Omega_{ak,\alpha'k'}(t)
\]

(5.16)

\[
+ (\Gamma_{\alpha'k'}^{<,+} - \Gamma_{\alpha'k'}^{<,+}) \Pi_{ak}(t) + (\Gamma_{ak}^{>,+} - \Gamma_{ak}^{>,+}) \Pi^\dagger_{ak}(t).
\]

In this expression the current matrices \( \Pi_\alpha \) are given by

\[
\Pi_\alpha(t) = \int_{t_0}^{t} dt_2 \left( G^>(t,t_2) \Sigma_\alpha^<(t_2,t) - G^<(t,t_2) \Sigma_\alpha^>(t_2,t) \right).
\]

(5.17)

In Eq. 5.14-5.16, the coefficients \( \chi \) and \( \gamma \) are described in detail in Appendix D. Here \( G^> \) and \( G^< \) denote the greater and lesser Green’s functions, respectively, and \( \Sigma^{\geq} \) are the corresponding self-energies. The
Green’s functions are defined in terms of system creation and annihilation operators

\[ G_{ij}^{<}(t_1, t_2) = \frac{i}{\hbar} \langle c_j^\dagger(t_1), c_i(t_2) \rangle, \quad (5.18) \]

\[ G_{ij}^{>(t_1, t_2) = -\frac{i}{\hbar} \langle c_i(t_1), c_j^\dagger(t_2) \rangle. \quad (5.19) \]

In terms of Green’s functions and reservoir self-energies the time-dependent current flowing from or to the lead \( \alpha \) is given by \([239]\)

\[ I_{\alpha}(t) = \frac{2e}{\hbar} \text{Re} \text{Tr} \left\{ \int_{-\infty}^{\infty} dt_1 \left[ G^{<}(t_1, t) \Sigma_{\alpha}^\alpha(t_1, t) + G^R(t, t_1) \Sigma_{\alpha}^{\leq}(t_1, t) \right] \right\} \quad (5.20) \]

where the subscripts \( a \) and \( r \) refer to the advanced and retarded versions of the respective Green’s function or the self-energy. In terms of the current matrices, \( \Pi_{\alpha} \), the time dependent current can be written as \([82, 131]\) \( I_{\alpha}(t) = \frac{2e}{\hbar} \text{Re} \text{Tr} \{ \Pi_{\alpha k}(t) \} \).

The mean current through the system, as reported in the results section, is given by \( I(t) = \left[ I_L(t) - I_R(t) \right]/2 \).

### 5.1.3 Elastic dephasing model

The vibronic dephasing NEGF approach (VD-NEGF) is a time-independent formalism and the respective quantities are defined in the energy rather than in the time domain as for the TD-NEGF. The system Hamilton is the same as defined in Eq.5.2 but with time-independent energies and couplings. The corresponding retarded and advanced Green’s functions are defined by \([?]\)

\[ G^R(\epsilon) = \left[ 1 - \hat{H}_S - \Sigma^R_L(\epsilon) - \Sigma^R_R(\epsilon) - \Sigma^R_{\text{deph}}(\epsilon) \right]^{-1}, \quad (5.21) \]

\[ G^A(\epsilon) = (G^R(\epsilon))^\dagger, \quad (5.22) \]

where \( \Sigma^R_L/R \) describes the retarded self-energy of the left/right lead and \( \Sigma^R_{\text{deph}} \) the influence of dephasing. For the calculation of transport properties we use the many-body nonequilibrium Green function formalism \([231, 232]\). Within this theory, the steady-state current can be expressed using the Meir-Wingreen-Jauho formula

\[ I = \frac{ie}{\hbar} \int_{-\infty}^{\infty} \text{Tr} \left\{ \left( \Gamma_L(\epsilon) - \Gamma_R(\epsilon) \right) G^I(\epsilon) \right\} \left( (f_L(\epsilon) I_L(\epsilon) - f_R(\epsilon) I_R(\epsilon)) (G^R(\epsilon) - G^A(\epsilon)) \right) d\epsilon, \quad (5.23) \]

where the greater and lesser green functions are defined by the Keldysh equation

\[ G^\geq(\epsilon) = G^R(\epsilon) \Sigma_{\text{tot}}(\epsilon) G^A(\epsilon). \quad (5.24) \]
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Here \( \Sigma_{\text{tot}} \) represents the total self-energy containing contributions from the leads as well as the decoherence effects. The former are defined similar to Eq. 5.11

\[
\Sigma_<(\epsilon) = i f_{\alpha}(\epsilon) \Gamma_{\alpha}(\epsilon),
\]

(5.25)

\[
\Sigma_>(\epsilon) = -i (1 - f_{\alpha}(\epsilon)) \Gamma_{\alpha}(\epsilon),
\]

(5.26)

where \( \Gamma_{\alpha} \) denotes the above defined broadening functions and \( f_{\alpha}(\epsilon) \) the equilibrium Fermi functions of the leads. As in Sec. 5.1.2, we consider decoherence effects by electron-phonon interactions, Eq. 5.6, and also assume a bath of independent oscillators. The corresponding lesser self-energy then reads [232]

\[
\Sigma_{\text{vib}}^<_<(\epsilon) = \sum_{q} \frac{i}{2\pi} \int M^q G^<_<(\epsilon - \epsilon') M^q D_{\alpha,q}^<(\epsilon') d\epsilon',
\]

(5.27)

where \( (M^q)_{ij} \equiv \xi_{ij,q} \) are the coupling matrix elements between electrons and phonons. We use an elastic Vibronic Dephasing (VD) model, [213–216] i.e., we assume that the energy of the phonons \( \hbar \omega_q \) is small compared to all other energy scales, so that no phonons are excited inelastically. Furthermore it is assumed that the electron-phonon interaction is uniform and occurs just site-locally, i.e., \( i = j \). With these approximations we can study the influence of pure dephasing which is comparable to the model described in Sec. 5.1.2. The corresponding self-energy reads

\[
\left[ \Sigma_{\text{VD}}^{R<}(\epsilon) \right]_{ij} = \gamma^2 G_{ii}^{R<}(\epsilon) \delta_{ij},
\]

(5.28)

where \( \gamma \) is the strength of the dephasing. It can be estimated as [213, 216]

\[
\gamma \approx \sqrt{k_B T \nu_{e-v}}.
\]

(5.29)

As depicted in Fig. 5.2.1, both methods describe decoherence effects caused by electron-phonon interactions but in different ways. While the time-dependent formalism assumes that dephasing is caused by site fluctuations, the steady-state formulation describes dephasing by the coupling of the electronic system to an equilibrium bath of vibrations as. In order to compare the two dephasing models, we find that the squared dephasing strength \( \gamma^2 \) can be expressed in terms of the phonon spectral density

\[
\gamma^2 = \int \left[ (f_B^{0}(-\omega) + 1) J(-\omega) + f_B^{0}(\omega) J(\omega) \right] d\omega.
\]

(5.30)

For spectra densities such as the Drude spectral density (see below) with \( J(-\omega) = -J(\omega) \), the squared dephasing strength \( \gamma^2 \) simplifies to

\[
\gamma^2 = \int 2 f_B^{0}(\omega) J(\omega) d\omega
\]

(5.31)

This formula allows to estimate the dephasing strength \( \gamma \) from a given polaron shift \( \epsilon_p^i = \frac{\xi^2_{ii}}{\omega} \) and thus a direct comparison of both methods.

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5.2 Modeling the environment

To be able to compare the time-independent vibronic dephasing model and the time-dependent approach with fluctuating site, one needs parameters for which an easy comparison is possible. In a previous study [156] part of the present authors have compared the population dynamics in a dimer system coupled to local bosonic baths determined using the HEOM density matrix approach with an ensemble-averaged wave packet approach which is equivalent to Ehrenfest dynamics without feedback from the baths to the primary system. The present study adds fermionic reservoirs to both ends of the dimer and thus the current through the dimer is the quantity of primary interest and not the population dynamics though this quantity can be analyzed as well. The present time-dependent Green’s function scheme TDGF in terms of the coupling to the bosonic baths is identical to the previously studied dimer without fermionic reservoirs. Treating the vibrational effects with a time-independent Hamiltonian is a common feature of the present vibronic dephasing model and the HEOM density matrix approach in case of the dimer. In the limit of vanishing molecule-lead couplings, the present molecular junction system with two sites reduced to the previously investigated dimer model. Thus, most of the results obtained earlier for the dimer model will be of quite some interest in interpreting the present results.

Moreover, as in the earlier study we will use Drude spectral densities for coupling the individual sites to bosonic baths. The Drude spectral density has the clear advantage, that the time-dependent noise being equivalent to this spectral density can easily be created numerically. At small frequencies the Drude spectral density is linearly increasing as function of frequency while it is decreasing exponentially for large frequencies. Each site \(i\) in the tight-binding system is coupled to an individual spectral density \(J_i(\omega)\) given by

\[
J_i(\omega) = \frac{2}{\pi} \lambda_i \gamma_i \frac{\omega}{\omega^2 + \gamma_i}. \tag{5.32}
\]

Here the inverse correlation time \(\gamma_i = \tau_i^{-1}\) is related to the width of the spectral density and \(\lambda_i\) denotes the reorganization energy as defined in Eq. 5.10. In the comparisons below all sites of the system will be connected to equivalent thermal baths and thus the index \(i\) will be dropped in the following. As discussed previously [156], the Drude spectral density corresponds to site energy fluctuations with an exponentially decaying autocorrelation function, i.e., \(C(t) = \langle \Delta E(t) \Delta E(0) \rangle = \langle (\Delta E(0))^2 \rangle \exp(-t/\tau) = C(0) \exp(-t/\tau)\). In case of the Drude spectral density, the autocorrelation function is given by

\[
C(t) = \frac{2\lambda}{\beta} e^{-t/\tau} \tag{5.33}
\]

with the inverse temperature \(\beta\). In the limit of vanishing \(\tau\) this colored noise goes over into white noise. In the energy domain we assume that the noise can be described by a Gaussian distribution centered at a value of 5 eV with a variance of \(\langle (\Delta E(0))^2 \rangle = C(0) = 2\lambda/\beta\). For the creation of the exponentially time-correlated noise we employed an approach by Fox et al. [240]. As an example, the fluctuating site energies of two sites are shown in Fig. 5.2.
Figure 5.2: Time dependence of the site energies of two sites with average energies $E_1=5.1$ eV and $E_2=4.9$ eV. The noise with a reorganization energy of 5000 cm$^{-1}$ (0.620 eV) at a temperature of 300 K was generated with a time step of 0.01 fs.
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5.2.1 Results

The VD-NEGF and the TD-NEGF approach are compared using the tight-binding model depicted in Fig. . In all test cases below, the temperature is assumed to be 300 K and the chemical potentials of the leads are fixed to $\mu_L=6$ eV at left side and $\mu_L=4$ eV at the right side. Thus, the conduction window has a width of 2 eV. All intersite couplings $\Delta$ in the tight-binding model of the molecular wire in the junction are fixed to a value of $\Delta = 100$ cm$^{-1}$ (0.0124 eV). Moreover, the coupling between molecular wire and leads are the same in all test cases since both schemes, i.e., the VD-NEGF as well as the TD-NEGF approach, do not perform any approximation in the molecule-lead coupling strength. For simplicity, the wide-band limit is assumed which in the TD-NEGF formalism is mimicked by a single broad Lorentzian function of width $W = 10$ eV centered in the middle of the conduction band, i.e., at 5 eV (see also Eq. 5.13). The coupling strength $\Gamma$ to both leads was set to $\Gamma_\alpha = 0.01$ eV.

In a first test we compare the TD-NEGF approach to the vibronic dephasing model for a two-site model. For the latter model the time-independent site energies are set to $E_1=5.1$ eV and $E_2=4.9$ eV while in the time-dependent scheme these values define the time-averaged values (see also Fig. 5.2).
The currents are determined for varying reorganization energies while the site energy fluctuations and the reorganization energy $\lambda$ are related by $\langle (\Delta E(0))^2 \rangle = 2\lambda/\beta$. As mentioned already, the sites are coupled to individual phonon baths which, however, have the same reorganization energies in the present numerical investigation. For a proper comparison of the VD-NEGF and the TD-NEGF schemes, one has to probe the agreement between the VD-NEGF scheme and a time-averaged current from the TD-NEGF formalism. The average is calculated starting from the time when the initial transient period ends which is also present in case of vanishing reorganization energies. This would be the time when steady state is achieved without noise and it depends on coupling to the leads and the initial populations of the sites which was chosen to be 0.5 in all cases. Following this philosophy, the current in the present examples was averaged from 1000 fs to 50,000 fs in the case of two-site systems (and from 1000 fs to 100,000 fs in the case of three and four-site systems).

The comparison for a molecular wire consisting of two sites is shown in Fig. 5.4. A large variety of parameters is actually shown. Three different correlation times with two unlike setups of average site energies as function of the reorganization energy. Let us start with the two different setups for the (average) site energies. In one case, the site energies are equal which in case of the time-dependent scheme needs to be interpreted as equal average site energies. Due to this favorable configuration, the current is largest with a value of about 1 $\mu$A when no noise is present. Coupling to the phonon baths decreases the respective current with increasing reorganization energy. The situation is different when the site energies are initially detuned by 0.2 eV. Then the transfer between the sites is quite small when no noise is present and increases to a maximum at a reorganization energy of about 0.4 eV before it decreases again. In the time-dependent scenario this maximum can be rationalized that at this reorganization energy, the most events of (nearly) resonant site energies happen. For site energies in resonance, the transfer between the site is largest. When the site energies are fluctuating with a smaller or amplitude, the frequency of (near) degeneracies is smaller leading to a smaller current. The results the TD-NEGF and the VD-NEGF approaches are almost identical. Only at larger reorganization energies, small differences are visible while we have to admit that the averaging of the time-dependent currents at large reorganization energies might not be as accurate as for smaller noise due to the large fluctuations involved. The differences for the results of different correlation times is quite small.

For the vibronic dephasing model the effect of the coupling to the bosonic bath can be seen in the so-called current spectral density.

To see if the excellent agreement between the TD-NEGF and the VD-NEGF schemes is only present for the two-site model, we also performed simulations with molecular wires consisting of three and four sites. The (average) site energies in case of the three-site system were $E_1=5.2$ eV, $E_2=5.0$ eV, and $E_3=4.8$ eV while for the four-site system the values were $E_1=5.3$ eV, $E_2=5.1$ eV, $E_3=4.9$ eV and $E_4=4.7$ eV. Thus, there was always a difference of 0.2 eV between the (average) site energies and a symmetry with respect to the middle of the conduction. As can be seen in Fig. 5.5, the agreement between the two models is again excellent while the $E_1=5.2$ eV, $E_2=5.0$ eV, and $E_3=5.2$ eV absolute currents decay with the number of sites. If one wants to interpret in the time-dependent picture, the current decays with any additional site which is not in resonance on average. The energy levels have to come into close resonance by the fluctuations which is only the case part of the time, thus reducing the
Figure 5.4: Currents through a two-site junction as function of the reorganization energy $\lambda$. Shown are three different panels for varying correlation times. The results for the vibronic dephasing model as well as the TD-NEGF approach are shown for two scenarios of average site energies, i.e., equal site energies of $E_1 = E_2 = 5$ eV and unequal ones $E_1 = 5.1$ eV and $E_2 = 4.9$ eV. The insets show the behavior for large reorganization energies in some more detail.

To better understand the high degree of similarity of the results in Fig. 5.4 for the three different noise autocorrelation time of 1 fs, 50 fs and 100 fs, we turn to estimates of the dephasing time. A clear relation can be found between the energy gap fluctuations and an estimate of the dephasing time for exciton and charge transfer systems [241–243]. The investigated charge transfer systems using a multi-scale approach were DNA, photolyase, and cryptochrome [242]. The energy gap fluctuations $\sqrt{\langle (\Delta E(0))^2 \rangle}$ in these systems ranged from 0.15 eV to 0.35 eV. Using $\langle (\Delta E(0))^2 \rangle = 2\lambda/\beta$ this results to reorganization energies in the range of roughly 0.4 eV to 2.4 eV. The numerical autocorrelation functions are not purely exponential but a fit to an exponentially decaying function leads to correlation times in the order of 10 fs [242]. Dephasing times between 3 fs and 7 fs were determined for the mentioned
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Figure 5.5: Currents as function of reorganization energy for a three and a four-site system.

An excellent agreement between the TD-NEGF and the time-independent VD-NEGF approach was observed. This agreement was only clear from the onset because the two schemes seem quite different when looking at the formulas. In both models, however, the sites are coupled to individual baths which is an important coincidence in the model building step. Moreover, both models are pure dephasing models. The coupling to a bath usually leads to a fast dephasing accompanied by an often slower
relaxation process. This second component is missing in both schemes, i.e., no inelastic processes are involved. In molecular junctions the significance of inelastic processes increases with increasing bias voltage. Moreover, in case of very small molecule-lead couplings, energy relaxation effects become more important since the electrons have more time to relax on the wire. For the extreme case of vanishing molecule-lead coupling (which would no longer describe a molecular junction) the problems of the missing relaxation terms in the time-dependent formalism have been discussed earlier \cite{156}. Actually, for the latter dimer model, corrections to include relaxation in models with fluctuating site energies have been discussed in the literature \cite{156, 244, 245}. It would be interesting to see if and how these correction terms could be applied to molecular junctions as well.

It is very reassuring, however, that the two studied and apparently difference schemes do yield the same results when it comes to the (average) current through the device. If one is only interested in the average current, the VD-NEGF schemes is surely the simpler way to go since no time propagation is needed. In this case one needs to have model system as described above with a known spectral density which does not need to be of the Drude form. In recent years, descriptions of molecular wires such as DNA were developed which were based on a time-dependent multi-scale description of the system of interest \cite{93, 246, 247}. The present results show that using the fluctuations from such an approach directly within the TD-NEGF approach yields results comparable to those of the vibronic dephasing model without going the detour through determining spectral densities including the underlying assumption such as harmonic baths. In addition, the TD-NEGF approach would offer a direct way how to couple dephasing effects and other time-dependent influences such as laser pulses \cite{62, 248} although a proper ensemble average would have to be performed.
Conclusion and outlook

The main new development presented in this thesis is methodological in nature. From the theoretical perspective, this development amounted to use of the Chebyshev expansion technique for the derivation of equations of motion and their subsequent numerical implementation. This novel approach is used to calculate the time evolution of systems attached to reservoirs. We mainly discussed three different theories of transport applied to two different kinds of particle systems, namely fermionic and bosonic systems, and calculated the charge transport dynamics through molecular wires as well as exciton transfer dynamics in molecular aggregates attached to phonon baths.

The approach presented in this thesis was first applied to the second-order QME [113] for fermionic systems. Here we show the extension of the Chebyshev scheme to a number of other transport theories and the corresponding applications. Specifically, in this work we present a Chebyshev based TD-NEGF scheme for fermionic systems, as well as Chebyshev based QMEs based on a second-order treatment of the environmental coupling and hierarchical equations of motion scheme for bosonic systems. The key advantages gained by the application of the Chebyshev decomposition and the comparative limitations of the standard approaches are discussed as well. One of the main strengths of the discussed Chebyshev decomposition approach is that it allows any kind of molecule-lead or system-reservoir coupling. This coupling is present in the spectral density or the level-width function, which describe the external properties of the reservoirs. In schemes such as the exponential decomposition, the spectral density needs to be approximated using Lorentzian functions. Although this scheme suffices for mimicking smooth spectral densities, in cases where the spectral densities show a nonlinear behavior, Lorentzian fitting does not perform well. In fact, it is only efficient if the spectral density can be represented accurately using only a few Lorentzian functions. Furthermore, the temperature range is restricted to low temperatures since a high number of terms are needed in the decomposition of the Fermi or Bose-Einstein function. Although other parametrization schemes exist that make use other kinds of functions to fit the energy profiles stemming from superohmic behavior, the fitting procedures for mimicking experimental or numerically obtained spectral densities are highly complicated, at least for systems that display a strongly varying peak structure.

The Chebyshev decomposition method basically consists of a different expansion of the reservoir self-energies or correlation functions using Chebyshev polynomials and bessel functions. This scheme does not involve an expansion of the Fermi function or of the spectral density function but rather incorporates them in their natural forms. The expansion of the Fermi function faces a limitation at low temperatures since the Fermi function becomes highly steep, and its series expansion requires a
large number of terms resulting in a highly inefficient numerical treatment. The Chebyshev based approach removes the restriction of having to use simple forms of spectral densities as well and enables the treatment of systems with rapidly fluctuating environmental energy profiles. Thus there remain no limitations regarding the simulation of arbitrarily low temperatures and truly arbitrary forms of spectral densities. Moreover, one is able to treat sharp gaps, peaks and discontinuities in the spectral density at exactly the same numerical cost as it takes to treat smoothly varying functions. This ability is in stark contrast to the exponential decomposition approach, where one needs a large number of terms to mimic sharply varying energy profiles. This property of the Chebyshev approach has high practical relevance and can be used to calculate the dynamics of realistic systems. For example, the energy profile of gold has a sharp gap in it which can easily be dealt with within the Chebyshev approach. Furthermore, for the case of bosonic systems, complex spectral densities extracted from experiments [165, 166] or from a combination of classical molecular dynamics simulations and quantum chemistry calculations [167–171] show highly complex structures that can only be approximated by sum of Lorentzian functions [172], while the Chebyshev approach can incorporate any level of complexity of the spectral densities including those that are experimental or numerically obtained in an exact manner. Thus this scheme can have highly relevant use-cases in both fermionic as well as bosonic systems.

To validate the C-NEGF scheme we used a single resonant level and tested the obtained time-dependent current against the usual E-NEGF results. As both theories are able to deal with time-dependent system Hamiltonians we performed comparisons for systems under external influences, such as monochromatic and pulsed laser fields. Moreover, we applied the C-NEGF for the calculation of charge transport properties in a multi-site system. This situation corresponds to having a DNA system in water [90] with site energies of the system obtained by using molecular dynamics (MD) and quantum chemical simulations. To mimic the scenario of a molecular chain between two leads immersed in a solvent [?] we model site energy trajectories using Gaussian distributed trajectories. Moreover, the obtained site energies are exponentially correlated in time. We put this system in contact with two types of reservoir band structures or spectral densities. The simple case of the wide-band limit with an energy-independent spectral density, which can also be studied using the E-NEGF scheme, was employed to test and confirm the C-NEGF results. Next we used a spectral density with a gap and sharp edges. While the E-NEGF scheme is not able to simulate such a band structure, the C-NEGF scheme can handle it without any additional numerical effort as compared to the simulation of the above-mentioned energy-independent molecule-lead coupling. Thus, complex and realistic band structures can be simulated at the computational cost of trivial band structures using the Chebyshev approach.

It is to be noted that C-HEOM scheme as well as the NEGF scheme presented herein can be computationally on the expensive side, depending on the system parameters. Especially for larger systems the computational requirements become a considerable hinderance. One of the ways in which this can be overcome is by the modification of the implementation of these schemes such that they can be run on parallel computers or graphical processing units (GPUs). The distribution of computational load would render these highly useful theories to larger systems by bringing about a significant speed-up in the simulation time. The newly developed Chebyshev HEOM would especially benefit from a GPU implementation. If higher tiers of the C-HEOM could be implemented, they would enable the
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calculation of population dynamics in strongly coupled systems. Moreover, more realistic scenarios using experimental or numerically obtained spectral densities could be dealt with in an exact manner.

Another useful and pertinent extension of the theories presented would be the implementation of a charge feedback loop between the charge transport step and the classical molecular dynamics (MD) simulations. This loop would feed the influence of the charge on the wire as well as the voltage across it into the quantum chemistry calculations. These effects are pertinent since the applied voltage may cause polarization in the solvent solvent molecules and the charge residing on the wire may bring about the formation of polarons. Thus, this improvement to the scheme would lead to a more complete picture of the charge transport by taking into account polaron effects.

The main drawback of the Chebyshev approach is that the simulation time is limited by the number of polynomials used in the expansion. The scheme has a quasi-linear dependence on the simulation time as well as on the spectral range $\Omega$ of the system. Thus, the computational time is adversely affected for larger system-reservoir coupling strength and positively affected for systems with a narrow spectral range. Moreover, the scheme brakes down after a specific simulation time, governed by the number of Chebyshev polynomials used. This, however, presents no limitations as such on the accuracy of the Chebyshev based schemes before the breakdown point.

The motivation behind applying the Chebyshev decomposition approach to the NEGF scheme was the need for an improved implementation of the TD-NEGF scheme as well as the advantages observed for the CDTL [113] scheme. The latter include a speed-up in computational time as well as the ability to incorporate any kind of lead spectral density at low temperatures. Although the C-NEGF approach neither contains a temperature dependence nor a dependence on frequency behavior of the molecule-lead coupling, it does not show a computational time speed-up like the CDTL for the aforementioned reasons. A useful scheme [129] that transforms all matrices in the NEGF scheme to vectors or scalars was coupled to the C-NEGF scheme to obtain considerable computational advantage including a linear dependence on the size of the system. This trick was applied to the faster E-NEGF scheme as well to further improve its numerical efficiency. The new vectorized NEGF schemes become highly suitable for the calculation of charge transport through larger and more realistic systems such as oligomers, peptides and DNA. Moreover, better, more quantitative descriptions of the molecule-lead coupling could be incorporated within the improved NEGF scheme in the future to understand the effect of non-wide band limit on charge transport.
A. Derivations of quantities within the NEGF framework

Here a derivation of the expressions for the quantities that appear in the Chapter 3 of this thesis as part of the TD-NEGF scheme is presented. These include the average time-dependent current through the system given in terms of Green’s functions and self-energies, the derivation of the EOMs of the NEGF framework derived using the Chebyshev expansion scheme. Further, the equations for the boundary cases of the first and second tier of the NEGF are given as well that arise due to the slightly different equations for the starting and ending cases within the sum over Chebyshev polynomials that is used to expand the self-energies.

A.1 Derivation of current and other relevant GF quantities in the TD-NEGF scheme.

Derivation of the to-be-used expression for the time dependent current, \( I_\alpha \), from Ref. 72.

\[
I_\alpha (t) = 2 eReTr\left( \int_{-\infty}^{\infty} dt_2 \left[ G^< (t, t_2) \Sigma_\alpha^a (t_2, t) + G^r (t, t_2) \Sigma_\alpha^< (t_2, t) \right] \right) = 2 eReTr\left( \Pi_\alpha (t) \right) \tag{A.35}
\]

where

\[
\Sigma_\alpha^a (t_2, t) = \Theta (t - t_2) \left[ \Sigma^\alpha_\alpha (t_2, t) - \Sigma^\alpha_a (t_2, t) \right]
\]

\[
G^r (t, t_2) = \Theta (t - t_2) \left[ G^> (t, t_2) - G^< (t, t_2) \right]
\]

and

\[
\Pi_\alpha (t) = \int_{-\infty}^{\infty} dt_2 G^< (t, t_2) \Sigma_\alpha^a (t_2, t) + G^r (t, t_2) \Sigma_\alpha^< (t_2, t)
\]

\[
= \int_{-\infty}^{\infty} dt_2 \left[ G^< (t, t_2) \Theta (t - t_2) \left[ \Sigma^\alpha_\alpha (t_2, t) - \Sigma^\alpha_a (t_2, t) \right] + \Theta (t - t_2) \left[ G^> (t, t_2) - G^< (t, t_2) \right] \Sigma^\alpha_\alpha (t_2, t) \right]
\]

\[
= \int_{-\infty}^{\infty} dt_2 \left[ \Theta (t - t_2) \Sigma^\alpha_a (t_2, t) G^< (t, t_2) - \Theta (t - t_2) \Sigma^\alpha_a (t_2, t) G^< (t, t_2) \right]
\]

\[
+ \Theta (t - t_2) G^> (t, t_2) \Sigma^\alpha_< (t_2, t) - \Theta (t - t_2) G^< (t, t_2) \Sigma^\alpha_< (t_2, t)
\]
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\[ \int_{-\infty}^{\infty} dt_2 \Theta(t - t_2) \left( G^>(t, t_2) \Sigma^\alpha_\alpha(t_2, t) - G^<(t, t_2) \Sigma^\alpha_\alpha(t_2, t) \right) \]

Thus

\[ \Pi^\alpha(t) = \int_{t_0}^{t} dt_2 \left( G^>(t, t_2) \Sigma^\alpha_\alpha(t_2, t) - G^<(t, t_2) \Sigma^\alpha_\alpha(t_2, t) \right) \] (A.36)

Given in the book of Di Ventra [230], for example, are the equations for the advanced and retarded Green’s functions. These can be used to derive the equations for the derivatives of the more relevant to this work lesser and greater Green’s functions.

\[ G^-(t, \tau) = G^a(t, \tau) = \frac{i}{\hbar} \Theta(\tau - t)e^{-\frac{i}{\hbar}H(t-\tau)} \] (A.37)

\[ G^+(t, \tau) = G^r(t, \tau) = -\frac{i}{\hbar} \Theta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} . \] (A.38)

Time derivatives of the advanced and regarted Green’s functions read:

\[ \frac{\partial}{\partial t} G^a(t, \tau) = \frac{\partial}{\partial t} \left[ \frac{i}{\hbar} \Theta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} \right] \]

\[ = \frac{i}{\hbar} [\delta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} + \Theta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)}( - \frac{iH}{\hbar})] \]

\[ = \frac{i}{\hbar} \delta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} - \frac{i}{\hbar} HG^a(t, \tau) \] (A.39)

\[ \frac{\partial}{\partial t} G^r(t, \tau) = \frac{\partial}{\partial t} \left[ -\frac{i}{\hbar} \Theta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} \right] \]

\[ = -\frac{i}{\hbar} [\delta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} + \Theta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)}( - \frac{iH}{\hbar})] \]

\[ = -\frac{i}{\hbar} \delta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} + HG^r(t, \tau) \] (A.40)

The time derivatives of \( G^\leq(t, \tau) \) can then be written as:

\[ \frac{\partial}{\partial t} G^\leq(t, \tau) = \frac{\partial}{\partial t} \left[ \Theta(t - \tau)(G^a(t, \tau) - G^r(t, \tau)) \right] \]

\[ = \left[ \delta(t - \tau)(G^a(t, \tau) - G^r(t, \tau)) \right] \] (A.41)
+\Theta(\tau - t) \left[ \frac{i}{\hbar}\delta(\tau - t)e^{-\frac{i}{\hbar}H(t-\tau)} - \frac{i}{\hbar}HG^a(t,\tau) + \frac{i}{\hbar}\delta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} + \frac{i}{\hbar}HG^r(t,\tau) \right] \\
= [\delta(\tau - t)G^a(t,\tau) - \delta(t - \tau)G^a(t,\tau)] + \Theta(\tau - t)\left[ -\frac{i}{\hbar}HG^a(t,\tau) + \frac{i}{\hbar}HG^r(t,\tau) \right] \\
= -\frac{i}{\hbar}HG^<(t,\tau) \\

\frac{\partial}{\partial t} G^>(t,\tau) = \frac{\partial}{\partial t} \left[ \Theta(t - \tau)(G^r(t,\tau) - G^a(t,\tau)) \right] \\
= \left[ \delta(t - \tau)(G^r(t,\tau) - G^a(t,\tau)) \right] + ... \\
... + \Theta(t - \tau) \left[ -\frac{i}{\hbar}\delta(t - \tau)e^{-\frac{i}{\hbar}H(t-\tau)} - \frac{i}{\hbar}HG^r(t,\tau) - \frac{i}{\hbar}\delta(\tau - t)e^{-\frac{i}{\hbar}H(t-\tau)} + \frac{i}{\hbar}HG^a(t,\tau) \right] \\
= \left[ \delta(t - \tau)G^r(t,\tau) - \delta(\tau - t)G^r(t,\tau) \right] + \Theta(t - \tau)\left[ -\frac{i}{\hbar}HG^r(t,\tau) + \frac{i}{\hbar}HG^a(t,\tau) \right] \\
= -\frac{i}{\hbar}HG^>(t,\tau) \\

Knowing that \\
\frac{\partial}{\partial t} \rho_S(t) = -\frac{i}{\hbar}[H_S(t),\rho_S(t)] + \frac{1}{\hbar}\sum_\alpha \left( \Pi_\alpha(t) + \Pi_\alpha^\dagger(t) \right) \\
(A.43) \\

\Pi_\alpha(t) = \frac{1}{\hbar} \int_{t_0}^t dt_2 \left( G^>(t,\tau_2)\Sigma^<_\alpha(t_2,t) - G^<(t,\tau_2)\Sigma^>_\alpha(t_2,t) \right) \\
(A.44) \\

and the Chebyshev decomposition of self-energies \\

\Sigma^<_\alpha(t) = \sum_{n=0}^{\infty} I^<_{\alpha,n} \Sigma^<_n(t) \\
\Sigma^>_\alpha(t) = \sum_{n=0}^{\infty} I^>_ {\alpha,n} \Sigma^>_n(t) . \\

We need to split the expression in the equation for \Pi_\alpha(t) as follows \\

\Pi_\alpha(t) = \tilde{\Pi}^<_\alpha(t) - \tilde{\Pi}^>_\alpha(t) = \frac{1}{\hbar} \int_{t_0}^t dt_2 \left( G^>(t,\tau_2)\Sigma^<_\alpha(t_2,t) - \frac{1}{2} \int_{t_0}^t dt_2 \left( G^<(t,\tau_2)\Sigma^>_\alpha(t_2,t) \right) \right) \\
(A.45)
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Which leaves the EOM for $\rho_S(t)$ as

$$\frac{\partial}{\partial t} \rho_S(t) = -\frac{i}{\hbar} [H_S(t), \rho_S(t)] + \frac{1}{\hbar} \sum_{\alpha} \left( (\Pi_\alpha^<(t) - \Pi_\alpha^>(t)) + (\Pi_\alpha^>(t) - \Pi_\alpha^<(t))^\dagger \right)$$

Inserting expressions of the self-energies given above we get

$$\Pi_\alpha^<(t) - \Pi_\alpha^>(t) = \frac{1}{\hbar} \sum_{\alpha,n} I_{\alpha,n} \left( \int_{t_0}^t dt_2 \, G^>(t, t_2)\Sigma_n^<(t_2, t) \right) - \frac{1}{\hbar} \sum_{\alpha,n} I_{\alpha,n} \left( \int_{t_0}^t dt_2 \, G^<(t, t_2)\Sigma_n^>(t_2, t) \right)$$

Grouping the terms inside the brackets in the above equations and defining auxiliary operators

$$\Pi_\alpha^<(t) - \Pi_\alpha^>(t) = \frac{1}{\hbar} \sum_{\alpha,n} I_{\alpha,n} \Pi_{\alpha,n}^<(t) - \frac{1}{\hbar} \sum_{\alpha,n} I_{\alpha,n} \Pi_{\alpha,n}^>(t)$$

where the auxiliary operators are

$$\Pi_{\alpha,n}^<(t) = \int_{t_0}^t dt_2 \, G^>(t, t_2)\Sigma_n^<(t_2, t) \quad (A.46)$$

$$\Pi_{\alpha,n}^>(t) = \int_{t_0}^t dt_2 \, G^<(t, t_2)\Sigma_n^>(t_2, t) \quad (A.47)$$

Finally, taking the time derivatives of $\Pi_\alpha^\Xi$

$$\frac{\partial}{\partial t} \Pi_{\alpha,n}^<(t) = \frac{1}{\hbar} \sum_{\alpha,n} I_{\alpha,n} \frac{\partial}{\partial t} \left( \Pi_{\alpha,n}^<(t) \right) \quad (A.48)$$

$$\frac{\partial}{\partial t} \Pi_{\alpha,n}^>(t) = \frac{1}{\hbar} \sum_{\alpha,n} I_{\alpha,n} \frac{\partial}{\partial t} \left( \Pi_{\alpha,n}^>(t) \right) \quad (A.49)$$

which contain the time derivatives of the lesser and greater Green’s functions and self-energies and thus can be written as:

$$\frac{\partial}{\partial t} \Pi_{\alpha,n}^<(t) = \int_{t_0}^t dt_2 \frac{\partial}{\partial t} \left( G^>(t, t_2) \Sigma_n^<(t_2, t) \right) + \int_{t_0}^t dt_2 \, G^>(t, t_2) \frac{\partial}{\partial t} \left( \Sigma_n^<(t_2, t) \right) + G^>(t, t) \Sigma_n^>(t, t)$$

$$= \int_{t_0}^t dt_2 \left( -\frac{i}{\hbar} HG^>(t, \tau) \right) \Sigma_n^<(t_2, t) + \int_{t_0}^t dt_2 \, G^>(t, t_2) \frac{\partial}{\partial t} \left( \Sigma_n^<(t_2, t) \right) + i(\rho_S(t) - 1)\delta_{n=0}$$
\[
\frac{\partial}{\partial t} (\Pi_{\alpha,n}^\omega(t)) = \int_{t_0}^t dt' \frac{\partial}{\partial t'} (G< (t, t_2)) \Sigma_n^< (t_2, t) + \int_{t_0}^t dt' G< (t, t_2) \frac{\partial}{\partial t'} (\Sigma_n^> (t_2, t)) + G< (t, t) \Sigma_n^> (t, t)
\]

\[
= \int_{t_0}^t dt' (- \frac{i}{\hbar} HG< (t, \tau)) \Sigma_n^> (t_2, t) + \int_{t_0}^t dt' G< (t, t_2) \frac{\partial}{\partial t'} (\Sigma_n^> (t_2, t)) + i \rho_S(t) \delta_{n=0}
\]

Plugging in the following derivatives of the Green’s functions and the self-energies in the above equations

\[
\frac{\partial}{\partial t} G^\omega (t, \tau) = - \frac{i}{\hbar} H_S(t) G^\omega (t, \tau)
\]

\[
- \frac{i}{\hbar} \int dt' \Sigma_{\text{loc}}^\omega (t, t_2) G^\omega (t_2, \tau)
\]

\[
- \frac{i}{\hbar} \int dt' \Sigma_{\text{col}}^\omega (t, t_2) G^\omega (t_2, \tau)
\]

\[
\frac{d}{dt} \Sigma^<_0 (t) = - i \omega \Sigma^<_0 (t) - \Omega \Sigma^<_1 (t)
\]

\[
\frac{d}{dt} \Sigma^<_0 (t) = i \omega \Sigma^<_0 (t) - \Omega \Sigma^<_1 (t)
\]

\[
\frac{d}{dt} \Sigma^<_n (t) = - i \omega \Sigma^<_n (t) + \frac{\Omega}{2} \Sigma^<_n (t) - \frac{\Omega}{2} \Sigma^<_n (t)
\]

\[
\frac{d}{dt} \Sigma^> (t) = i \omega \Sigma^<_n (t) + \frac{\Omega}{2} \Sigma^<_n (t) - \frac{\Omega}{2} \Sigma^<_n (t)
\]

while for the case where \( n = N_{\text{ch}} \) we drop the leading term from the derivatives of \( \Sigma_n \).

Thus the time derivatives of \( \Pi_{\alpha,n} (t) \) read

\[
\frac{\partial}{\partial t} \Pi_{\alpha,0}^< (t) = \int_{t_0}^t dt' ( - \frac{i}{\hbar} HG^> (t, \tau)) \Sigma_n^< (t_2, t) + \int_{t_0}^t dt' G^< (t, t_2) (- \frac{i}{\hbar} \Sigma^<_0 (t) - \Omega \Sigma^<_1 (t)) + i (\rho_S(t) - 1)
\]

\[
\frac{\partial}{\partial t} \Pi_{\alpha,0}^> (t) = \int_{t_0}^t dt' ( - \frac{i}{\hbar} HG^< (t, \tau)) \Sigma_n^> (t_2, t) + \int_{t_0}^t dt' G^< (t, t_2) (i \omega \Sigma^<_0 (t) - \Omega \Sigma^<_1 (t)) + i \rho_S(t)
\]

\[
\frac{\partial}{\partial t} \Pi_{\alpha,n}^< (t) = \int_{t_0}^t dt' ( - \frac{i}{\hbar} HG^> (t, \tau)) \Sigma_n^< (t_2, t) + \int_{t_0}^t dt' G^> (t, t_2) (- \frac{i}{\hbar} \Sigma^<_0 (t) + \Omega \Sigma^<_n (t) - \frac{\Omega}{2} \Sigma^<_n (t) - \frac{\Omega}{2} \Sigma^<_n (t))
\]

\[
\frac{\partial}{\partial t} \Pi_{\alpha,n}^> (t) = \int_{t_0}^t dt' ( - \frac{i}{\hbar} HG^< (t, \tau)) \Sigma_n^> (t_2, t) + \int_{t_0}^t dt' G^< (t, t_2) (i \omega \Sigma^<_0 (t) + \Omega \Sigma^>_n (t) + \frac{\Omega}{2} \Sigma^>_n (t) - \frac{\Omega}{2} \Sigma^>_n (t))
\]

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Finally, we get for \( n = 0 \) and \( n = N_{ch} \) (where \( N_{ch} \) is the total number of Chebyshev polynomials used in the expansion while \( n \) is the index that runs over those polynomials)

\[
\frac{\partial}{\partial t} \bar{\Pi}_{\alpha,0}^<(t) = i(\rho_S(t) - 1) - i\bar{\omega} \bar{\Pi}_{\alpha,0}^<(t) - \Omega \bar{\Pi}_{\alpha,1}^<(t) - \frac{i}{\hbar} H_S(t) \bar{\Pi}_{\alpha,0}^<(t) \tag{A.51}
\]

\[
\frac{\partial}{\partial t} \bar{\Pi}_{\alpha,0}^>(t) = i\rho_S(t) + i\bar{\omega} \bar{\Pi}_{\alpha,0}^>(t) - \Omega \bar{\Pi}_{\alpha,1}^>(t) - \frac{i}{\hbar} H_S(t) \bar{\Pi}_{\alpha,0}^>(t) \tag{A.52}
\]

\[
\frac{\partial}{\partial t} \bar{\Pi}_{\alpha,n}^<(t) = -i\bar{\omega} \bar{\Pi}_{\alpha,n}^<(t) + \Omega \bar{\Pi}_{\alpha,n-1}^<(t) - \frac{\Omega}{2} \bar{\Pi}_{\alpha,n+1}^<(t) - \frac{i}{\hbar} H_S(t) \bar{\Pi}_{\alpha,n}^<(t) \tag{A.53}
\]

\[
\frac{\partial}{\partial t} \bar{\Pi}_{\alpha,n}^>(t) = i\bar{\omega} \bar{\Pi}_{\alpha,n}^>(t) + \Omega \bar{\Pi}_{\alpha,n-1}^>(t) - \frac{\Omega}{2} \bar{\Pi}_{\alpha,n+1}^>(t) - \frac{i}{\hbar} H_S(t) \bar{\Pi}_{\alpha,n}^>(t) \tag{A.54}
\]

In the above, the terms resulting from the derivatives of the integrals present in the derivatives of the Green’s functions are not written out. These terms are responsible for coupling the first and the second tiers of the NEGF scheme. They are given in the next section.

The \( \bar{\Pi}_{\alpha,n}(t) \) are multiplied by the respective \( I_n \) and the sum over \( n \) is taken:

\[
\frac{\partial}{\partial t} \bar{\Pi}_{\alpha}^<(t) = \frac{1}{\hbar} \sum_n I_{\alpha,n} \frac{\partial}{\partial t} \bar{\Pi}_{\alpha,n}^<(t)
\]

\[
\frac{\partial}{\partial t} \bar{\Pi}_{\alpha}^>(t) = \frac{1}{\hbar} \sum_n I_{\alpha,n} \frac{\partial}{\partial t} \bar{\Pi}_{\alpha,n}^>(t)
\]
Appendix A. Derivations of quantities within the NEGF framework

A.2 Derivation of the EOMs of the NEGF scheme using Chebyshev expansion.

Starting from the expressions of the self-energies given in Section 3,

\[ \Sigma_\alpha^<(t, \tau) = \frac{i}{2 \pi} \int_{-\infty}^{\infty} d\epsilon \ f_\alpha(\epsilon - \mu_\alpha)e^{i\epsilon(t-\tau)/\hbar} J_\alpha \]  
(A.55)

\[ \Sigma_\alpha^>(t, \tau) = -\frac{i}{2 \pi} \int_{-\infty}^{\infty} d\epsilon \ f_\alpha(-\epsilon - \mu_\alpha)e^{-i\epsilon(t-\tau)/\hbar} J_\alpha \]  
(A.56)

The Chebyshev expansion of self-energies requires choosing a specific maximum and minimum frequency/energy spectrum of the bath states

\[ \Sigma_\alpha^<(t, \tau) = \frac{i}{2 \pi} \int_{\omega_{min}}^{\omega_{max}} d\epsilon \ f_\alpha(\epsilon - \mu_\alpha)e^{-i\epsilon(t-\tau)/\hbar} J_\alpha \]  
(A.57)

\[ \Sigma_\alpha^>(t, \tau) = -\frac{i}{2 \pi} \int_{\omega_{min}}^{\omega_{max}} d\epsilon \ f_\alpha(-\epsilon - \mu_\alpha)e^{-i\epsilon(t-\tau)/\hbar} J_\alpha \]  
(A.58)

Taking \( \tau = 0 \), changing variable \( \omega = \Omega x + \bar{\omega} \), the interval \([\omega_{min}, \omega_{max}]\) is mapped onto \([-1, 1]\).

\[ \Sigma_\alpha^<(t) = \frac{i \hbar \Omega}{2 \pi} \int_{-1}^{1} dx \ f_\alpha(h\Omega x + h\bar{\omega} - \mu_\alpha)e^{-i\Omega xt} e^{-i\bar{\omega}t} J_\alpha(h\Omega x + h\bar{\omega}) , \]  
(A.59)

\[ \Sigma_\alpha^>(t) = -\frac{i \hbar \Omega}{2 \pi} \int_{-1}^{1} dx \ f_\alpha(-(h\Omega x + h\bar{\omega} - \mu_\alpha))e^{-i\Omega xt} e^{-i\bar{\omega}t} J_\alpha(h\Omega x + h\bar{\omega}) . \]  
(A.60)

Using the Jacobi-Anger identity given by

\[ e^{-i\Omega xt} = J_0(\Omega t) + \sum_{n=1}^{\infty} 2(-i)^n J_n(\Omega t)T_n(x) . \]  
(A.61)

Taking out the time-dependent part from the integral with \( x \) being the integration variable
\[ \Sigma_\leq(t) = J_0(\Omega t) e^{-i\omega t} \frac{ih\Omega}{2\pi} \int_{-1}^{1} dx \ f_\alpha(h\Omega x + h\omega - \mu_\alpha) J_\alpha(h\Omega x + h\omega) \]

\[ + \sum_{n=1}^{\infty} J_n(\Omega t) e^{-i\omega t} \frac{ih\Omega}{2\pi} \int_{-1}^{1} dx \ 2(i)^n T_n(x) f_\alpha(h\Omega x + h\omega - \mu_\alpha) J_\alpha(h\Omega x + h\omega) \]

\[ + \sum_{n=1}^{\infty} J_n(\Omega t) e^{-i\omega t} \frac{ih\Omega}{2\pi} \int_{-1}^{1} dx \ 2(-i)^n T_n(x) f_\alpha(-(h\Omega x + h\omega - \mu_\alpha)) J_\alpha(h\Omega x + h\omega) \]

\[ \Sigma_\geq(t) = J_0(\Omega t) e^{-i\omega t} \frac{(-i)h\Omega}{2\pi} \int_{-1}^{1} dx \ f_\alpha(-(h\Omega x + h\omega - \mu_\alpha)) J_\alpha(h\Omega x + h\omega) \]

\[ + \sum_{n=1}^{\infty} J_n(\Omega t) e^{-i\omega t} \frac{(-i)h\Omega}{2\pi} \int_{-1}^{1} dx \ 2(-i)^n T_n(x) f_\alpha(-(h\Omega x + h\omega - \mu_\alpha)) J_\alpha(h\Omega x + h\omega) \]

Using the above the self-energies can be written as

\[ \Sigma_\leq(t) = \sum_{n=0}^{\infty} I_{\leq,n}^\leq(t) \Sigma_n^\leq(t) \]

(A.62)

\[ \Sigma_\geq(t) = \sum_{n=0}^{\infty} I_{\geq,n}^\geq(t) \Sigma_n^\geq(t) \]

(A.63)

Taking the time derivative of the reduced self-energies

\[ \frac{d}{dt} \Sigma_0^\leq(t) = -i\omega \Sigma_n^\leq(t) - \Omega \Sigma_1^\leq(t) = \frac{d}{dt} \Sigma_0^\geq(t) \]

\[ \frac{d}{dt} \Sigma_n^\leq(t) = -i\omega \Sigma_n^\leq(t) + \frac{\Omega}{2} \Sigma_{n-1}^\leq(t) - \frac{\Omega}{2} \Sigma_{n+1}^\leq(t) = \frac{d}{dt} \Sigma_n^\geq(t) \]

Using the new definitions of the self-energies, we form a new definition for the current matrices:

\[ \Pi_\leq(t) = \frac{1}{\hbar} \sum_{n} I_{\leq,n}^\leq \int_{t_0}^{t} dt_2 \ G_\leq(t, t_2) \Sigma_n^\leq(t_2, t) = \frac{1}{\hbar} \sum_{n} I_{\leq,n}^\leq \Pi_{\leq,n}(t) \]

\[ \Pi_\geq(t) = \frac{1}{\hbar} \sum_{n} I_{\geq,n}^\geq \int_{t_0}^{t} dt_2 \ G_\geq(t, t_2) \Sigma_n^\geq(t_2, t) = \frac{1}{\hbar} \sum_{n} I_{\geq,n}^\geq \Pi_{\geq,n}(t) \]

\[ \Pi_\leq(t) - \Pi_\geq(t) = \frac{1}{\hbar} \sum_{n} I_{\leq,n}^\leq \Pi_{\leq,n}(t) - \frac{1}{\hbar} \sum_{n} I_{\geq,n}^\geq \Pi_{\geq,n}(t) \]

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Thus

$$\tilde{\Pi}_\alpha^<(t) - \tilde{\Pi}_\alpha^>(t) = \frac{1}{\hbar} \sum_n^\infty I_{\alpha,n}^<(\int_{t_0}^t dt_2 G^>(t, t_2) \Sigma_{\alpha}^<(t_2, t)) - \frac{1}{\hbar} \sum_n^\infty I_{\alpha,n}^<(\int_{t_0}^t dt_2 G^<(t, t_2) \Sigma_{\alpha}^>(t_2, t))$$

and

$$\Pi_\alpha(t) = \tilde{\Pi}_\alpha^<(t) - \tilde{\Pi}_\alpha^>(t)$$

$$\Pi_\alpha(t) = \frac{1}{\hbar} \int_{t_0}^t dt_2 \left(G^>(t, t_2) \Sigma_{\alpha}^<(t_2, t) - G^<(t, t_2) \Sigma_{\alpha}^>(t_2, t)\right)$$

where $\tilde{\Pi}_\alpha^>(t)$ may be called the auxiliary current matrices.

Thus we have

$$\frac{\partial}{\partial t} \rho_s^{s.p.} = -\frac{i}{\hbar} [H_S(t), \rho_s^{s.p.}] + \frac{1}{\hbar} \sum_\alpha \left((\tilde{\Pi}_\alpha^< - \tilde{\Pi}_\alpha^>) + (\tilde{\Pi}_\alpha^> - \tilde{\Pi}_\alpha^<)^\dagger\right)$$ (A.64)

where

$$\frac{\partial}{\partial t} \tilde{\Pi}_\alpha^<(t) = \frac{1}{\hbar} \sum_n^\infty I_{\alpha,n}^< \frac{d}{dt} \left(\tilde{\Pi}_\alpha^<(t)\right)$$

$$\frac{\partial}{\partial t} \tilde{\Pi}_\alpha^>(t) = \frac{1}{\hbar} \sum_n^\infty I_{\alpha,n}^> \frac{d}{dt} \left(\tilde{\Pi}_\alpha^>(t)\right)$$

To continue we need an EOM for $\Pi_{\alpha,n}^\pm$.

$$\frac{\partial}{\partial t} \tilde{\Pi}_{\alpha,n}^< = -i\omega \tilde{\Pi}_{\alpha,n}^< + \frac{\Omega}{2} \tilde{\Pi}_{\alpha,n-1}^< - \frac{\Omega}{2} \tilde{\Pi}_{\alpha,n+1}^< - \frac{i}{\hbar} H_S(t) \tilde{\Pi}_{\alpha,n}^< - \frac{i}{\hbar} \left(\chi_{\alpha,\alpha'}(t) - \chi_{\alpha,\alpha'}^<(t)\right)$$ (A.65)

$$\frac{\partial}{\partial t} \tilde{\Pi}_{\alpha,n}^> = -i\omega \tilde{\Pi}_{\alpha,n}^> + \frac{\Omega}{2} \tilde{\Pi}_{\alpha,n-1}^> - \frac{\Omega}{2} \tilde{\Pi}_{\alpha,n+1}^> - \frac{i}{\hbar} H_S(t) \tilde{\Pi}_{\alpha,n}^> - \frac{i}{\hbar} \left(\chi_{\alpha,\alpha'}(t) - \chi_{\alpha,\alpha'}^>(t)\right)$$ (A.66)
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\[ \frac{\partial}{\partial t} \Phi_{\alpha,0}^\leq(t) = i \rho_{S}^{p} \left( \Phi_{\alpha,0}^\leq(t) - 1 \right) \]
\[ - i \omega \Phi_{\alpha,0}^\leq(t) - \Omega \Phi_{\alpha,1}^\leq(t) \]
\[ - \frac{i}{\hbar} H_S(t) \Phi_{\alpha,0}^\leq(t) \]
\[ - \frac{i}{\hbar} \left( \chi_{\alpha,\alpha'}^\leq(t) - \chi_{\alpha',\alpha}^\leq(t) \right) \]  
\[ (A.67) \]

\[ \frac{\partial}{\partial t} \Phi_{\alpha,0}^\gtr(t) = i \rho_{S}^{p} \left( \Phi_{\alpha,0}^\gtr(t) \right) \]
\[ - i \omega \Phi_{\alpha,0}^\gtr(t) - \frac{i}{\hbar} H_S(t) \Phi_{\alpha,0}^\gtr(t) \]
\[ - \frac{i}{\hbar} \left( \chi_{\alpha,\alpha'}^\gtr(t) - \chi_{\alpha',\alpha}^\gtr(t) \right) \]  
\[ (A.68) \]

The quantities \( X \) and \( Y \) are given as:
\[ X_{\alpha,\alpha'}^\leq(t) - Y_{\alpha,\alpha'}^\leq(t) = \sum_{n'=0}^{N} \int_{t_0}^{t} dt_2 \left[ \int_{t_0}^{t} dt_1 \Sigma_{\alpha,\alpha'}(t,t_1) G_{n,n'}^\gtr(t_1,t_2) + \int_{t_0}^{t_2} dt_1 \Sigma_{\alpha,\alpha'}(t,t_1) G_{n,n'}^\gtr(t_1,t_2) \right] \Sigma_{n,n'} \]
\[ (A.67) \]

The source of the second tier terms are both the integrals present in the EOM of Green’s functions. These integral terms can be seen in the square brackets below. Expansion of the self-energies and regrouping of the terms follows.
\[ X_{\alpha,\alpha'}^{>}(t) - Y_{\alpha,\alpha'}^{>}(t) = \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha,\alpha'}^{<}(t, t_1) G^{<}(t_1, t_2) \Sigma_{\alpha}^{<}(t_2, t) - \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha,\alpha'}^{<}(t, t_1) G^{<}(t_1, t_2) \Sigma_{\alpha}^{<}(t_2, t) \]
\[ + \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{\alpha,\alpha'}^{>}(t, t_1) G^{<}(t_1, t_2) \Sigma_{\alpha}^{<}(t_2, t) - \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha,\alpha'}^{>}(t, t_1) G^{<}(t_1, t_2) \Sigma_{\alpha}^{<}(t_2, t) \]

\[ X_{\alpha,\alpha'}^{<}(t) - Y_{\alpha,\alpha'}^{<}(t) = \sum_{n'=0}^{\infty} I_{\alpha',n'}^{>} \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha'}^{>}(t, t_1) G^{<}(t_1, t_2) \Sigma_{n\alpha}^{<}(t_2, t) - \sum_{n'=0}^{\infty} I_{\alpha',n'}^{<} \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha'}^{<}(t, t_1) G^{>}(t_1, t_2) \Sigma_{n\alpha}^{>}(t_2, t) \]
\[ + \sum_{n'=0}^{\infty} I_{\alpha',n'}^{<} \left[ \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{\alpha'}^{<}(t, t_1) G^{<}(t_1, t_2) \Sigma_{n\alpha}^{<}(t_2, t) - \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha'}^{<}(t, t_1) G^{>}(t_1, t_2) \Sigma_{n\alpha}^{>}(t_2, t) \right] \]

\[ X_{\alpha,\alpha'}^{>}(t) - Y_{\alpha,\alpha'}^{>}(t) = \sum_{n'=0}^{\infty} I_{\alpha',n'}^{>} \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha'}^{>}(t, t_1) G^{<}(t_1, t_2) \Sigma_{n\alpha}^{<}(t_2, t) - \sum_{n'=0}^{\infty} I_{\alpha',n'}^{<} \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha'}^{<}(t, t_1) G^{>}(t_1, t_2) \Sigma_{n\alpha}^{>}(t_2, t) \]
\[ + \sum_{n'=0}^{\infty} I_{\alpha',n'}^{<} \left[ \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{\alpha'}^{<}(t, t_1) G^{<}(t_1, t_2) \Sigma_{n\alpha}^{<}(t_2, t) - \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{\alpha'}^{<}(t, t_1) G^{>}(t_1, t_2) \Sigma_{n\alpha}^{>}(t_2, t) \right] \]

In the above the terms with similar \( I_n \)'s are grouped together such that

\[ X_{\alpha,\alpha'}^{<}(t) - Y_{\alpha,\alpha'}^{<}(t) = \sum_{n'=0}^{\infty} I_{\alpha',n'}^{>} X_{n,n'}^{<} - \sum_{n'=0}^{\infty} I_{\alpha',n'}^{<} Y_{n,n'}^{<} \]  \hspace{1cm} (A.69)

\[ X_{\alpha,\alpha'}^{>}(t) - Y_{\alpha,\alpha'}^{>}(t) = \sum_{n'=0}^{\infty} I_{\alpha',n'}^{>} X_{n,n'}^{>} - \sum_{n'=0}^{\infty} I_{\alpha',n'}^{<} Y_{n,n'}^{>} \]  \hspace{1cm} (A.70)

Therefore, we end up with

\[ X_{n,n'}^{<} = \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{n,n'}^{<}(t, t_1) G^{>}(t_1, t_2) \Sigma_{n}^{>}(t_2, t) \]
\[ + \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{n,n'}^{<}(t, t_1) G^{<}(t_1, t_2) \Sigma_{n}^{<}(t_2, t) - \Sigma_{n,n'}^{<}(t_1, t_2) G^{<}(t_1, t_2) \Sigma_{n}^{<}(t_2, t) \]

\[ Y_{n,n'}^{<} = \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 \Sigma_{n,n'}^{<}(t, t_1) G^{>}(t_1, t_2) \Sigma_{n}^{>}(t_2, t) \]
Note that

\[ \frac{\partial}{\partial t} \mathcal{X}^<_{n,n'} = \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{n,\alpha}^<(t_1, t_1) G^<(t_1, t_2) \Sigma_{n'}^>(t_2, t) \]

\[ \mathcal{Y}^>_{n,n'} = \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{n,\alpha}^<(t_1, t_1) G^<(t_1, t_2) \Sigma_{n'}^>(t_2, t) \]

\[ - \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \Sigma_{n,\alpha}^<(t_1, t_1) G^<(t_1, t_2) \Sigma_{n'}^>(t_2, t) - \Sigma_{n,\alpha}^<(t_1, t_1) G^>(t_1, t_2) \Sigma_{n'}^>(t_2, t) \]

Using the above equations we calculate the time derivatives of the second tier quantities:

Note that \( \Sigma_{0,\alpha}^<(t, t) = 1 \) while the rest of \( \Sigma_{0,\alpha}^<(t, t) = 0. \)

\[ \frac{\partial}{\partial t} \mathcal{X}^<_{n,n'} = 2i\tilde{\omega} \mathcal{X}^<_{n,n'} + \frac{\Omega}{2} \mathcal{X}^<_{n,n'-1} + \frac{\Omega}{2} \mathcal{X}^<_{n-1,n'} - \frac{\Omega}{2} \mathcal{X}^<_{n,n'+1} - \frac{\Omega}{2} \mathcal{X}^<_{n+1,n'} \]

\[ + \underbrace{\Sigma_{n,\alpha}^<(t, t)}_{=1} \int_{t_0}^t dt_2 G^>(t, t_2) \Sigma_{n'}^>(t_2, t) \]

\[ + \int_{t_0}^t dt_1 \Sigma_{n,\alpha}^<(t, t_1) G^>(t_1, t) \underbrace{\Sigma_{n'}^<(t, t)}_{=1} - \int_{t_0}^{t_2=t} dt_1 \Sigma_{n,\alpha}^<(t, t_1) G^>(t_1, t) \underbrace{\Sigma_{n'}^<(t, t)}_{=1} \]

\[ + \int_{t_0}^{t_2=t} dt_1 \Sigma_{n,\alpha}^<(t, t_1) G^>(t_1, t) \underbrace{\Sigma_{n'}^<(t, t)}_{=1} \]

\[ \frac{\partial}{\partial t} \mathcal{Y}^<_{n,n'} = 2i\tilde{\omega} \mathcal{Y}^<_{n,n'} + \frac{\Omega}{2} \mathcal{Y}^<_{n,n'-1} + \frac{\Omega}{2} \mathcal{Y}^<_{n-1,n'} - \frac{\Omega}{2} \mathcal{Y}^<_{n,n'+1} - \frac{\Omega}{2} \mathcal{Y}^<_{n+1,n'} \]

\[ + \underbrace{\Sigma_{n,\alpha}^<(t, t)}_{=1} \int_{t_0}^t dt_2 G^>(t, t_2) \Sigma_{n'}^>(t_2, t) \]

\[ + \int_{t_0}^t dt_1 \Sigma_{n,\alpha}^<(t, t_1) G^>(t_1, t) \underbrace{\Sigma_{n'}^<(t, t)}_{=1} \]

\[ + \int_{t_0}^t dt_1 \Sigma_{n,\alpha}^<(t, t_1) G^>(t_1, t) \underbrace{\Sigma_{n'}^<(t, t)}_{=1} \]
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\[
\frac{\partial}{\partial t} \chi_{n,n'}^> = 2i\tilde{\omega} \chi_{n,n'}^> + \frac{\Omega}{2} \chi_{n,n'-1}^> + \frac{\Omega}{2} \chi_{n-1,n'}^> - \frac{\Omega}{2} \chi_{n,n'+1}^> - \frac{\Omega}{2} \chi_{n+1,n'}^>
\]

\[
+ \sum_{\alpha'} \int_{t_0}^{t} dt_2 G^<(t, t_2) \Sigma_{\alpha'}^>(t_2, t) \int_{t_0}^{t} dt_3 \Sigma_{\alpha,n}^>(t_3, t) = 1
\]

\[
+ \int_{t_0}^{t} dt_1 \Sigma_{\alpha,n}^>(t_1, t) G^<(t_1, t) \Sigma_{\alpha,n}^>(t, t) = 1
\]

\[
\frac{\partial}{\partial t} \mathcal{Y}_{n,n'}^> = 2i\tilde{\omega} \mathcal{Y}_{n,n'}^> + \frac{\Omega}{2} \mathcal{Y}_{n,n'-1}^> + \frac{\Omega}{2} \mathcal{Y}_{n-1,n'}^> - \frac{\Omega}{2} \mathcal{Y}_{n,n'+1}^> - \frac{\Omega}{2} \mathcal{Y}_{n+1,n'}^>
\]

\[
+ \sum_{\alpha'} \int_{t_0}^{t} dt_2 G^<(t, t_2) \Sigma_{\alpha'}^>(t_2, t) \int_{t_0}^{t} dt_3 \Sigma_{\alpha,n}^>(t_3, t) = 1
\]

\[
+ \int_{t_0}^{t} dt_1 \Sigma_{\alpha,n}^>(t_1, t) G^<(t_1, t) \Sigma_{\alpha,n}^>(t, t) = 1
\]

\[
+ \int_{t_0}^{t} dt_1 \Sigma_{\alpha,n}^>(t_1, t) G^<(t_1, t) \Sigma_{\alpha,n}^>(t, t) = 1
\]

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The EOM for the general case \([n, n]\) and the boundary cases, \([0, 0], [N, N'], [0, N'], [N, 0], [N, n'], [n, N'], [0, n'], [n, 0]\), are as follows: EOMs of quantities \(X, Y\) for \([n, n'] = [1, 2, ..., N - 1; 1, 2, ..., N' - 1]\):

\[
\frac{\partial}{\partial t} X^<_{n,n'} = -2i\omega X^<_{n,n}(t) + \frac{\Omega}{2} X^<_{n,n' - 1} + \frac{\Omega}{2} X^<_{n,n' + 1} - \frac{\Omega}{2} X^<_{n+1,n'}
\]

\[
\frac{\partial}{\partial t} Y^<_{n,n'} = -2i\omega Y^<_{n,n}(t) + \frac{\Omega}{2} Y^<_{n,n' - 1} + \frac{\Omega}{2} Y^<_{n,n' + 1} - \frac{\Omega}{2} Y^<_{n+1,n'}
\]

\[
\frac{\partial}{\partial t} X^>_{n,n'} = -2i\omega X^>_{n,n}(t) + \frac{\Omega}{2} X^>_{n,n' - 1} + \frac{\Omega}{2} X^>_{n,n' + 1} - \frac{\Omega}{2} X^>_{n+1,n'}
\]

\[
\frac{\partial}{\partial t} Y^>_{n,n'} = -2i\omega Y^>_{n,n}(t) + \frac{\Omega}{2} Y^>_{n,n' - 1} + \frac{\Omega}{2} Y^>_{n,n' + 1} - \frac{\Omega}{2} Y^>_{n+1,n'}
\]

Starting case \([n, n'] = [0, 0]\)

\[
\frac{\partial}{\partial t} X^<_{0,0} = -2i\omega X^<_{0,0}(t) - \Omega X^<_{0,1'} - \Omega X^<_{1,0'} + v^i_{\alpha'} \bar{\Pi}^>_{\alpha,n}(t) + \bar{\Pi}^<_{\alpha',n'}(t) v_{\alpha'}
\]

\[
\frac{\partial}{\partial t} Y^<_{0,0} = -2i\omega Y^>_{0,0}(t) - \Omega Y^<_{0,1'} - \Omega Y^<_{1,0'} + v^i_{\alpha'} \bar{\Pi}^<_{\alpha,n}(t) + \bar{\Pi}^>_{\alpha',n'}(t) v_{\alpha'}
\]

\[
\frac{\partial}{\partial t} X^>_{0,0} = -2i\omega X^>_{0,0}(t) - \Omega X^>_{0,1'} - \Omega X^>_{1,0'} + v^i_{\alpha'} \bar{\Pi}^>_{\alpha,n}(t) + \bar{\Pi}^<_{\alpha',n'}(t) v_{\alpha'}
\]

\[
\frac{\partial}{\partial t} Y^>_{0,0} = -2i\omega Y^>_{0,0}(t) - \Omega Y^>_{0,1'} - \Omega Y^>_{1,0'} + v^i_{\alpha'} \bar{\Pi}^<_{\alpha,n}(t) + \bar{\Pi}^>_{\alpha',n'}(t) v_{\alpha'}
\]

EOMs of quantities \(X, Y\) for \([n, 0] = [1, 2, ..., N - 1; 0]\):

\[
\frac{\partial}{\partial t} X^<_{n,0} = -2i\omega X^<_{n,0}(t) + \frac{\Omega}{2} X^<_{n-1,0} - \Omega X^<_{n,1} - \Omega X^<_{n+1,0} + v^i_{\alpha'} \bar{\Pi}^<_{\alpha,n}(t)
\]

\[
\frac{\partial}{\partial t} Y^<_{n,0} = -2i\omega Y^<_{n,0}(t) + \frac{\Omega}{2} Y^<_{n-1,0} - \Omega Y^<_{n,1} + v^i_{\alpha'} \bar{\Pi}^<_{\alpha,n}(t)
\]

\[
\frac{\partial}{\partial t} Y^>_{n,0} = -2i\omega Y^>_{n,0}(t) + \frac{\Omega}{2} Y^>_{n-1,0} - \Omega Y^>_{n,1} + v^i_{\alpha'} \bar{\Pi}^>_{\alpha,n}(t)
\]
Appendix A. Derivations of quantities within the NEGF framework

\[ \frac{\partial}{\partial t} Y_{n,0}^> = -2i\omega Y_{n,0}^< + \frac{\Omega}{2} Y_{n-1,0}^> - \frac{\Omega}{2} Y_{n+1,0}^> - \Omega Y_{n,1}^> + V_{\alpha,1}^\dagger \Pi_{n,n}^> (t) \]

EOMs of quantities \( X, Y \) for \([0, n'] = [0; 1, 2, ..., N' - 1]\):

\[ \frac{\partial}{\partial t} X_{0,n'}^< = -2i\omega X_{0,n'}^< (t) + \frac{\Omega}{2} X_{0,n'-1}^> - \frac{\Omega}{2} X_{0,n'+1}^> - \Omega X_{1,n'}^> + \Pi_{\alpha,n'}^> (t) v_{\alpha'} \]

\[ \frac{\partial}{\partial t} Y_{0,n'}^< = -2i\omega Y_{0,n'}^< (t) + \frac{\Omega}{2} Y_{0,n'-1}^> - \frac{\Omega}{2} Y_{0,n'+1}^> - \Omega Y_{1,n'}^> + \Pi_{\alpha,n'}^> (t) v_{\alpha'} \]

\[ \frac{\partial}{\partial t} X_{0,n'}^> = -2i\omega X_{0,n'}^> (t) + \frac{\Omega}{2} X_{0,n'-1}^> - \frac{\Omega}{2} X_{0,n'+1}^> - \Omega X_{1,n'}^> + \Pi_{\alpha,n'}^> (t) v_{\alpha'} \]

\[ \frac{\partial}{\partial t} Y_{0,n'}^> = -2i\omega Y_{0,n'}^> (t) + \frac{\Omega}{2} Y_{0,n'-1}^> - \frac{\Omega}{2} Y_{0,n'+1}^> - \Omega Y_{1,n'}^> + \Pi_{\alpha,n'}^> (t) v_{\alpha'} \]

EOMs of quantities \( X, Y \) for \([n, N'] = [1, 2, ..., N - 1; N']\):

\[ \frac{\partial}{\partial t} X_{n,N'}^< = -2i\omega X_{n,N'}^< (t) + \frac{\Omega}{2} X_{n-1,N'}^> - \frac{\Omega}{2} X_{n+1,N'}^> + \frac{\Omega}{2} X_{n,N'-1}^> \]

\[ \frac{\partial}{\partial t} Y_{n,N'}^< = -2i\omega Y_{n,N'}^< (t) + \frac{\Omega}{2} Y_{n-1,N'}^> - \frac{\Omega}{2} Y_{n+1,N'}^> + \frac{\Omega}{2} Y_{n,N'-1}^> \]

\[ \frac{\partial}{\partial t} X_{n,N'}^> = -2i\omega X_{n,N'}^> (t) + \frac{\Omega}{2} X_{n-1,N'}^> - \frac{\Omega}{2} X_{n+1,N'}^> + \frac{\Omega}{2} X_{n,N'-1}^> \]

\[ \frac{\partial}{\partial t} Y_{n,N'}^> = -2i\omega Y_{n,N'}^> (t) + \frac{\Omega}{2} Y_{n-1,N'}^> - \frac{\Omega}{2} Y_{n+1,N'}^> + \frac{\Omega}{2} Y_{n,N'-1}^> \]

EOMs of quantities \( X, Y \) for \([N, n'] = [N; 1, 2, ..., N' - 1]\):

\[ \frac{\partial}{\partial t} X_{N,n'}^< = -2i\omega X_{N,n'}^< (t) + \frac{\Omega}{2} X_{N,n'-1}^> - \frac{\Omega}{2} X_{N,n'+1}^> + \frac{\Omega}{2} X_{N-1,n'}^< \]

\[ \frac{\partial}{\partial t} Y_{N,n'}^< = -2i\omega Y_{N,n'}^< (t) + \frac{\Omega}{2} Y_{N,n'-1}^> - \frac{\Omega}{2} Y_{N,n'+1}^> + \frac{\Omega}{2} Y_{N-1,n'}^< \]

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Appendix A. Derivations of quantities within the NEGF framework

\[ \frac{\partial}{\partial t} \chi_{N,n'}^> = -2i\bar{\omega}\chi_{N,n'}^<(t) + \frac{\Omega}{2} \chi_{N,n'-1}^> - \frac{\Omega}{2} \chi_{N,n'+1}^> + \frac{\Omega}{2} \chi_{N-1,n'}^> \]

\[ \frac{\partial}{\partial t} \gamma_{N,n'}^> = -2i\bar{\omega}\gamma_{N,n'}^<(t) + \frac{\Omega}{2} \gamma_{N,n'-1}^> - \frac{\Omega}{2} \gamma_{N,n'+1}^> + \frac{\Omega}{2} \gamma_{N-1,n'}^> \]

EOMs of quantities \( \chi, \gamma \) for \([0, N']\):

\[ \frac{\partial}{\partial t} \chi_{0,N'}^<(t) = -2i\bar{\omega}\chi_{0,N'}^<(t) + \frac{\Omega}{2} \chi_{0,N'-1}^<(t) - \Omega \chi_{1,N'}^<(t) + \bar{\Pi}_{\alpha',N'}^\dagger(t) \, \nu_{\alpha'} \]

\[ \frac{\partial}{\partial t} \gamma_{0,N'}^<(t) = -2i\bar{\omega}\gamma_{0,N'}^<(t) + \frac{\Omega}{2} \gamma_{0,N'-1}^<(t) - \Omega \gamma_{1,N'}^<(t) + \bar{\Pi}_{\alpha',N'}^\dagger(t) \, \nu_{\alpha'} \]

\[ \frac{\partial}{\partial t} \chi_{0,N'}^>(t) = -2i\bar{\omega}\chi_{0,N'}^>(t) + \frac{\Omega}{2} \chi_{0,N'-1}^>(t) - \Omega \chi_{1,N'}^>(t) + \bar{\Pi}_{\alpha',N'}^\dagger(t) \, \nu_{\alpha'} \]

\[ \frac{\partial}{\partial t} \gamma_{0,N'}^>(t) = -2i\bar{\omega}\gamma_{0,N'}^>(t) + \frac{\Omega}{2} \gamma_{0,N'-1}^>(t) - \Omega \gamma_{1,N'}^>(t) + \bar{\Pi}_{\alpha',N'}^\dagger(t) \, \nu_{\alpha'} \]

EOMs of quantities \( \chi, \gamma \) for \([N, 0]\):

\[ \frac{\partial}{\partial t} \chi_{N,0}^<(t) = -2i\bar{\omega}\chi_{N,0}^<(t) + \frac{\Omega}{2} \chi_{N-1,0}^<(t) - \Omega \chi_{N,1}^<(t) + \nu_{\alpha}^\dagger \bar{\Pi}_{\alpha,N}^<(t) \]

\[ \frac{\partial}{\partial t} \gamma_{N,0}^<(t) = -2i\bar{\omega}\gamma_{N,0}^<(t) + \frac{\Omega}{2} \gamma_{N-1,0}^<(t) - \Omega \gamma_{N,1}^<(t) + \nu_{\alpha}^\dagger \bar{\Pi}_{\alpha,N}^<(t) \]

\[ \frac{\partial}{\partial t} \chi_{N,0}^>(t) = -2i\bar{\omega}\chi_{N,0}^>(t) + \frac{\Omega}{2} \chi_{N-1,0}^>(t) - \Omega \chi_{N,1}^>(t) + \nu_{\alpha}^\dagger \bar{\Pi}_{\alpha,N}^>(t) \]

\[ \frac{\partial}{\partial t} \gamma_{N,0}^>(t) = -2i\bar{\omega}\gamma_{N,0}^>(t) + \frac{\Omega}{2} \gamma_{N-1,0}^>(t) - \Omega \gamma_{N,1}^>(t) + \nu_{\alpha}^\dagger \bar{\Pi}_{\alpha,N}^>(t) \]

EOMs of quantities \( \chi, \gamma \) for \([n, n'] = [N; N']\):

\[ \frac{\partial}{\partial t} \chi_{n,n'}^< = -2i\bar{\omega}\chi_{N,N'}^<(t) + \frac{\Omega}{2} \chi_{n,n'-1}^< + \frac{\Omega}{2} \chi_{n-1,n'}^< \]
Appendix A. Derivations of quantities within the NEGF framework

\[ \frac{\partial}{\partial t} Y_\langle n,n' \rangle = -2i\bar{\omega}Y_\langle N,N' \rangle (t) + \frac{\Omega}{2} Y_\langle n,n'-1 \rangle + \frac{\Omega}{2} Y_\langle n-1,n' \rangle \]

\[ \frac{\partial}{\partial t} X_\rangle n,n' \rangle = -2i\bar{\omega}X_\rangle N,N' \rangle (t) + \frac{\Omega}{2} X_\rangle n,n'-1 \rangle + \frac{\Omega}{2} X_\rangle n-1,n' \rangle \]

\[ \frac{\partial}{\partial t} Y_\rangle n,n' \rangle = -2i\bar{\omega}Y_\rangle N,N' \rangle (t) + \frac{\Omega}{2} Y_\rangle n,n'-1 \rangle + \frac{\Omega}{2} Y_\rangle n-1,n' \rangle \]
B. Efficient vector based method for NEGF

In this Appendix, we discuss in some detail the derivation of a method which replaces all matrices in the NEGF scheme developed in Ref. 129 by vectors or scalars. This method renders the NEGF scheme capable of dealing with larger systems by improving the scaling of the required numerical effort as compared to the size of the system. A linear scaling is achieved and reported in Ref. along with the development of the mentioned vectors- and scalars-based scheme. Here we derive the scheme in a simplified manner using the notation used within this work.

Beginning with regular the EOM for NEGF,

\[
\frac{\partial}{\partial t} \rho_S(t) = -\frac{i}{\hbar} [H_S(t), \rho_S(t)] + \frac{1}{\hbar} \sum_\alpha \left( \Pi_\alpha(t) + \Pi_\alpha^\dagger(t) \right) \tag{B1}
\]

\[
\Pi_\alpha(t) = \frac{1}{\hbar} \int_{t_0}^t dt_2 \left( G^>_{\alpha}(t, t_2) \Sigma_<^\alpha(t_2, t) - G^<_{\alpha}(t, t_2) \Sigma^>_\alpha(t_2, t) \right) \tag{B2}
\]

Where the self-energies are given by

\[
\Sigma_<^\alpha(t, \tau) = \frac{i}{2\pi} \int_{-\infty}^\infty d\epsilon f_\alpha(\epsilon - \mu_\alpha) e^{i\epsilon(t-\tau)/\hbar} J_\alpha(\epsilon) \tag{B3}
\]

\[
\Sigma^>_\alpha(t, \tau) = -\frac{i}{2\pi} \int_{-\infty}^\infty d\epsilon f_\alpha(-\epsilon - \mu_\alpha) e^{-i\epsilon(t-\tau)/\hbar} J_\alpha(\epsilon) \tag{B4}
\]

Here \( J_\alpha(\epsilon) \) is the level-width function (or the spectral density) of reservoir \( \alpha \), given in terms of the reservoir density of states, \( (T_i(\epsilon) \) is the coupling of wire level \( i \) to reservoir state at energy \( \epsilon )):

\[
J_{\alpha,ij}(\epsilon) = 2\pi \sum_i T_i(\epsilon) T_j^\dagger(\epsilon) \delta(\epsilon - \epsilon_i) \tag{B5}
\]

\( J_\alpha(\epsilon) \) is present in the above given EOM in the form of an \( N \times N \) matrix, i.e.

\[
J_{\alpha,ij}(\epsilon) = \left[ N \times N \right] \tag{B6}
\]
Appendix B. Efficient vector based method for NEGF

For 1D systems, this matrix is already in diagonal form

\[
J_{L,ij}(\epsilon) = \begin{bmatrix}
J_{L,11}(\epsilon) & \cdots & \\
\vdots & \ddots & \\
J_{L,N_1}(\epsilon) & \cdots & J_{L,N_N}(\epsilon)
\end{bmatrix}, \quad J_{R,ij}(\epsilon) = \begin{bmatrix}
\cdots & \cdots & J_{R,N}(\epsilon)
\end{bmatrix}
\]

The non-zero elements in the above, \(J_{L,11}(\epsilon)\) and \(J_{R,NN}(\epsilon)\), are to be fitted using Lorentzians. All other elements except for the ones mentioned above are zero.

In general, a level width function may be diagonalized as follows:

\[
J_{\alpha}(\epsilon) = \sum_{c=1}^{N_c} \xi_{\alpha c}(\epsilon) v_{\alpha c}(\epsilon) \xi_{\alpha c}^\dagger(\epsilon)
\]

\[
J_{\alpha}(\epsilon) = \sum_{c=1}^{N_c} \sum_{l=1}^{N_l} \xi_{\alpha c}(\epsilon) \frac{A_{\alpha l c} W_{\alpha l c}^2}{(\epsilon - \epsilon_{\alpha l c})^2 + W_{\alpha l c}^2} \xi_{\alpha c}^\dagger(\epsilon)
\]

(B7)

Where \(\xi_{\alpha c}\) are transversal wave-vectors of dimension \(N_c\), and \(v_{\alpha c}(\epsilon)\) is directly proportional to the group velocity in channel \(c\). For the 1D case there is one transport channel per lead \((N_c = 1)\), which means that the level-width function has only one non-zero element, given by \(v(\epsilon)\).

For the 1D case the level width function is already diagonal, so it follows in general that:

\[
J_{\alpha}(\epsilon) = \xi_{\alpha}(\epsilon) v_{\alpha}(\epsilon) \xi_{\alpha}^\dagger(\epsilon)
\]

Assuming a single Lorentzian for a simplified derivation,

\[
J_{\alpha}(\epsilon) = \xi_{\alpha}^\dagger(\epsilon) v_{\alpha}(\epsilon) \xi_{\alpha}^\dagger(\epsilon) \frac{A_{\alpha} W_{\alpha}^2}{(\epsilon - \epsilon_{\alpha})^2 + W_{\alpha}^2}
\]

(B8)

the matrix form of the spectral density is then written as

\[
J_{L,ij}(\epsilon) = \begin{bmatrix}
1 \\
\vdots \\
\vdots
\end{bmatrix} \begin{bmatrix}
J_{L,11}(\epsilon) & \cdots & \\
\vdots & \ddots & \\
J_{L,N}(\epsilon) & \cdots & J_{L,N}(\epsilon)
\end{bmatrix} \begin{bmatrix}
1 \\
\vdots \\
1
\end{bmatrix}, \quad J_{R,ij}(\epsilon) = \begin{bmatrix}
\cdots & \cdots & \cdots \\
1
\end{bmatrix}
\]

The non-zero element in the above is decomposed using one or more Lorentzians, similar to the procedure before. This element is essentially the same as what it was pre-matrix diagonalization.

Inserting Eq. B7 in Eq. B3 and Eq. B4, we get,

\[
\Sigma_{\alpha}^{<}(t, \tau) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\epsilon \ f_{\alpha}(\epsilon - \mu_{\alpha}) e^{i(t-\tau)/\hbar} \xi_{\alpha}^\dagger(\epsilon - \epsilon_{\alpha})^2 + W_{\alpha}^2 \xi_{\alpha}^\dagger
\]

(B9)
Following Jordan’s lemma brings the greater/lesser self-energies into the following form

$$\Sigma_\alpha^\pm (t, \tau) = \frac{1}{\hbar} \sum_x \xi_\alpha^\pm \exp \left\{ \frac{i}{\hbar} \chi_{ax}(t) \right\} \xi_\alpha^\dagger$$

(B11)

Inserting the above in the definition of $\Pi_\alpha$ and defining auxiliary-mode wave-vectors $\tilde{\Pi}_{\alpha x}$:

$$\Pi_\alpha(t) = \frac{1}{\hbar} \sum_x \left[ \int_{t_0}^t dt_2 \left( G^\geq_\alpha(t, t_2) \xi_\alpha^\dagger \exp \left\{ \frac{i}{\hbar} \chi_{ax}(t) \right\} \xi \right) - G^\leq_\alpha(t, t_2) \xi_\alpha^\dagger \exp \left\{ \frac{i}{\hbar} \chi_{ax}(t) \right\} \xi_\alpha^\dagger \right]$$

(B12)

$$\Pi_\alpha(t) = \frac{1}{\hbar} \sum_x \tilde{\Pi}_{\alpha x}(t) \xi_\alpha^\dagger$$

(B14)

The vector $\tilde{\Pi}_{\alpha x}(t)$ with dimension $N$ is given as

$$\tilde{\Pi}_{\alpha x}(t) = \int_{t_0}^t dt_2 \left( G^\geq_\alpha(t, t_2) \Gamma^\geq_\alpha - G^\leq_\alpha(t, t_2) \Gamma^\leq_\alpha \right) \exp \left\{ \frac{i}{\hbar} \chi_{ax}(t) \right\} \xi_\alpha$$

(B15)

Its equation of motion is found to be

$$\frac{\partial \tilde{\Pi}_{\alpha x}(t)}{\partial t} = -\frac{i}{\hbar} [H_S(t) - \chi^+_{ax}] \tilde{\Pi}_{\alpha x}(t) - i \Gamma^\leq_\alpha \xi_\alpha - i (\Gamma^\geq_\alpha - \Gamma^\leq_\alpha) \rho_{S,p}(t) \xi_\alpha^\dagger - \frac{i}{\hbar^2} \sum_{\alpha',x'} \Omega_{\alpha x,\alpha' x'}(t) \xi_{\alpha'}^\dagger$$

(B16)

While the EOM for the quantity $\Omega_{\alpha x,\alpha' x'}(t)$ is given as

$$\frac{\partial \Omega_{\alpha x,\alpha' x'}(t)}{\partial t} = -\frac{i}{\hbar} [\chi^+_{\alpha' x'} - \chi^+_{ax}] \Omega_{\alpha x,\alpha' x'}(t) + (\Gamma^\geq_{\alpha' x'} - \Gamma^\leq_{\alpha' x'}) \xi_\alpha^\dagger \tilde{\Pi}_{\alpha x}(t)$$

$$+ (\Gamma^\geq_{ax} - \Gamma^\leq_{ax}) \tilde{\Pi}_{\alpha x}(t) \xi_{\alpha'}^\dagger$$

(B17)

In this approach the quantities $\Omega_{\alpha x,\alpha' x'}(t)$ are scalars rather than matrices.

Thus we have for the following quantities the dimensions:

$\Omega_{\alpha x,\alpha' x'}(t) \rightarrow 1 \times 1. \quad \tilde{\Pi}_{\alpha x}(t) \rightarrow N \times 1. \quad \xi_\alpha \rightarrow N \times 1.$
C. Derivation of the exponential HEOM

In this Appendix, we discuss in some detail the derivation of the exponential decomposed HEOM scheme. The derivation of this scheme using the Feynmann-Vernon influence functional method is given in several works [98, 107, 177, 178]. This derivation follows the initial steps shown in Chapter 4 in the derivation of the C-HEOM and is shown for greater consistency in the derivation. In contrasts to Chapter 4, here the regular form of the correlation functions is adopted, i.e., its given in terms of sum of weighted exponentials. A detailed version of this derivation may be found in Ref. ?, from where this, more simplified derivation is adapted from.

The time evolution of the reduced density matrix \( \rho_S(t) \) is given by

\[
\rho_S(t) = \text{tr}_{\text{bath}} \{ U(t, t_0) \rho(0) U^\dagger(t, t_0) \} = \tilde{U}(t, t_0) \rho_S(t_0).
\]

(B1)

The Liouville space propagator above, \( \tilde{U}(t, t_0) \), depends on the system part as well as the system-bath interaction part of the total system. The Feynman-Vernon influence functional formalism [199] is used to factorize the total system by rewriting \( \tilde{U}(t, t_0) \) in the path integral formalism. The time evolution operator \( U(t, t_0) \) in path integral representation is given as [76]

\[
U(t, t_0) = \int_{\alpha_0}^{\alpha_t} D\alpha e^{i\pi S[\alpha]},
\]

(B2)

where \( \alpha \) denotes arbitrary paths in phase space with the respective fixed starting and ending points \( \alpha_0 \) and \( \alpha_t \). The action functional \( S[\alpha] \) describes the evolution of the total system but can be decomposed into system, bath, and system-bath interaction parts. The time evolution of the full density matrix in path integral formalism therefore reads [177]

\[
\rho_{\alpha,\alpha',t} = \int_{\alpha_0}^{\alpha_t} D\alpha \int_{\alpha_0'}^{\alpha'_t} D\alpha' e^{i(S_S[\alpha]+S_B[\alpha]+S_{SB}[\alpha])} \rho_{\alpha_0,\alpha'_0,t_0} e^{-i(S_S[\alpha']+S_B[\alpha']+S_{SB}[\alpha'])}
\]

(B3)

By tracing over the bath DOFs one gets [178]

\[
\mathcal{U}(\alpha, \alpha', t; \alpha_0, \alpha'_0, t_0) = \int_{\alpha_0}^{\alpha_t} D\alpha \int_{\alpha_0'}^{\alpha'_t} D\alpha' e^{iS[\alpha]F(\alpha, \alpha')e^{S[\alpha']}}
\]

(B4)

Here the Feynman-Vernon influence functional \( F(\alpha, \alpha') \) represents the system-bath interaction [199].
Appendix C. Derivation of the exponential HEOM

It should be noted that it is necessary to keep track of the order of the terms in Liouville space as for instance the time evolution operator and the density operator do not commute.

Employing the Caldeira-Leggett model for the system-bath interaction and using a single system operator $K$, the influence functional can be written as (adopting an arbitrary Liouville space representation $\alpha = (\alpha, \alpha')$)

$$F[\alpha(t)] = \exp \left\{ - \int_{t_i}^{t} d\tau K^\times[\alpha(\tau)]\Lambda[\alpha(\tau)] \right\}. \quad (B5)$$

Taking the time derivative of $\rho_S(t)$ leads to an equation of motion describing the time evolution of the system coupled to an external bath. Therefore, the derivative of the time evolution operator defined earlier, $U(\alpha_t, \alpha'_t; \alpha_0, \alpha'_0, t_0)$, needs to be evaluated. $U(\alpha_t, \alpha'_t; \alpha_0, \alpha'_0, t_0)$ basically contains the influence functional $F(\alpha, \alpha')$ and the time derivatives of the action term describing the evolution of the unperturbed system, given by

$$\frac{\partial}{\partial t} e^{iS[\alpha]} = -iH_S e^{iS[\alpha]}, \quad (B6)$$

while the time derivative of influence functional, containing the effects of the system-bath interaction, is given by

$$\frac{\partial}{\partial t} F[\alpha(t)] = -K^\times[\alpha(\tau)]\Lambda[\alpha(\tau)] F[\alpha(t)]. \quad (B7)$$

The above equation provides no closed solution and one needs to introduce the so-called auxiliary influence functional $F_1$ to obtain the formal solution

$$\frac{\partial}{\partial t} F[\alpha(t)] = -K^\times[\alpha(\tau)] F_1[\alpha(t)]. \quad (B8)$$

The above does not provide a closed solution and formally exact solution as well, which can nonetheless be obtained by taking the derivatives of $F$ up to the $n^{th}$ order. Consequently one obtains an infinite hierarchy of auxiliary influence functionals $F_n$. If an exponential form of the correlation function present inside the operators $A[\alpha(t)]$ is adopted then one can construct a hierarchical equation of motion up to an arbitrary order. $A^\times[\alpha(\tau)]$ is given as

$$A^\times[\alpha(t)] = A[\alpha(t)] - A[\alpha(t)] \quad (B9)$$

and

$$A[\alpha(t)] = \int_{t_0}^{t} d\tau C(t - \tau) K[\alpha(\tau)] \quad (B10)$$

where $C(t - \tau)$ is the correlation function and can be written in terms of a weighted sum of exponentials.
Appendix C. Derivation of the exponential HEOM

as follows

\[ C(t - \tau) = \sum_{l=1}^{\mathcal{C}} C_l(t_0) e^{-\frac{i}{\hbar} \gamma_l t} \]  \hspace{1cm} (B11)

In the following we assume that \( l = 1 \), i.e. the number of exponential terms or the number of poles of the fermi function and the spectral density combined is set to 1. This is an approximation but the end result is no different for a higher number of poles utilized in the expansion as compared to a lower number, except for the presence of a sum over the number of poles in the appropriate places. In the above \( C_l(t_0) \) and \( \gamma_l \) are constants. Continuing with Eq. B8, where \( \mathcal{F}_1[\alpha(t)] \) is defined, we can see this first auxiliary operator being composed of basically two terms

\[ \mathcal{F}_1[\alpha(t)] = -i \Lambda^X[\alpha(t)] \mathcal{F}[\alpha(t)] \]  \hspace{1cm} (B12)

Taking the time derivative of the above, i.e. \( \partial_t \mathcal{F}_1[\alpha(t)] \) reads

\[ \frac{\partial}{\partial t} \mathcal{F}_1[\alpha(t)] = -i \left( \frac{\partial}{\partial t} \Lambda^X[\alpha(t)] \right) \mathcal{F}[\alpha(t)] - i(K[\alpha(\tau)] - K[\alpha'(\tau)]) \mathcal{F}_2[\alpha(t)] \]  \hspace{1cm} (B13)

Using the exponential form of the correlation function present in \( \Lambda^X[\alpha(t)] \) one can obtain the time derivative of the \( \Lambda^X[\alpha(t)] \) in a straightforward manner using the fact that the derivative of an exponential is again an exponential

\[ \frac{\partial}{\partial t} \mathcal{F}_1[\alpha(t)] = 
- i(C(t_0)K[\alpha(\tau)] - C^*(t_0)K[\alpha(\tau)]) \mathcal{F}[\alpha(t)] - \gamma \mathcal{F}[\alpha(t)] - i(K[\alpha(\tau)] - K[\alpha'(\tau)]) \mathcal{F}_2[\alpha(t)] \]  \hspace{1cm} (B14)

The same procedure as above is then used to calculate the time derivative of the 2nd tier auxiliary influence functionals (AIF) and so on up till the time derivative of the \( n^{th} \) tier AIF, \( \mathcal{F}_n[\alpha(t)] \), which is given as follows

\[ \frac{\partial}{\partial t} \mathcal{F}_n[\alpha(t)] = 
- i(C(t_0)K[\alpha(\tau)] - C^*(t_0)K[\alpha(\tau)]) \mathcal{F}_{n-1}[\alpha(t)] - n\gamma \mathcal{F}[\alpha(t)] - i(K[\alpha(\tau)] - K[\alpha'(\tau)]) \mathcal{F}_{n+1}[\alpha(t)] \]  \hspace{1cm} (B15)

In the above, \( n \) is an index vector and denotes the level of the hierarchy. Each tier is coupled to a higher and lower tier via the \( n - 1 \) and \( n + 1 \) terms respectively. The obtained infinite hierarchy of influence functionals gives rise to an infinite hierarchy of auxiliary reduced density matrices,

\[ \rho_n(t) = U_n \rho(t_0) \]  \hspace{1cm} (B16)

in the above the auxiliary time evolution operator are obtained by replacing the influence functional by the corresponding auxiliary influence functionals. The time evolution of the above can be obtained by plugging in Eq. B16 the time derivative of the time evolution operator (Eq. B4) which can be obtained
Appendix C. Derivation of the exponential HEOM

by using Eq. B6 and B15. We obtain the following

$$\rho_n(t) = -(i\mathcal{L} + n\gamma)\rho_n - i[K[\alpha(\tau)],\rho_{n+1}] - in[C(t_0)K[\alpha(\tau)]\rho_{n-1} - C^*(t_0)\rho_{n-1}K[\alpha(\tau)]]$$

(B17)

The Liouville superoperator, $\mathcal{L}$, denotes the commutator with the Hamiltonian. The general form of the HEOM for an arbitrary number of poles used in the exponential form of the correlation function is as follows:

$$\rho_n(t) = -i\mathcal{L}\rho_n + \gamma_n\rho_n + \rho_n^+ + \rho_n^-$$

(B18)

The index array $n = (n_1, ..., n_L)$ denotes the leading order of system-bath coupling. The coefficients $\gamma$ result from the exponential expansion of the correlation functions and are written in the above in short-hand notation, i.e.,

$$\gamma_n = \sum_{l=1}^L n_l\gamma_l$$

(B19)

The coupling to the lower and higher tiers $\rho_n^-$ and $\rho_n^+$ are given by

$$\rho_n^- = -i\sum_{l=1}^L n_l(C_lK_l\rho_{n_l}^- - C_l^*\rho_{n_l}^-K_l)$$

(B20)

$$\rho_n^+ = -i\sum_{l=1}^L [K_l, \rho_{n_l}^+]$$

(B21)
D. Auxiliary material

Fluctuation-dissipation theorem

The spectral density function can also be considered as the Fourier transform of the reservoir response function. If the latter is as follows

$$\Phi_{\alpha ij}(t) \equiv \langle [B^\sigma_{\alpha i}(t), B^\sigma_{\alpha j}(0)] \rangle .$$ (D.22)

Then

$$J^\sigma_{\alpha ij}(\omega) \equiv \mathcal{F}\{\Phi_{\alpha ij}(t)\} .$$ (D.23)

Expanding the anticommutator and splitting the average

$$\mathcal{F}\{[[B^\sigma_{\alpha i}(t), B^\sigma_{\alpha j}(0)]]\} = \mathcal{F}\{\langle B^\sigma_{\alpha i}(t)B^\sigma_{\alpha j}(0)\rangle + \langle B^\sigma_{\alpha j}(0)B^\sigma_{\alpha i}(t)\rangle\}$$

$$= \mathcal{F}\{\langle B^\sigma_{\alpha i}(t)B^\sigma_{\alpha j}(0)\rangle\} + \mathcal{F}\{\langle B^\sigma_{\alpha j}(0)B^\sigma_{\alpha i}(t)\rangle\}$$

$$= \mathcal{F}\{C^\sigma_{\alpha ij}(t)\} + \mathcal{F}\{C^\sigma_{\alpha ji}(-t)\} = C^\sigma_{\alpha ij}(\omega) + C^\sigma_{\alpha ji}(-\omega) .$$ (D.24)

Using an expression of $C^\sigma_{\alpha ji}(-\omega)$

$$C^\sigma_{\alpha ji}(-\omega) = e^{\sigma\beta_\alpha(h\omega - \mu_\alpha)}C^\sigma_{\alpha ij}(\omega)$$ (D.25)

and inserting (D.25) in (D.24)

$$J^\sigma_{\alpha ij}(\omega) = C^\sigma_{\alpha ij}(\omega)\left(1 + e^{\sigma\beta_\alpha(h\omega - \mu_\alpha)}\right) .$$ (D.26)

The above can be rewritten as

$$C^\sigma_{\alpha ij}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{1}{1 + e^{\sigma\beta_\alpha(h\omega - \mu_\alpha)}} e^{\sigma i\omega t} J^\sigma_{\alpha ij}(\omega)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega f_\alpha(\beta_\alpha(h\omega - \mu_\alpha)) e^{\sigma i\omega t} J^\sigma_{\alpha ij}(\omega) ,$$ (D.27)

where $f_\alpha$ is the Fermi-Dirac function of reservoir $\alpha$. Eq. (D.27) is one of the specific forms of the fluctuation-dissipation theorem. The main idea behind the FDT is that the fluctuations of a physical
quantity (quantified here by the correlation function) and the response of this quantity to an external perturbation are directly related.

Exponential decomposed NEGF scheme

The coefficients \( \chi^{\pm}_{ak} \) are the poles from the upper (lower) half plane of both spectral density and Fermi function (for the latter the Matsubara poles are given below)

\[
\chi^{\pm}_{ak} = \{ \epsilon_a \pm iW_a \text{ for } k = 1, \pm \frac{2(k-1) - 1}{\beta} \pi i + \mu_a \text{ for } k = 2, \ldots, N_F + 1 \},
\]

whereas the other factors are given by

\[
I^{<,+}_{ak} = \left\{ \frac{1}{2} i \Gamma_a W_a f_a (\epsilon_a + iW_a + \mu_a) \text{ for } k = 1, \frac{1}{\beta} J_a \left( \frac{2(k-1) - 1}{\beta} \pi i + \mu_a \right) \text{ for } k = 2, \ldots, N_F + 1 \right\},
\]

\[
I^{<,-}_{ak} = \left\{ \frac{1}{2} i \Gamma_a W_a f_a (\epsilon_a - iW_a + \mu_a) \text{ for } k = 1, -\frac{1}{\beta} J_a \left( -\frac{2(k-1) - 1}{\beta} \pi i + \mu_a \right) \text{ for } k = 2, \ldots, N_F + 1 \right\},
\]

\[
I^{>,+}_{ak} = \left\{ -\frac{1}{2} i \Gamma_a W_a f_a (-\epsilon_a - iW_a - \mu_a) \text{ for } k = 1, \frac{1}{\beta} J_a \left( \frac{2(k-1) - 1}{\beta} \pi i + \mu_a \right) \text{ for } k = 2, \ldots, N_F + 1 \right\},
\]

\[
I^{>,-}_{ak} = \left\{ -\frac{1}{2} i \Gamma_a W_a f_a (-\epsilon_a + iW_a - \mu_a) \text{ for } k = 1, -\frac{1}{\beta} J_a \left( -\frac{2(k-1) - 1}{\beta} \pi i + \mu_a \right) \text{ for } k = 2, \ldots, N_F + 1 \right\}.
\]

Density matrix elements

The expectation value of the number operator, or the occupation number, is defined as \( \langle n \rangle = \text{Tr} \{ c^\dagger_1 c_1 \rho \} \). For the sake of a simple example, we take a 2 \( \times \) 2 density matrix,

\[
\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}.
\]

The occupation number is then given as

\[
\langle n \rangle = \text{Tr} \left\{ \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \right\}
\]

\[
= \text{Tr} \left\{ \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \right\} = \text{Tr} \left\{ \begin{pmatrix} 0 & 0 \\ \rho_{21} & \rho_{22} \end{pmatrix} \right\} = \rho_{22}.
\]

Thus the occupation number is stored in the \( \rho_{22} \) element of the density matrix.
Number operator

If $N_\alpha$ is the number operator for reservoir $\alpha$ and $b_\alpha^\dagger, b_\alpha$ are the creation/annihilation operators then

$$
[N_\alpha, b_\alpha] = \sum_k [b_\alpha^\dagger b_\alpha, b_\alpha] = \sum_k (b_\alpha^\dagger \{b_\alpha, b_\alpha\} - \{b_\alpha^\dagger, b_\alpha\} b_\alpha) = \sum_k (-\{b_\alpha^\dagger, b_\alpha\}) = -b_\alpha,
$$

(D.28a)

$$
[N_\alpha, b_\alpha^\dagger] = \sum_k (b_\alpha^\dagger \{b_\alpha, b_\alpha^\dagger\} - \{b_\alpha^\dagger, b_\alpha^\dagger\} b_\alpha) = \sum_k b_\alpha^\dagger \delta kj = b_\alpha^\dagger
$$

(D.28b)

where we have used the fact that $[AB, C] = A\{B, C\} - \{A, C\} B$. The same relations hold also for the reservoir operators $B_{\alpha k}^{(l)}$ since they are linear combinations of $b_\alpha^{(l)}$

$$
[N_\alpha, B_{\alpha k}] = -B_{\alpha k} \quad , \quad [N_\alpha, B_{\alpha k}^\dagger] = B_{\alpha k}^\dagger
$$

(D.29)

Or in condensed notation

$$
[N_\alpha, B_{\alpha k}^\sigma] = \sigma B_{\alpha k}^\sigma
$$

(D.30)

Let us denote by $AB \equiv [A, B]$, the commutator of an arbitrary operator $B$ with $A$. Then by the definition of the exponential operator

$$
e^A B e^{-A} = e^A B = \sum_{n=0}^{\infty} \frac{1}{n!} A^n B
$$

(D.31)

If $N_\alpha B_{\alpha k}^\sigma \equiv [N_\alpha, B_{\alpha k}^\sigma]$, then using (D.31) one can write

$$
e^{\beta_\alpha \mu_\alpha} N_\alpha B_{\alpha k}^\sigma e^{-\beta_\alpha \mu_\alpha} N_\alpha = e^{\beta_\alpha \mu_\alpha} N_\alpha B_{\alpha k}^\sigma = \sum_{n=0}^{\infty} \frac{(\beta_\alpha \mu_\alpha)^n}{n!} N_\alpha^n B_{\alpha k}^\sigma
$$

(D.32)

Then by (D.30) it follows

$$
e^{\beta_\alpha \mu_\alpha} N_\alpha B_{\alpha k}^\sigma e^{-\beta_\alpha \mu_\alpha} N_\alpha = \sum_{n=0}^{\infty} \frac{(\beta_\alpha \mu_\alpha)^n}{n!} \sigma^n B_{\alpha k}^\sigma = e^{\sigma \beta_\alpha \mu_\alpha} B_{\alpha k}^\sigma
$$

(D.33)

The identity above shall prove itself valuable in the next section when discussing the detailed-balance equation for the correlation functions.
Bibliography


Bibliography


Bibliography


List of Publications

Publications included in the present thesis:


Publications not related to the present thesis:


Poster Presentations
