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## Keldysh-Langevin Approach to Nuclear Dynamics in Molecular Junctions

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Thesis submitted to the College of Science and Engineering

at

### James Cook University

in partial fulfillment of the requirements for the degree of

### **Doctor of Philosophy (Physical Sciences)**



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Primary advisor: A/Prof. Daniel Kosov Secondary advisor: Prof. Ronald White

### **Declaration of originality**

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institute of tertiary education. Every reasonable effort has been made to gain permission and acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

It is not down on any map; true places never are.

Herman Melville, Moby-Dick

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## Abstract

The quintessential system which is used to observe and study the effects of quantum transport is that of the molecular junction: a molecular bridge bonded between two macroscopic conducting leads. Molecules in molecular junctions are subject to current-induced forces that can break chemical bonds, induce reactions, destabilize molecular geometry, and halt the operation of the junction. Additionally, novel phenomena such as telegraphic switching between conformations and localised heating have the possibility of being exploited for device functionality. We develop a nonequilibrium Green's function based transport theory in which atoms on the molecular bridge are allowed to move. This is achieved by utilising the inherent separation of timescales between slow nuclear motion and fast electronic dynamics, allowing us to solve for the adiabatic Green's functions along with non-adiabatic dynamical corrections. To make the theoretical approach fully self-consistent, the same time-separation approach is used to develop expressions for the adiabatic, dissipative, and stochastic components of current-induced forces in terms of adiabatic Green's functions. Using these current induced forces, the equation of motion for the nuclear degrees of freedom is cast in the form of a Langevin equation. This model is applied for both static and AC driving in the leads, and incorporates the motion of the atoms in the central region along with the atoms on the leads interface. Furthermore, we utilise a Fokker-Planck description for the classical coordinate in order to calculate Kramers' first-passage times and reaction rates. We observe localized heating effects and the formation of bi-stable effective potentials for the classical coordinates which are analysed through the use of the measured noise in the current. Negative viscosities are shown to emerge under an applied voltage bias in a variety of systems, which demonstrate the lack of a possible steady-state for certain configurations. An applied AC driving is shown to be capable of producing a cooling effect to the molecular bridge, increasing the stability and longevity of the system. We assess the validity of the Langevin approach in different regimes by applying a novel time-stepping algorithm to solve for the classical Ehrenfest dynamics of the molecular bridge, and find that the results produced by the Langevin method are accurate provided that the applicable regimes are not abused.

## **Research output**

### **Publications**

- Current-induced atomic motion, structural instabilities, and negative temperatures on moleculeelectrode interfaces in electronic junctions,
   R.J. Preston, V.F. Kershaw, D.S. Kosov, Phys. Rev. B, 101, 155415 (2019)
- [2] Cooling molecular electronic junctions by AC current,
  R.J. Preston, T.D. Honeychurch, D.S. Kosov, J. Chem. Phys., 153, 121102 (2020)
- [3] First-passage time theory of activated rate chemical processes in electronic molecular junctions, R.J. Preston, M.F. Gelin, D.S. Kosov, J. Chem. Phys., 154, 114108 (2021)
- [4] Emergence of negative viscosities and colored noise under current-driven Ehrenfest molecular dynamics,
   B.I. Broeten, T.D. Honeychurch, D.S. Kosoy, arXiv proprint, arXiv:2204.08278

R.J. Preston, T.D. Honeychurch, D.S. Kosov, arXiv preprint, arXiv:2204.08278

### **Conference posters**

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## Introduction

#### **1.1** Setting the scene for a technological revolution

An age of unending technological innovation has lulled us into a false sense of security. The constant scaling down of electronic components since their inception has yielded a continuous growth to our computational prowess which allows society to cope with the demands of an increasingly data-driven world. However, we now stand on a precipice of our own construction, in which the past century of advancement in electronics converges towards its ultimate conclusion.

Computations at the most fundamental level are performed through the manipulation of charge states of transistors, of which there can be hundreds of millions of transistors on a single chip. The state of a single transistor is represented as either a 1 or a 0; this corresponds to whether or not a small applied voltage allows for current to flow across a gate within the transistor. This forms the basis for the so-called Boolean algebra in which calculations and operations are phrased in terms of logical statements, where a large number of transistors operate in unison to perform a desired function. A higher density of transistors on a given chip will thus correspond to a larger capacity for computation. In a crude sense, the goal for technological advancement is then clear; to cram as many transistors into as small an area as possible! The most commonly used architecture is the metal-oxide-semiconductor field-effect transistor (MOSFET), a schematic of which is shown in Figure 1.1. A single MOSFET consists of a silicon substrate which has been doped in regions at either end with phosphorous while the bulk of the substrate is doped with boron. The end regions are generally referred to as the source and drain, where a large chemical potential is applied to the source relative to the drain. The free electrons due to the phosphorous in the source and drain flow into the nearby surrounding holes in the substrate due to the boron. This creates an electromagnetic energy barrier for further electron flow, prohibiting any net current to flow from the source to the drain - the transistor is in the 0 state. In order to induce a current flow, we introduce a gate which is separated from the substrate by an insulating oxide layer. Application of a



Figure 1.1: Schematic of a generic MOSFET.

small voltage on the gate opens a conducting channel between the source and drain along the surface between the insulating layer and the substrate - the transistor is now in the 1 state. Computations are performed by manipulating the gate voltages of sets of transistors in tandem.

The size of a transistor is measured in terms of the distance between the source and the drain. Device miniaturisation then involves decreasing this distance while maintaining adequate device functionality. Undesirable short-channel effects arise as a result of the decreased source-drain separation. These include effects such as drain induced barrier lowering, which lowers the energy required for an electron to traverse the region from the source to the drain and blurs the distinction between 1 and 0 states within the device. Additionally, surface scattering along the oxide layer, the hot electron effect, and impact ionisation will decrease the device efficiency and degrade its performance over time. On very small scales, we must also directly compete with quantum mechanical effects such as quantum tunnelling in which an electron is capable of tunnelling directly from the source to the drain with little regard for the energy barrier dividing them. This results in a net leakage current even in the 0 state. While manufacturers have developed ingenious methods of circumventing short-channel effects while maintaining a steady rate of miniaturisation in accordance with Moore's law, we are approaching a fundamental limit in which transistors are constructed on the atomic scale and are entirely shackled by quantum laws. This then marks the end of the current era of electronics and a grand finale for Moore's law, and the rush is on to uncover the next great innovation.

A candidate with a name that has permeated even the general public is that of quantum computing. If the aim is to overcome quantum effects on the small scale, perhaps we can shift our perspective so that quantum effects are exploited to our own advantage. The quantum computer is an entirely novel architecture which does just that. Here, the bits in a classical computer are replaced by quantum bits or qubits, a superposition between two distinct quantum states. These qubits are subject to quantum logic gates which manipulate the state of the qubit according to applied electromagnetic fields in the device. Calculations are then performed via the manipulation and interaction of a large number of qubits.

Quantum computing is a stimulating concept worthy of exploration. It does, however, come with its own plethora of difficulties to be conquered such as decoherence and quantum error correction. The most powerful quantum computers today are still limited to less than 100 qubits; a factor of ten-thousand too small to serve as a practical replacement to the current technology. Additionally, a quantum computer is only as useful as the algorithms we feed it. While quantum computers do allow for specialised algorithms for tackling problems out of reach of classical computing, the infrastructure is not yet developed enough to provide benefits beyond niche applications. In its current state of infancy, the field of quantum computing is ill-equipped to take the reigns moving forward. A more immediate solution is desired.

#### **1.2 Molecular Electronics**

Another possible alternative elects to tread the middle ground between evolution and revolution; this is the field of molecular electronics. The concept is to replace the conventional semiconductor architecture by single molecules which act as the active elements in integrated circuits. The choice of molecule used is tailored to satisfy a particular purpose within the circuit by utilising its inherent structure and conducting properties. The idea presents a number of benefits. Firstly, electronic elements are designed and fabricated on the smallest possible scale with quantum effects already accounted for in the system. Quantum effects can then be utilised as an additional tool at our disposal for novel device applications, rather than something to be feared; especially since nanostructures which fall under the regime of quantum mechanics often show desirable electrical, optical, and thermal properties inaccessible to conventional classical systems [1]. Secondly, a ground-up method of device fabrication in which device elements are synthesised in large quantities in labs would yield a monumental decrease to costs in comparison to the expensive top-down approach of fabrication used currently. Finally, and in contrast to quantum computing, operations are still performed using classical bits and so the knowledge of classical computing built over the last half-century need not go to waste.

The basic building block of molecular electronics technology is the molecular junction, where two macroscopic electrodes or leads are connected by a molecular bridge as visualised in Figure 1.2. In experiments, the electrodes are generally composed of gold due to its inherent inertness which aids in the consistency and reproducibility of measurements [2], as well as its plasticity which further facilitates junction fabrication. However, silver [3, 4], platinum



Figure 1.2: Schematic of a molecular junction. The molecular bridge (green) connects two macroscopic leads (yellow).

[5–7], palladium [8], and variations of graphite [9, 10] have also been used experimentally due to their favourable conducting properties. The molecular bridge is then chosen to meet the desired function of the device. It's been observed that carbon-based molecules often display the required versatility and conduction properties to produce any number of novel functions [11]. The experimental construction of molecular junctions is facilitated by a number of techniques. Most prevalent in the literature is that of the scanning tunnelling microscope break-junction (STMBJ) in which the fine tip of a scanning tunnelling microscope is indented into a metal substrate, leading to the formation of chemical bonds between the substrate and tip. The tip is subsequently retracted, forming a short atomic wire between the tip and the substrate which each act as the source and the drain, respectively. An alternate method of almost equal popularity is that of the mechanically-controllable break-junction (MCBJ). Here, a metallic bridge is attached to a flexible substrate which is then slowly bent mechanically via a piezoelectric motor. Enough applied bending breaks the metallic bridge, forming a nanoscale gap. The molecular bridge is then generally deposited into the junction gap from solution. The MCBJ approach has the benefit of readily being able to include a gate electrode unlike STMBJ.

While the original concept of molecular electronics has been around since the 1950's, the great experimental charge was initiated by Aviram and Ratner with their theoretical description of a molecular rectifier [12], which demonstrated that molecular electronic devices, if constructible, could indeed mimic the operations of conventional electronic components. Since then, a raft of devices have been proposed and realised experimentally including but not limited to molecular switches induced both by voltage [13–15] and mechanical [16–18] means, molecular diodes [19–21], molecular field effect transistors via inclusion of an additional electrode acting as a gate [22], thermoelectric devices [23–25], and spintronic devices, which utilise the electronic spin as an additional degree of freedom [26–28].

Even beyond the domain of nanoelectronic devices, molecular junctions have found utility in theoretical pursuits as they are an ideal testing ground for quantum transport effects in non-equilibrium systems. They enable the study of the basic mechanisms of charge transport, yielding transport regimes otherwise inaccessible to classical systems [29–37], along with facilitating the probing of thermodynamical laws on the most fundamental scale [38, 39].

Unfortunately, if molecular electronics is to be thought of as a legitimate successor to silicon semiconductor technology, a number of hurdles must be overcome. Molecular junctions behave like insulators and require a high voltage bias for device operation [40]. As a result, the significant operational voltage bias of a few volts across the molecular length along with large electric current densities destroy the structural integrity of the device through chemical bond rupture, large scale molecular geometry alteration or electromigration of the leads interfacial atoms. Furthermore, while the construction of single molecular junctions is now achieved experimentally using various techniques, the fabrication of integrated circuits is another challenge altogether.

### 1.3 Current-induced forces/phenomena

#### 1.3.1 Experimental evidence for current-induced forces

In this section, we present a brief overview of some notable experimental demonstrations of the effects of current-induced forces in molecular junctions.

#### 1.3.1.1 Voltage-induced bond rupture and device breakdown

We first discuss the observed experimental breakdown of molecular junctions due to an applied voltage bias over the electrodes. Junction breakdown is generally observed experimentally via observation of the conductance through the device. Stepwise decreases to the conductance are indicative of bond-breakages along the molecular bridge which decreases the possible pathways of current through the system; zero measured conductance then implies that the molecular bridge has been severed completely. Statistical analysis over an ensemble of such systems then allows for the calculation of the average lifetime of the molecular bridge for a variety of parameters.

This approach was applied by Tsutsui et al. [41] in which they applied the MCBJ technique to construct molecular junctions consisting of a benzenedithiolate (BDT) molecular bridge connecting two gold electrodes. Measurements of the conductance indicated the presence of one or more BDT bridges in parallel in any given junction. The lifetime of a BDT bridge was then calculated by measuring the time spent at a given quantum of conductance before



Figure 1.3: Lifetime distributions of BDT junctions. The green lines are Gaussian fits to the single peak profile. The peak junction lifetime  $\tau_B$  is denoted by the arrows, which corresponds to the lifetime of BDT junctions with a certain configuration formed at a maximum likelihood. Reproduced with permission from Reference [41].

decaying to a lower value. Figure 1.3 is a reproduction of their results in which the distribution of junction lifetimes is observed for varying voltages. Increasing the voltage beyond  $V_e = 0.6V$  results in a dramatic decrease to the lifetime of the BDT bridge. Relevant theory suggests that the lifetime is dictated both by a voltage induced lowering of the energy barrier for dissociation which is approximately linear below 1V, and local heating of the vibrational modes along the molecular bridge which become important beyond a certain threshold voltage [42–44]. The authors reason that for  $V_e > 0.6V$ , local heating due to electron-phonon interactions becomes sufficiently large to trigger thermally-activated bond dissociation within the junction. They then use their measurements to estimate an effective temperature of the vibrations along the molecular bridge as a function of the voltage  $V_e$ , as shown in Figure 1.4.

Similar results have been produced by Smit et al. [45] and Sabater et al. [46] for molecular bridges consisting of Au or Pt chains again using the MCBJ technique. They observed the voltage induced breakdown for varying chain lengths, finding that longer chains were subject to bond rupture at smaller voltages.



Figure 1.4: Bias dependence of  $T_{\text{eff}}$  (circles) and  $\tau_B$  (triangles) of BDT molecular junctions (red) and Au single-atom contacts (blue). Reproduced with permission from Reference [41].

#### 1.3.1.2 Probing the vibrations

While vibrations along the molecular bridge cannot be observed directly, information about them can be garnered via measurement of the transport properties of the junction. The excitation of vibrational modes manifest as tiny variations in the transport properties of the system which become more obvious when measuring the conductance and higher derivatives of the current with respect to the voltage. An example of such an analysis is displayed in Figure 1.5 as reproduced from Kushmerick et al. [47]. In this study, they constructed crossed-wire tunnel junctions in which the junction separation is controllable via the Lorentz force generated by a small DC current. Deposited within the junction was oligo(phenylene ethynylene) (OPE), a molecular configuration which has been widely studied for possible technological applications [48–51]. Measurement of  $\frac{d^2I}{dV^2}$  shows prominent peaks at specific voltages indicating a change to the transport properties of the system. Comparison with previous experiments along with density functional theory calculations allowed the authors to associate the peaks with the excitation of vibrational modes of specific bonds along the OPE molecule.

There exists a vast array of literature which applies this technique for both the characterisation and identification of vibrational modes over various parameter regimes [52–61].

#### 1.3.1.3 Configurational changes and switching

Beyond affecting basic transport properties, the excitation of vibrational modes along the bridge can result in large-scale configurational changes to the molecular geometry. This is exhibited in experimental observations via the apparent switching of the electric current between two or more states. An appropriate example is an experiment performed by Stipe et al. [62] in which an STM tip was utilised to induce the reversible rotation of molecular oxygen


Figure 1.5: Inelastic electronic tunnelling spectrum of an OPE junction. Mode assignments are from density-functional theory calculations of the free molecule. Reproduced with permission from Reference [47].



Figure 1.6: Tunneling current during a 0.3V pulse above an isolated  $O_2$  molecule. Rotation is followed by dissociation (step at  $t \sim 610$ ms) Reproduced with permission from Reference [62].

on a platinum surface. They found that under the influence of a tunnelling current, the  $O_2$  molecules could occupy three separate energetically stable orientations. They propose that this is a result of the excitation of the rotational vibration mode due to the inelastic tunnelling of electrons. They additionally found that a large enough applied voltage could result in complete dissociation of the  $O_2$  molecule; an example trajectory of this is found in Figure 1.6 where the molecule dissociates after 610ms. The dissociation corresponds to the stretch mode of the  $O_2$  which has a larger energy barrier than the rotational modes. This is an example of the large-scale configurational changes which can occur under the influence of current-induced forces. However, the effects are not limited to the collective modes of a given molecule.

Auwärter et al. [14] considered a free-base tetraphenyl-porphyrin molecule which is anchored to a silver surface under the influence of an STM tip. Rather than inducing bulk vibrations in the molecular configuration, they were able manipulate the configuration of individual pro-



Figure 1.7: Model highlighting the position of the hydrogen pair (yellow) in configuration (a)  $H_{\alpha}$  and (b)  $H_{\kappa}$ . (c) Current versus time trace recorded at -1.9 V. A switching between two current levels representing the high (h) and low (l) conductance states is clearly discernible. Reproduced with permission from Reference [14].

tons, thus producing an atomic switch on the smallest possible scale. As shown in Figure 1.7a and 1.7b, the central pair of protons can exist in two possible states which they dub the  $H_{\alpha}$  and  $H_{\kappa}$  configurations. Careful placement of the STM tip and the application of a voltage over the junction produces an inelastic tunnelling current which yields the required energy to change between the configurations. This then results in a bi-stable switching in the current trajectory as observed in Figure 1.7c. Conductance switching in molecular junctions is ubiquitous in experimental literature for a range of different systems and molecular configurations [63–71].

#### 1.3.1.4 Current-induced chemical reactions

An intimate understanding of the effects of the current-induced forces allows for molecular engineering, in which complex chemical reactions are carried out in molecular junctions solely due to the controlled dissociation of specific bonds on the molecular bridge. With more development, this may allow for the precise construction of molecular-scale devices to suit a specific purpose. Additionally, the research can be applied to better understand problems in surface science. A pioneering experiment by Lauhon and Ho [72] saw a multi-step unimolecular reaction performed entirely using an STM tip. The main reaction discussed was a two step reaction from acetylene (HCCH) to produce molecular ethynyl (CCH) and subsequently,



Figure 1.8: Schematic illustration of the STM tip-induced synthesis steps of a biphenyl molecule. (a),(b) Electron-induced selective abstraction of iodine from iodobenzene. (c) Removal of the iodine atom to a terrace site by lateral manipulation. (d) Bringing together two phenyls by lateral manipulation. (e) Electron induced chemical association of the phenyl couple to biphenyl. (f) Pulling the synthesized molecule by its front end with the STM tip to confirm the association. Reproduced with permission from Reference [73].

dicarbon (CC). This was achieved by the application of precise voltages to excite vibrational modes in specific bonds:

$$HCCH \xrightarrow[V=2.8eV]{} CCH \xrightarrow[V=2.1eV]{} CC$$
(1.1)

Hla et al. [73] went a step further by synthesizing biphenyl from iodobenzene adsorbed on a Cu(111) substrate. This was achieved by first applying a tunnelling current to extract iodine from the iodobenzene, leaving a single phenyl molecule. Then, two phenyl molecules are brought into contact via lateral manipulation using the STM tip. The chemical association of the two phenyl molecules into biphenyl was then induced by another tunnelling current which rotated the molecules such that the appropriate orbitals were aligned to facilitate bonding. A schematic of the procedure is reproduced in Figure 1.8.

Finally, a more recent study by Aragonés et al. [74] used the applied external field present in an STMBJ to accelerate bond formation processes in a Diels–Alder reaction; demonstrating the importance of not only the current-induced forces, but also the electric field produced by the non-equilibrium leads.

# 1.3.2 Theoretical consideration of the current-induced Forces

### 1.3.2.1 Fully-Quantum methods

We find it appropriate to begin the discussion on the theoretical treatment of current-induced forces by considering methods which accurately account for the quantum nature of both the electronic environment and nuclei along the bridge; the goal being to minimise the number of assumptions being made about the system. Unfortunately, assumptions are a necessary requirement for the problem to be soluble and a fully-quantum treatment of the entire system often requires assumptions which are directly at odds with the experimentally observed phenomena which we seek to reproduce theoretically.

A class of numerically exact approaches relies on the calculation of the wavefunction describing a closed system via the propagation of the time-dependent Schrodinger equation:

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle,$$
 (1.2)

in which the system of interest is coupled to a bath represented by a finite number of bath modes. A notable propagation technique which has seen success is the multilayer multicon-figuration time-dependent Hartree approach (ML-MCTDH) [75–81]. Here, the wavefunction is subject to a recursive expansion into a hierarchy of single-particle functions which is truncated at a chosen layer determined by convergence testing for the given system. Expressing the base layer in terms of time-independent basis functions then allows each layer to be evolved according to its own equation of motion. While accounting for *all* desired quantum effects, such methods suffer from a number of drawbacks. Firstly, the baths must be finite since the system is closed. Many bath modes are required for convergence of the method at the cost of computational efficiency. In addition, numerical simulations are limited by electronic time-scales. Experimentally observed phenomena such as bond-rupture and large scale configuration changes on the molecular bridge instead occur over much longer nuclear time-scales which are inaccessible to the method due to convergence limitations [75].

In the context of our research, it is more appropriate to consider open quantum systems in which the molecular bridge is attached to infinite reservoirs of electrons which constitute the environment. The Hamiltonian for the bridge can be decomposed into electronic and vibrational components along with the coupling between the two:

$$\hat{H}_{\text{sys}} = \hat{H}_{el} + \hat{H}_{vib} + \hat{H}_{el-vib}, \tag{1.3}$$

The electronic-vibrational coupling  $\hat{H}_{el-vib}$  will in general have a complicated dependence on the vibrational coordinate itself. To simplify the problem and avoid the presence of two-body

and higher interaction terms, it's generally assumed that the amplitude of vibrational motion is small. The interaction is then expanded to first order in the deviations of nuclei from their equilibrium configuration [82], yielding

$$\hat{H}_{el-vib} = \lambda \hat{a}^{\dagger} \hat{a} (\hat{b} + \hat{b}^{\dagger}), \qquad (1.4)$$

where  $\lambda$  is the interaction strength as computed via electronic structure calculations. For ease of explanation, in the equations presented we explicitly consider the case of a single electronic level and vibrational mode on the molecular bridge in this section; this is known as the Holstein model. We use  $\hat{a}^{\dagger}$  to denote the fermionic creation operator corresponding to the electronic level on the bridge, while  $\hat{b}^{\dagger}$  is the bosonic creation operator for a vibrational mode, and likewise for the annihilation operators. The vibrational modes contained in  $\hat{H}_{vib}$ are commonly assumed to be harmonic [77, 78, 83–93] or limited to other generic vibrational potentials [94, 95]; the harmonic case is given by

$$\hat{H}_{vib} = \hbar\omega(\hat{b}^{\dagger}\hat{b} + \frac{1}{2}).$$
(1.5)

These assumptions emphasise the difficulties with a quantum treatment of the vibrations. Many-body interactions in the Hamiltonian present theoretical troubles which are circumvented by assuming that the vibrations are small and harmonic. Unfortunately, this is directly at odds with the experimental phenomena which we seek to reproduce with the model in which the current-induced forces may produce *large-scale* changes to the molecular geometry.

From this Hamiltonian, the system can be solved for via numerically exact or perturbative approaches. The hierarchical quantum master equation (HQME) approach is a numerically exact method [85, 95–102]. The system is described in terms of a density matrix which contains information on the coupling of the system to an environment. In a similar vein as ML-MCTDH, the full density matrix is decomposed into a hierarchy of auxiliary density matrices which are each calculated according to their own equations of motion and convergence tests again dictate where to truncate the hierarchy. While HQME provides a numerically exact scheme for simulating the dynamics of a system interacting with an environment over short time-scales, it is generally limited to the aforementioned simplistic descriptions of the molecular bridge. However, recent developments to the theory which utilise a discrete variable representation of vibrational modes have proved successful in moving beyond the harmonic approximation [95, 101, 102].

Beyond numerically exact methods, the introduction of a small parameter is often utilised to facilitate a perturbative treatment of the problem. This can lead to greater computational efficiency and allows for the consideration of larger and more complex systems. One such perturbative scheme is the self-consistent Born approximation, in which the interaction strength  $\lambda$  is assumed small relative to  $\Gamma$ ;  $\Gamma$  being the level broadening due to the interaction with the

leads while  $1/\Gamma$  is associated with the characteristic tunnelling time of an electron through the bridge. From here, the problem is then treated within an appropriate framework such as non-equilibrium Green's functions [77, 87, 103–108]. The converse case where  $\lambda \gg \Gamma$  can instead be treated using master equations [85, 90, 109–117].

#### 1.3.2.2 Quasi-Classical methods

A fully quantum treatment of the system is not conducive to the observation of experimental phenomena such as current-induced configurational changes and bond rupture. A semiclassical description for the nuclear dynamics allows for the description of such phenomena while greatly reducing the computational load since the vibrations can now be evolved in time according to classical equations of motion. This comes at the cost of neglecting quantum effects such as quantum tunnelling of the nuclei, coherences, and the quantized nature of the vibrational modes. However, this can often be justified depending on the parameter regime in which the system is operating. Quantum tunnelling of the nuclei generally only becomes relevant at very low temperatures where thermalization effects are decreased [118, 119], while coherences quickly dissipate over the long time-scales of nuclear motion [120]. The quantized nature of vibrational modes depends on the molecule considered; larger collective vibrations can be reasonably approximated as a continuum of vibrational states.

The consideration of classical vibrations allows for much manoeuvrability in the form of the Hamiltonian. The components of the Holstein model described in the previous section now become

$$\hbar\omega(\hat{b}^{\dagger}\hat{b} + \frac{1}{2}) \to \frac{1}{2}mv^2 + U(x),$$
 (1.6)

$$h_0\hat{a}^{\dagger}\hat{a} + \lambda\hat{a}^{\dagger}\hat{a}\underbrace{(\hat{b} + \hat{b}^{\dagger})}_{\hat{x}} \to V(x)\hat{a}^{\dagger}\hat{a}, \qquad (1.7)$$

where we have introduced the classical position and velocity, x and v. The advantages are clear, we are now able to consider arbitrary vibrational potentials U(x) as well as arbitrary functional dependence of the interaction V(x) without fear of having to consider many-body interactions, since the vibrational coordinates have been demoted from operators to variables. This provides a natural and intuitive means of exploring large-scale configurational changes within the system which are otherwise difficult to model on a quantum footing. The remaining task is to then appropriately model the forces acting on the classical coordinates such that they can be evolved according to

$$F = ma. \tag{1.8}$$

This is achieved through a variety of methods including surface-hopping schemes [121–131],

Ehrenfest dynamics [100, 132–140], and Langevin dynamics [141–152]. The electronic components of the Hamiltonian can be expressed in the form

$$\hat{H}_{el} + \hat{H}_{el-vib} = V_c(x)\hat{a}^{\dagger}\hat{a} - V_u(x)(\hat{a}^{\dagger}\hat{a} - 1),$$
(1.9)

where  $V_c$  is the charged potential and  $V_u$  is the uncharged potential. When the electronic level on the molecular bridge is occupied and  $\hat{a}^{\dagger}\hat{a} = 1$ , the classical coordinate vibrates in the charged potential and when it is unoccupied,  $\hat{a}^{\dagger}\hat{a} = 0$  and it oscillates in the uncharged potential. Surface-hopping schemes consider unperturbed classical vibrations in these potentials where at any given time, the potential may change from uncharged to charged (or vice versa) as determined by hopping rates which are usually computed in an ad-hoc manner to satisfy thermodynamic equilibrium conditions. Such schemes have found success in describing the vibrational relaxation of molecules near metal surfaces and with some extensions, has been applied to non-equilibrium transport [121]. However, the applicable regimes of the method are not always clear a priori since it lacks the rigorous theoretical foundation of other methods [153].

In contrast, Ehrenfest dynamics opts to only consider the average occupation at any given time as determined by the nuclear geometry. The average occupation of the electronic level  $\langle a^{\dagger}a \rangle$  varies continuously as a function of the classical vibrations, which then generates the time-dependent vibrational potential. Treating the interaction with the electronic environment on an average level in this way neglects the microscopic detail in the electronic density and does not account for the electron-nuclear correlations required to accurately describe effects such as joule heating [133, 134, 154–156]. However, extensions beyond Ehrenfest dynamics which account for electron-nuclear correlations via a perturbative expansion in the nuclear fluctuations about the mean trajectory have alleviated these issues [155, 156]. We will discuss the Ehrenfest approach in more detail in Section 7.

An approach which does accurately describe heating effects is the Langevin approach. Since Langevin dynamics is the primary focus of this study, we review the approach in significant detail in the following sections.

# **1.4** The Langevin equation

The Langevin equation was first applied to the study of Brownian motion. Here, we have a large particle such as a grain of pollen floating on the surface of water. The pollen can be observed to undergo rapid directional changes and unpredictable motion as it interacts with the constituent water molecules in the fluid. Treating this system on an exact footing would entail one to solve the coupled equations of motion for each of the many ( $\sim 10^{23}$ ) particles; an

unachievable and unnecessary goal, especially considering that we only desire a description of the motion of the single of grain of pollen. We instead opt to search for a reduced description of the system in which the interaction of the grain of pollen with the surrounding environment is treated on a phenomenological level.

The dynamics of the pollen is assumed to be governed chiefly by a velocity-proportional viscosity force. This is justified by the realisation that for some positive velocity v, the pollen will *on average* experience more collisions from in front than from behind, in which case the velocity at the next instant of time depends only on the current velocity and not on previous values. However, this implies that the velocity of the pollen should decay to zero after some time which contradicts our observations and intuition. This is because we are still not accounting for the random thermal vibrations within the fluid which are constantly buffeting our Brownian particle. These are accounted for by an additional stochastic force  $\delta f(t)$  which will act to re-energize the particle such that we observe a non-zero steady state temperature. The equation of motion now becomes

$$m\frac{dv}{dt} = -\xi v + \delta f(t). \tag{1.10}$$

The stochastic force is quantified according to its moments. By invoking the central-limit theorem, it is often a reasonable assumption to propose  $\delta f(t)$  to be a Gaussian process, meaning it is defined entirely by its first two moments. Thus, we assume that

$$\langle \delta f(t) \rangle = 0, \qquad \langle \delta f(t) \delta f(t') \rangle = D \delta(t - t'),$$
(1.11)

where  $\langle \rangle$  represents an average over many samples of the stochastic force. The zero mean can be justified by the realization that any directionality component should be appropriately captured by the frictional force, leaving only the homogeneous thermal vibrations to the stochastic force. The second moment describes the strength of the stochastic force and its correlations at different times. In accordance with the original description of Brownian motion, we have assumed that the stochastic force is uncorrelated at different times as described by  $\delta(t - t')$ . This amounts to assuming that the environment relaxes instantaneously with respect to the motion of the Brownian particle such that at any given time step, the environment has no memory of previous times.

Naturally, one would expect a relationship between the viscosity coefficient  $\xi$  and the diffusion coefficient *D*, since each emerge due to interactions with the same surrounding fluid. Additionally, they both act to entirely determine the dynamics of our Brownian particle and its steady-state temperature. This relationship is the aptly named fluctuation-dissipation theorem.

# **1.4.1** Fluctuation-Dissipation theorem

We aim to find a relationship between  $\xi$  and D along with the steady-state temperature. Let's begin with our Langevin equation as defined in (1.10) and first find an explicit expression for v(t). Using the conventional approach for a first-order differential equation, we find

$$v(t) = e^{-\frac{\xi}{m}t}v(0) + \frac{1}{m}\int_{0}^{t} dt' e^{-\frac{\xi}{m}(t-t')}\delta f(t').$$
(1.12)

In the hopes of relating v(t) to the kinetic energy, we now square the above equation to obtain

$$v(t)^{2} = e^{-\frac{-2\xi}{m}t}v(0)^{2} + \frac{2}{m}e^{-\frac{\xi}{m}t}v(0)\int_{0}^{t}dt'e^{-\frac{\xi}{m}(t-t')}\delta f(t')$$
(1.13)

$$+\frac{1}{m^2}\int_{0}^{t} dt' dt'' e^{-\frac{\xi}{m}(t-t')} e^{-\frac{\xi}{m}(t-t'')} \delta f(t') \delta f(t'').$$
(1.14)

Apply an average over many iterations of the stochastic force and leverage (1.11) to obtain

$$\left\langle v(t)^{2} \right\rangle = e^{-\frac{-2\xi}{m}t} v(0)^{2} + \frac{1}{m^{2}} \int_{0}^{t} dt' dt'' e^{-\frac{\xi}{m}(t-t')} e^{-\frac{\xi}{m}(t-t'')} \left\langle \delta f(t') \delta f(t'') \right\rangle$$
(1.15)

$$=e^{-\frac{-2\xi}{m}t}v(0)^{2}+\frac{D}{m^{2}}\int_{0}^{t}dt'dt''e^{-\frac{\xi}{m}(t-t')}e^{-\frac{\xi}{m}(t-t'')}\delta(t'-t'')$$
(1.16)

$$=e^{-\frac{-2\xi}{m}t}v(0)^{2}+\frac{D}{m^{2}}\int_{0}^{t}dt'e^{-\frac{2\xi}{m}(t-t')}$$
(1.17)

$$=e^{-\frac{-2\xi}{m}t}v(0)^{2}+\frac{D}{2m\xi}\left(1-e^{-\frac{2\xi}{m}t}\right).$$
(1.18)

In the long time limit as the system approaches equilibrium, the exponentials will disappear and we are left with

$$\langle v^2 \rangle = \frac{D}{2m\xi}.\tag{1.19}$$

According to the equipartition theorem, the temperature of our Brownian particle must satisfy

$$\frac{1}{2}T = \frac{m\langle v^2 \rangle}{2}.$$
(1.20)

Finally, substitution of (1.19) yields

$$T = \frac{D}{2\xi}.$$
 (1.21)

Equation (1.21) is the fluctuation-dissipation relation, which defines the equilibrium temperature of a Brownian particle according to the viscosity coefficient  $\xi$  and the diffusion coefficient D. It provides the delicate balance between excitational and dissipative forces. It must be



Figure 1.9: (a) Langevin dynamics in its original conception, applied to a grain of pollen undergoing forces from the surrounding fluid. (b) The application of Langevin dynamics in molecular junctions, where the quantum electronic environment induces vibrations in the nuclear degrees of freedom.

noted that this derivation assumes the Langevin coefficients to be constant. Our model allows for multiplicative noise, meaning the Langevin coefficients are dependent on the classical Brownian coordinate. In this regime, an explicit derivation of the fluctuation-dissipation relation is difficult to find. We do, however, find it convenient to define an *effective* temperature of the classical vibrations in analogy to the fluctuation-dissipation relation derived above.

# 1.4.2 Application to molecular electronics

The Langevin approach to modelling Brownian motion proved to be a great success, reproducing predictions obtained by Einstein and Smoluchowski via a Fokker-Planck equation. However, the approach is not limited to the study of particle diffusion or, in fact, the realms of physics whatsoever. Such is the generality of the method that the Brownian particle need not be a particle at all, but can describe some collective property of a system under the influence of approximately stochastic effects. Indeed, the Langevin equation has found applications in chemistry, biology and even finance.

In terms of the description of molecular junctions, the Brownian particle models the motion of a classical degree of freedom interacting with a quantum electronic environment as an electric current flows through the junction. A visualisation of the transition from conventional Brownian motion to Langevin dynamics in molecular junctions is presented in Figure 1.9. The choice of classical degree of freedom is dependent on the system under consideration; an ensemble of Langevin equations may be used to model the motion of the 3*N* degrees of freedom of the *N* nuclei present, or the motion could rather be considered collectively as a large-scale stretching or rotation of a molecular configuration. The choice is generally informed by the calculation of vibrational modes corresponding to the molecular bridge considered.

## 1.4.3 Langevin equation assumptions

#### 1.4.3.1 Memory effects

The Langevin approach is reliant on the inherent time-scale separation between the motion of the Brownian particle and the surrounding environment. If we were to consider exactly the motion of each particle in the environment according to the appropriate coupled equations of motion, then the evolution of the system would be entirely Markovian; the state of the system at the next instant of time would depend only on the current state of the system, and not on earlier times. This is because Newton's laws themselves are Markovian. When we choose to eliminate the individuality of the particles in the fluid and consider them collectively as an environment acting on our Brownian particle, this property of Markovianity is lost. However, equation (1.10) itself is Markovian. Clearly then, the description as it stands is incomplete.

A more accurate description may be obtained via a generalised Langevin equation, such as:

$$m\frac{dv}{dt} = -\int_0^t dt' Z(t-t')v(t') + \delta f(t).$$
(1.22)

Here, Z(t - t') replaces our usual viscosity coefficient. The frictional force then not only depends on the current velocity of the Brownian particle, but also the velocity at previous times. In such a case, the environment is not required to equilibrate instantaneously with respect to the motion of the Brownian particle. Rather, the Brownian particle is capable of influencing a flow in the environmental degrees of freedom which can affect the forces at a later time. Generalised Langevin equations prove especially useful in the modelling of molecular junctions when one wants to also consider the nuclear vibrations in the baths themselves [157–160]. However, solving for the generalised Langevin coefficients in a self-consistent manner is computationally costly and the Markovian description is usually adequate.

Memory in the environment will also have an effect on the correlations in the stochastic force presented in (1.11). Our assumption of delta-correlation was again predicated on the environment equilibrating instantaneously. This is the so-called white-noise approximation. The separation of time-scales implied in the usage of a Langevin description is usually used as justification for the white-noise approximation. We analyse the validity of this approximation in molecular junctions in Section 7.

#### 1.4.3.2 Stochastic force as a Gaussian process

Assuming that the stochastic force is a Gaussian process enables us to entirely quantify it in terms of its first two moments shown in (1.11). Over the time-scales of the motion of the Brownian particle it will experience many random forces due to the surrounding environment; then over any given time-step, the stochastic force acting on the particle will be the *mean* of the individual random forces from the environment over that time-step. The central-limit theorem states that the distribution of the mean of random samples from a distribution will approach a Gaussian in the limit of many large samples [161]. As a result, the stochastic force  $\delta f$  which acts as the mean of the random forces experienced over a time-step, must approach a Gaussian process in the limit of a large time-scale separation.

This property is also demonstrated in the following section in a more rigorous manner, in which the stochastic force is shown to become Gaussian in the classical limit of vibrations.

# 1.4.4 Quantum mechanically motivated derivation of the Langevin Equation

Our intuition which guided us to a Langevin description of a classical Brownian particle immersed in a fluid becomes somewhat obfuscated when we delve into the quantum regime present inside molecular junctions in which forces due to the environment arise from interactions with tunnelling electrons. It is not immediately clear that the approach is applicable in the case where the environment is quantum in nature. Fortunately, the path-integral formulation of quantum mechanics allows us to derive a Langevin description for a vibrational coordinate in the classical limit, starting from first principles. In this section, we illustrate the main conceptual steps of the derivation as guided by Reference [162]. We will not cover the derivation in any detail; rather, we only hope to get a sense of the procedure. The approach has been applied by a number of authors [157, 163–167].

Let's consider a quantum system with a nuclear degree of freedom interacting with an electronic bath. The reduced density matrix for the nuclear vibrations is found by taking a trace over the bath states of the full density matrix,  $\text{Tr}_B \{\hat{\rho}\}$ . An arbitrary element in the coordinate representation is then given by

$$\rho_{vib}(x_2, y_2) = \int dx_1 \int dy_1 \mathcal{K}(x_2, y_2; x_1, y_1) \rho_{vib}(x_1, y_1).$$
(1.23)

Here,  $\mathcal{K}$  is the nuclear propagation kernel defined as

$$\mathcal{K}(x_2, y_2; x_1, y_1) = \int_{(x_1, y_1)}^{(x_2, y_2)} \mathcal{D}(x, y) e^{i(S(x) - S(y))} \mathcal{F}(x, y),$$
(1.24)



Figure 1.10: Nuclear coordinates on time-ordered, x(t), and anti-time-ordered, y(t), branches of the Keldysh contour. Reproduced with permission from Reference [162].

where S(x) is the classical action associated with the path x and  $\mathcal{F}$  is the influence functional which describes the influence of the bath on the time evolution of the vibrational density matrix. We use x to denote the trajectory for the time-ordered segment of the Keldysh contour, while y is the trajectory for the anti time-ordered segment, and  $\int \mathcal{D}(x, y)$  is the integral over paths for both x and y. The influence functional is found to be

$$\mathcal{F}(x,y) = \langle U_C(\tau'_0,\tau_0;t) \rangle_B, \tag{1.25}$$

where  $U_C(\tau'_0, \tau_0; t)$  denotes a time-evolution from  $\tau_0$  ( $t_0$  on the top part of the contour) forwards in time t, then backwards to  $\tau'_0$  ( $t_0$  on the bottom part of the contour). Since we have traced over the bath degrees of freedom, the time evolution of the system is now non-unitary and the evolution along the top and bottom parts of the contour will deviate from each other. This is shown diagrammatically in Figure 1.10. We introduce the Wigner coordinates for the position as

$$Q = \frac{x+y}{2}, \qquad \xi = x-y,$$
 (1.26)

where Q and  $\xi$  are the average and difference paths of the nuclear degree of freedom, respectively. The average path corresponds to the diagonal elements of the density matrix. We can also interpret these coordinates in terms of classical and quantum contributions, where the off-diagonals of the density matrix correspond to deviations away from the classical path. To see this, let's consider the nuclear propagation kernel as per (1.24) in the absence of a coupling to the bath, meaning  $\mathcal{F} = 1$ . Taking the classical limit corresponds to assuming that deviations away from the classical trajectory, as described by  $\xi$ , are small. Let's consider the classical action terms in the exponent; taking a linear expansion in  $\xi$  results in

$$S(x) - S(y) = S[Q + \frac{\xi}{2}] - S[Q - \frac{\xi}{2}]$$
(1.27)

$$\approx -\int_{t_0}^t dt' \left( m\ddot{Q}(t') + V'(Q(t')) \right) \xi(t'), \tag{1.28}$$

where we have expressed *S* as a time integral over the Lagrangian and used a functional Taylor series to expand each to the first order in  $\xi$ . The reduced density matrix, now expressed in terms of the Wigner coordinates, is then given by

$$\rho_{vib}(Q_2,\xi_2) = \int dQ_1 \int d\xi_1 \rho_{vib}(x_1,y_1) \int_{Q_1}^{Q_2} \mathcal{D}Q \int_{\xi_1}^{\xi_2} \mathcal{D}\xi e^{-i\int_{t_0}^t dt' \left(m\ddot{Q}(t') + V'(Q(t'))\right)\xi(t')}.$$
 (1.29)

We can define a functional Dirac-delta function according to

$$\delta(G(t_1)) = \int \mathcal{D}\Sigma e^{i\int dt_1\Sigma(t_1)G(t_1)}.$$
(1.30)

The functional integral over  $\xi$  in (1.29) can then be expressed as  $\delta(m\ddot{Q}(t') + V'(Q(t')))$ , which dictates that the only trajectory which has a non-zero contribution to  $\rho_{vib}$  is the one that satisfies

$$m\ddot{Q}(t') = -V'(Q(t')).$$
 (1.31)

In the absence any influence from the bath, our average coordinate Q of the system can be interpreted to be undergoing classical motion according to Newton's laws. Now, if we account for the interaction with the bath such that  $\mathcal{F} \neq 1$ , instead of producing a functional Diracdelta function we will instead find a Gaussian with a width characteristic of the bath and interactions considered. To solve for a classical equation of motion in a similar vein as above while including effects due to the bath, we require the influence functional to be of the form

$$\mathcal{F} = e^{i\phi} \tag{1.32}$$

where  $\phi$  is the influence phase. With significant work and again taking expansions to first order in  $\xi$ , the influence functional is found as

$$\mathcal{F} = \exp\left\{-i\int_{0}^{t} dt_{1}\xi(t_{1})\operatorname{Tr}_{B}\left\{\partial_{Q}H_{el}^{I}(Q(t_{1}))\rho_{B}(t_{1})\right\} - \frac{1}{2}\int_{0}^{t} dt_{1}\int_{0}^{t} dt_{2}\xi(t_{1})\Pi(t_{1},t_{2})\xi(t_{2})\right\},\tag{1.33}$$

where

$$\Pi(t_1, t_2) = \operatorname{Tr}_B\left(\left[\partial_Q H^I_{el}(Q(t_1)), \partial_Q H^I_{el}(Q(t_2))\right]_+ \rho_B(0)\right),$$
(1.34)

and  $H_{el}^{I}$  denotes the electronic Hamiltonian in the interaction picture. Since we now have  $\mathcal{F}$  in the form given by (1.32), it may seem that the problem just requires a straight forward application of the functional Dirac-delta function. However, if we recall (1.30), we require the exponential to be first order in our integration variable  $\xi$ . Clearly, the second term in (1.33)

is quadratic in  $\xi$ . To define an effective equation of motion for the system we would like the influence functional to be expressed in the form

$$\mathcal{F} = e^{i \int_0^t dt_1 \xi(t_1) \chi(Q(t_1))}, \tag{1.35}$$

where  $\chi$  is some place-holder function. This would allow us to apply (1.30), meaning that the only trajectory which contributes must satisfy

$$m\ddot{Q}(t_1) = -\partial_Q V(Q(t_1)) + \chi(Q(t_1)).$$
(1.36)

This is the classical equation of motion we desire. Thus, we must see if we can find a way to re-express the last quadratic term in  $\xi$  instead in a form linear in  $\xi$ :

$$\kappa = -\frac{1}{2} \int_0^t dt_1 \int_0^t dt_2 \xi(t_1) \Pi(t_1, t_2) \xi(t_2) = i \int_0^t dt_1 \xi(t_1) \eta(t_1).$$
(1.37)

As it turns out, there is no such function  $\eta$  that satisfies this while also being independent of  $\xi$ . In other words, there is no way for us to obtain a *deterministic* effective equation of motion for Q while accounting for the influence of the bath. However, we can instead consider the possibility that  $e^{\kappa}$  is the average of some stochastic term. Specifically, we can interpret it as the characteristic function of a probabilistic process describing a random variable  $\eta$ :

$$e^{\kappa} = \langle e^{i \int_0^t dt_1 \xi(t_1) \eta(t_1)} \rangle, \qquad (1.38)$$

where  $\langle \rangle$  denotes a statistical average over  $\eta$ . Thus, the unwieldy quadratic term becomes

$$e^{-\frac{1}{2}\int_{0}^{t}dt_{1}\int_{0}^{t}dt_{2}\xi(t_{1})\Pi(t_{1},t_{2})\xi(t_{2})} = \langle e^{i\int_{0}^{t}dt_{1}\xi(t_{1})\eta(t_{1})} \rangle,$$
(1.39)

where  $\eta$  becomes a Gaussian stochastic variable quantified according to

$$\langle \eta(t) \rangle = 0, \qquad \langle \eta(t_1)\eta(t_2) \rangle = \Pi(t_1, t_2). \tag{1.40}$$

This is formally known as the Hubbard-Stratonovich transformation, which takes a deterministic non-local exponent and transforms it to one involving local stochastic terms that must be averaged over a distribution. The Hubbard-Stratonovich transformation maps the true propagator to the average of a set of stochastic propagations. By averaging over the trajectories these propagators generate, one is able to obtain the reduced density matrix. We now observe that (1.39) is linear in  $\xi$  as desired. This allows us to introduce a functional Dirac-delta function which enforces Q to satisfy the *stochastic* equation of motion,

$$m\ddot{Q}(t_1) = -\partial_Q V(Q(t_1)) - \langle \partial_Q H^l_{el}(Q(t_1)) \rangle + \eta(t_1).$$
(1.41)

This can then be transformed into a Langevin equation by applying a time-scale separation in

the system, which allows for the second term on the right-hand side to be decomposed into an adiabatic force and a frictional force, while the autocorrelations in the stochastic force can be assumed to be delta-correlated.

So, we have seen that a classical equation of motion for a vibrational degree of freedom can be found in the classical limit; the caveat being that the resultant equation must contain a stochastic term. This is then manipulated into the form of a Langevin equation. The allure of the described method is the rigorous application of the classical limit which leads naturally to a classical equation of motion. Our method, described in section 2, instead applies an ad-hoc approach in which an equation for the quantum force operator is mapped onto a classical equation.

# 1.5 Outline

The purpose of this study is to further elucidate the effects of current-induced forces in molecular junctions from a theoretical standpoint to gain a better understanding of stability/instability, heating effects, and novel device applications.

We begin in Chapter 2 by deriving the framework of our model: the theory describing the evolution of the non-equilibrium Green's functions. From this scaffolding, we then in Chapter 3 derive a Langevin description for an arbitrary classical coordinate. This involves the assumption of a time-scale separation between slow classical and fast electronic degrees of freedom, in which the Green's functions are decomposed into adiabatic components and non-adiabatic corrections. This additionally allows us to calculate the electric current through the system in terms of an adiabatic component and a first-order non-adiabatic correction due to the non-zero velocity of the classical coordinate.

In Chapter 4, we pay particular attention to the effects of nuclear motion on the leads interface. We observe the emergence of negative viscosity coefficients at high voltages as a direct result of this motion. Additionally, we quantify parameter regimes in which the potential for the classical degree of freedom becomes bistable. Calculation of the Fano factor shows that the noise becomes highly non-Poissonian in the bistable regime, producing Fano factors of over 400.

Chapter 5 sees the addition of a time-dependent sinusoidal driving to the leads energy levels with the goal being to utilise the driving to actively cool the junction and prolong the device stability. The effective temperature of the classical coordinate is calculated in analogy with the fluctuation-dissipation theorem, where the viscosity and diffusion coefficients are calculated self-consistently with the time-dependent driving. We observe that a slow AC driving can

have the effect of cooling the vibrations in the system while maintaining the same average current through the device.

Chapter 6 instead focuses on chemical reaction rates in molecular junctions, where the energy required for a reaction to occur is provided by the current-induced forces due to tunnelling electrons. A Fokker-Planck description allows us to derive expressions for the mean first-passage time of a reaction coordinate, describing the average amount of time passed before the reaction occurs. We find that the reaction rate is determined by the size of the energy barrier as determined by electronic occupations within the system, along with the inhomogeneous effective temperature over the reaction potential.

Finally, in Chapter 7 we utilise Ehrenfest dynamics via a novel algorithm as a means of benchmarking our time-scale separation and in doing so, once again observe the emergence of negative viscosities. Furthermore, the approach allows us to observe and quantify the coloured noise in the stochastic force, from which we can assess the validity of the white-noise approximation. We find that the white-noise approximation is valid when there is a clear time-scale separation within the system.

From this point forward we will be fluid with our use of operator notation, applying the  $\hat{}$  notation to denote an operator only when it is not contextually clear already. We also use atomic units for all presented results and calculations which allows us to set  $\hbar = e = m_e = 1$ , where *e* is the charge of an electron and  $m_e$  is the electron mass.

# Application of non-equilibrium Green's functions to quantum transport

In this chapter, we introduce the theoretical backbone required for our model. The content presented in this section is well established in the literature. After discussing in detail the tunnelling junction model, we introduce the formalism of non-equilibrium Green's functions for quantum transport in Section 2.3 as aided by Reference [168], the goal being to derive explicit equations of motion for the Green's functions. We then apply the formalism to the tunnelling junction in Section 2.4.

# 2.1 The tunnelling junction model

We will now introduce and justify the tunnelling junction model. Let's begin by considering a completely general Hamiltonian for the system shown in Figure 1.2. The Hamiltonian can be split into the contributions from nuclei and electrons as well as the inter-particle interactions according to

$$H = H_e + H_N + H_{eN} + H_{NN} + H_{ee}.$$
 (2.1)

Here,  $H_e$  and  $H_N$  correspond to the kinetic energies of electrons and nuclei, respectively, while  $H_{eN}$ ,  $H_{NN}$  and  $H_{ee}$  are two-body interaction terms between each particle. Let's first focus on the nuclear terms; we have [169]

$$H_N = \sum_i \frac{\hat{P}_i^2}{2M_i}, \qquad H_{NN} = \sum_{i < j} \frac{Z_i Z_j}{|\hat{X}_i - \hat{X}_j|},$$
(2.2)

where  $\hat{P}_i$  and  $\hat{X}_i$  are the momentum and position operators for the *i*<sup>th</sup> nuclei, while  $M_i$  is the mass and  $Z_i$  is the atomic number. However, the modelling of a many-body open system is generally insoluble when considering the above nuclear components exactly. We opt to treat the nuclei as behaving according to some classical degree of freedom, demoting the  $\hat{P}$  and  $\hat{X}$ 

operators to variables. We can then encapsulate the behaviour of the nuclei according to a chosen classical Hamiltonian:

$$H_{cl} = \sum_{i} \frac{P_i^2}{2M_i} + U_{cl}(\mathbf{X}),$$
(2.3)

where the sum over *i* is a sum over the classical degrees of freedom and **X** is the vector of classical coordinates. Note that  $U_{cl}$  will necessarily contain the contribution from  $H_{NN}$  as well as contributions from  $H_{eN}$  due to electron-nuclear attraction, and can be thought of as the classical bonding potential for the nuclei.

The electronic component of the Hamiltonian is treated on a quantum-mechanical footing. However, we choose to neglect the two-body electron-electron interactions in the system. While it has been shown theoretically that the inclusion of electron-electron interactions can have a large effect on the conductance profile of the system as well as allowing for interesting phenomena such as negative differential resistance and Kondo effect [84, 170–172], we do not include them in our model. We do, however, note that electron-electron interactions have been shown to affect the friction tensor which is a major object of this study [149]. While the exact two-body electron-electron interactions are not included, the electron-electron repulsion is included implicitly into the model via the elements of the electronic Hamiltonian which are input for a given system. The electronic Hamiltonian is given by

$$H_{el} = H_e + \underbrace{H_{eN} + H_{ee}}_{H_{eN,ee}},$$
(2.4)

where we have grouped the electron-nuclear attraction and electron-electron repulsion into  $H_{eN,ee}$ . In terms of creation and annihilation operators in the position basis, we then re-express this as

$$H_{el} = H_e + H_{eN,ee} = \int dx a^{\dagger}(x) \frac{\hat{p}^2}{2m} a(x) + \int dx a^{\dagger}(x) U(\hat{x}) a(x),$$
(2.5)

where  $\hat{p}$  and  $\hat{x}$  are the operators for the electronic momentum and position, respectively, while  $U(\hat{x})$  represents the coulomb potential experienced by an electron due to the surrounding nuclei and electrons. Using  $\hat{p} = -i\hbar \frac{d}{dx}$  and integrating by parts, we find

$$H_{el} = \frac{\hbar^2}{2m} \int dx \frac{d}{dx} a^{\dagger}(x) \frac{d}{dx} a(x) + \int dx a^{\dagger}(x) U(\hat{x}) a(x).$$
(2.6)

It is mathematically convenient for us to instead consider a discrete position basis such that for an arbitrary integrand f(x), the integrals become summations over a grid of position points according to

$$\int dx f(x) = \lim_{\Delta x \to 0} \Delta x \sum_{n} f_{n},$$
(2.7)

while the derivatives become

$$\frac{d}{dx}f_n = \lim_{\Delta x \to 0} \frac{f_{n+1} - f_{n-1}}{2\Delta x}.$$
(2.8)



Figure 2.1: The system has been partitioned into a central region and left/right leads, where we choose to focus on only the dynamics of the central region. Electron tunnelling between the leads and central region is facilitated by non-local terms in (2.11). The leads are now described by a continuum of electronic states as quantified in terms of an average electronic temperature and chemical potential.

Our electronic Hamiltonian in the discrete basis is then given by

$$H_{el} = \lim_{\Delta x \to 0} \frac{\hbar^2}{8m\Delta x} \sum_n (a_{n+1}^{\dagger} - a_{n-1}^{\dagger})(a_{n+1} - a_{n-1}) + \Delta x \sum_n a_n^{\dagger} U(\hat{x}) a_n$$
(2.9)

$$= \lim_{\Delta x \to 0} \frac{\hbar^2}{8m\Delta x} \Big( \sum_n 2a_n^{\dagger} a_n - \sum_n (a_{n-1}^{\dagger} a_{n+1} + h.c.) \Big) + \Delta x \sum_n a_n^{\dagger} U(\hat{x}) a_n.$$
(2.10)

Thus, we observe that the kinetic energy component of the electronic Hamiltonian contributes both local and non-local terms. Let's then express the electronic Hamiltonian in terms of separate local and non-local components in accordance with

$$H_{el} = \sum_{n} \epsilon_n a_n^{\dagger} a_n + \sum_{ij} \left( t_{ij} a_i^{\dagger} a_j + h.c. \right), \tag{2.11}$$

where we have grouped any scaling constants into  $\epsilon$  and t. We can now begin to construct the tunnelling junction. Our observations concern only the dynamics of the molecular bridge which spans the length between the macroscopic leads. As such, we choose to partition the system into three components; the left and right leads, and the central region (sometimes referred to as the scattering region). This partition is demonstrated in Figure 2.1. In doing so, our electronic Hamiltonian in (2.11) is separated into components describing the leads and the central region, along with a term which describes the coupling between them:

$$H_{el} = H_M + H_L + H_R + H_{ML} + H_{MR}.$$
 (2.12)

 $H_M$  is the Hamiltonian for the molecular bridge as described by

$$H_M = \sum_{ij} h_{ij} a_i^{\dagger} a_j, \qquad (2.13)$$

which contains both local contributions from the diagonal components of h, along with nonlocal components where  $h_{ij}$  is the hopping amplitude of an electronic jump between states iand j in the central region. The Hamiltonians for the left and right leads are given by  $H_L$  and  $H_R$ , respectively, and take the form

$$H_L + H_R = \sum_k \epsilon_{kL} a_{kL}^{\dagger} a_{kL} + \sum_k \epsilon_{kR} a_{kR}^{\dagger} a_{kR}, \qquad (2.14)$$

where the summation is taken over the leads states *k*. The leads act as a macroscopic reservoir for electrons; macroscopic in the sense that the state of the central region has no tangible effect on the leads. The electronic population of the leads can be described by a Fermi-Dirac distribution, such that the state of the leads is characterised entirely by the macroscopic temperature and chemical potential. Additionally, we will make frequent use of the wide-band approximation when describing the leads. This implies that the conducting band of each lead is taken to be infinitely wide. While a theoretical treatment which goes beyond the wide-band limit is often necessary when trying to reproduce the results of a specific experimental configuration [100, 173, 174], it is not necessary in our case.

Finally, the coupling between the central region and the leads arises via non-local components in (2.11). These are given by

$$H_{ML} = \sum_{ik} t_{i,kL} a_{kL}^{\dagger} a_i + h.c., \qquad H_{MR} = \sum_{ik} t_{i,kR} a_{kR}^{\dagger} a_i + h.c..$$
(2.15)

The *t* coupling elements are generally taken as a parameter for the model, which is informed by experiment.

Note that upon partitioning the system into central region and leads, we also neglect the classical vibrational component of the Hamiltonian arising from the leads and consider only the component which emerges due to the molecular bridge. In general, the contribution due to nuclear vibrations within the leads is significantly overshadowed by the electronic contribution and can be reasonably neglected [82]. Thus, our theoretical tunnelling junction is shown diagrammatically in Figure 2.2.

# 2.2 Important time-scales

As we will see, the self-consistent modelling of vibrations within the system in tandem with the quantum electronic environment requires the identification of a small parameter which can be leveraged to find a perturbative solution. The desired small parameter naturally emerges from our assumption of classical vibrations. In this case, the time-scale for nuclear motion is large relative to the time-scale in which electrons tunnel through the junction, whereby the



Figure 2.2: The theoretical description of the tunnelling junction. The central region contains a number of electronic levels described by  $H_M$ , which are coupled to the leads according to  $H_{ML}$  and  $H_{MR}$ . The central levels along with the couplings are allowed to be dependent on the nuclear vibrations in the central region, described by  $\vec{x}$ . The electronic populations of the leads are described by Fermi-Dirac distributions and nuclear vibrations within the leads are neglected.

electrons "observe" the nuclei as almost stationary. The traversal time for an electron can be reasonably estimated by the following [11, 82]:

$$\tau = \frac{\hbar}{\sqrt{\Delta E^2 + \Gamma^2}}.$$
(2.16)

Here,  $\Delta E$  is the injection energy of the electron while  $\Gamma$  is the level broadening;  $\Gamma$  will be introduced rigorously in Section 3.1.3. The concept of a traversal time is generally limited to coherent tunnelling regimes in which electrons tunnel quickly through the system; this is valid for our model. Likewise, the time-scale for classical vibration can be encapsulated by

$$\tau_{\rm cl} = \frac{1}{\Omega'} \tag{2.17}$$

where we use  $\Omega$  to denote the vibrational frequency. Thus, we exploit the fact that  $\tau \ll \tau_{cl}$  and our condition for perturbative expansion becomes

$$\frac{\Omega}{\Gamma} \ll 1,$$
 (2.18)

where we have assumed that  $\Delta E$  becomes negligible in the resonance regime. In any case, the inclusion of  $\Delta E$  will only serve to further justify our small parameter. Interestingly, the quantum nature of the nuclei once again becomes important in the limit of very small  $\Omega$ . In



Figure 2.3: Categorisation of modelling regimes in terms of  $\Omega/\Gamma$ . Green: Our operating regime where  $\Omega < \Gamma$ , such that nuclear vibrations are slow but quantum tunnelling of nuclei is negligible. Red: Quantum tunnelling becomes non-negligible - the theory breaks down. Yellow:  $\Omega > \Gamma$  such that our perturbative treatment is no longer valid - the theory breaks down.

this limit, quantum tunnelling of the nuclei starts to dominate over the classical diffusion due to interaction with the electronic environment [118, 119]. However, this can safely be ignored in our theory since we consider leads temperatures on the order of 300K such that  $\Omega$  is still sufficiently high to disregard tunnelling effects. The modelling regimes are summarised in Figure 2.3.

# 2.3 Non-equilibrium Green's functions

In this section, we will formally derive the underlying theory of non-equilibrium Green's functions, before applying it directly to the problem of our theoretical tunnelling junction. The Green's function is a mathematical object which contains the desired information about any observables within our system. In order to be able to solve for the Green's functions, we must first express them as a solution to integro-differential equations; namely, the Dyson equations and Kadanoff-Baym equations. Arriving at these equations is our first goal.

# 2.3.1 Motivation: Green's functions in first quantization

The ultimate goal of a theory is to model the time evolution of the dynamical variables of a system. In classical mechanics this amounts to the solution of Newton's laws, while in quantum mechanics we seek the solution to the Schrödinger equation.

Using the Schrodinger equation, we can define a time evolution operator which acts on a quantum state according to

$$|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle. \tag{2.19}$$

Through the use of the resolution of identity, we can instead define the time evolution of the

wavefunction as

$$\Psi(x,t) = \int dx' \underbrace{\langle x | U(t,t_0) | x' \rangle}_{G(xt,x't_0)} \Psi(x',t_0).$$
(2.20)

Here,  $\langle x|U(t,t_0)|x'\rangle$  or  $\langle xt|x't_0\rangle$  is known as the propagator or Green's function. It contains information on the probability for a state at position x' at time  $t_0$  to evolve to position x at time t. Clearly, knowledge of the Green's function in tandem with the initial conditions yields all information about the system. Thus, the modelling of the system reduces to the calculation of the Green's function.

# 2.3.2 Green's functions in a many-body open system

The problem is significantly complexified when the consideration is shifted to an open quantum system, in which we trace out the environmental degrees of freedom. The Green's functions are now expressed in the language of second quantization where one must now consider the hierarchy of many-body correlation functions of the creation and annihilation operators. However, application of Wick's theorem often simplifies the problem, requiring us to calculate only the single-body correlation functions depending on the problem. In connection with (2.20), the single-body correlation function expressed in the language of second quantization is

$$\operatorname{Tr}\left[\rho(t_0)\psi(x,t)\psi^{\dagger}(x',t')\right],\tag{2.21}$$

where we have introduced the creation and annihilation operators in the position basis as  $\psi^{\dagger}$ and  $\psi$ , respectively, and the system is prepared in an ensemble described by density matrix  $\rho(t_0)$  at time  $t = t_0$ . Thus, our consideration for a many-body system is shifted to the calculation of these correlation functions. Let's consider what this calculation entails explicitly by introducing the time evolution operators:

$$\operatorname{Tr}\left[\rho(t_{0})U(t_{0},t)\psi(x)U(t,t_{0})U(t_{0},t')\psi^{\dagger}(x')U(t',t_{0})\right],$$
(2.22)

Thus, the calculation involves both an evolution forwards and backwards in time from  $t_0$ , as visualised in Figure 2.4. The mathematical treatment with the full interacting density matrix at  $t_0$  is generally difficult. The problem is simplified by implementing assumptions. We will exemplify this with the following Hamiltonian:

$$h = h_0 + h' + V(t).$$
(2.23)

We use  $h_0$  to denote the Hamiltonian for a non-interacting system such as the central region in our molecular junction, while h' contains the coupling of that system to some environment (such as our macroscopic leads). For generality, we also include some external time-dependent



Figure 2.4: A visualisation of the time evolution involved in the calculation of (2.21).

potential which is switched on at time  $t_0$  - the inclusion of this is relevant to our study of AC driving in Section 5. We do not include any two-body interaction terms in any of the derivations presented. We assume that in the infinite past the system is in a state of thermal equilibrium according to a Gibbs distribution such that the density matrix takes the form

$$\rho_0 = \frac{e^{-\beta h_0}}{\operatorname{Tr} e^{-\beta h_0}}.$$
(2.24)

We then assume that the full density matrix at time  $t_0$  can be generated by evolving the initial non-interacting density matrix  $\rho_0$  in time after turning on the interaction with the macroscopic environment. Thus, the density matrix  $\rho(t_0)$  is found according to

$$\rho = \lim_{t' \to -\infty} U(t_0, t') \rho_0 U(t', t_0), \qquad (2.25)$$

$$\frac{e^{-\beta(h_0+h')}}{\operatorname{Tr} e^{-\beta(h_0+h')}} = \lim_{t'\to-\infty} e^{-i(h_0+h')(t_0-t')} \frac{e^{-\beta h_0}}{\operatorname{Tr} e^{-\beta h_0}} e^{-i(h_0+h')(t'-t_0)}.$$
(2.26)

The assumption of (2.26) greatly simplifies the mathematical treatment, allowing the correlation function in (2.21) to be expressed according to

$$= \operatorname{Tr}\left[\rho(t_0)\psi(x,t)\psi^{\dagger}(x',t')\right]$$
(2.27)

$$= \operatorname{Tr} \left[ U(t_0, -\infty) \rho_0(-\infty) U(-\infty, t_0) \psi(x, t) \psi^{\dagger}(x', t') \right]$$
(2.28)

$$= \operatorname{Tr} \Big[ \rho_0(-\infty) U(-\infty, t_0) \psi(x, t) \psi^{\dagger}(x', t') U(t_0, -\infty) \Big].$$
(2.29)

Thus, we see that only  $\rho_0$  needs to be considered, at the cost of the evolving the system to  $-\infty$ . We are additionally free to insert  $I = U(t_{max}, \infty)U(\infty, t_{max})$  anywhere into the equation where  $t_{max} = \max\{t, t'\}$  and I is the identity operator, such that the evolution is from  $-\infty \rightarrow \infty \rightarrow -\infty$ . This is the so-called Keldysh contour which forms the basis for all of our calculations



Figure 2.5: The four possibilities for defining the Green's function along the Keldysh contour.

using non-equilibrium Green's functions. Naturally, our choice of where to insert I dictates which segment (forwards or backwards) the times t and t' lie on. For arbitrary t and t', there are four possibilities as represented in Figure 2.5. These possibilities are quantified mathematically according to

$$G_{++}(x_1t_1, x_2t_2) = -i\left\langle T\left(a_H(x_1t_1)a_H^{\dagger}(x_2t_2)\right)\right\rangle,$$
(2.30)

$$G_{--}(x_1t_1, x_2t_2) = -i\left\langle \tilde{T}\left(a_H(x_1t_1)a_H^{\dagger}(x_2t_2)\right) \right\rangle,$$
(2.31)

$$G_{-+}(x_1t_1, x_2t_2) = -i\left\langle a_H(x_1t_1)a_H^{\dagger}(x_2t_2)\right\rangle,$$
(2.32)

$$G_{+-}(x_1t_1, x_2t_2) = i \left\langle a_H^{\dagger}(x_2t_2) a_H(x_1t_1) \right\rangle,$$
(2.33)

where *T* is the time ordering operator and  $\tilde{T}$  is the anti-time ordering operator. We use  $\langle ... \rangle$  to denote an average over the non-interacting density matrix  $\rho_0$ . The indices on  $G_{nm}$  inform us as to whether the corresponding times lie on the top (+) or bottom (-) parts of the contour. In general, the calculation of dynamical properties of a system involves the calculation of the  $G_{+-}$  component due to its correspondence with the number operator in second quantization; this is shown in the top-right of Figure 2.5. As we shall see,  $G_{+-}$  is inevitably coupled with the other real-time representations. Each real-time representation can together be encapsulated according to

$$G(x_1\tau_1, x_2\tau_2) = -i\left\langle T_c\left(a_H(x_1\tau_1)a_H^{\dagger}(x_2\tau_2)\right)\right\rangle, \qquad (2.34)$$

where we have introduced the contour time  $\tau$  and the contour time ordering operator  $T_c$  which orders operators according to their point of occurrence along the contour. This is the formal definition of the non-equilibrium Green's function. The mapping between the contour

time representation and real-time is defined explicitly according to

$$G(x_1\tau_1, x_2\tau_2) = \begin{pmatrix} G_{++}(x_1t_1, x_2t_2) & G_{+-}(x_1t_1, x_2t_2) \\ G_{-+}(x_1t_1, x_2t_2) & G_{--}(x_1t_1, x_2t_2) \end{pmatrix},$$
(2.35)

where the right-hand side is expressed in the Keldysh-Schwinger space. Thus far, it appears as though our treatment has only served to further complicate the problem! However, we will soon see that from this foundation we are able to derive integro-differential equations for the components of *G*. This then enables the possibility of a perturbative solution via an identified small parameter in the system or in some cases, a numerically exact solution is possible.

# 2.3.3 Evolving the system along the contour

# 2.3.3.1 The interaction picture

Consider a system described by the Hamiltonian:

$$H(t) = h + H'(t).$$
 (2.36)

Here we have split the full Hamiltonian H into a time independent non-interacting component h and a time dependent interacting component H'(t). We will take the general time evolution operator for a time-dependent Hamiltonian and partition it into interacting and non-interacting components as follows:

$$U(t, t_0) = T \left\{ e^{-i \int_{t_0}^t dt' H(t')} \right\}$$
  
=  $T \left\{ e^{-i \int_{t_0}^t dt' (h + H'(t'))} \right\}$   
=  $e^{-ih(t-t_0)} S(t, t_0),$  (2.37)

where  $S(t, t_0)$  is yet to be determined. The form of  $S(t, t_0)$  can be found via the consideration of the full time evolution operator as a solution to the Schrödinger equation and utilising (2.37),

$$i\frac{d}{dt}U(t,t_0) = H(t)U(t,t_0)$$
 (2.38)

$$i\frac{d}{dt}\left(e^{-ih(t-t_0)}S(t,t_0)\right) = \left(h + H'(t)\right)e^{-ih(t-t_0)}S(t,t_0).$$
(2.39)

Some menial rearrangement leads to

$$i\frac{d}{dt}S(t,t_0) = H'_h(t)S(t,t_0),$$
(2.40)

where we have let  $H'_h(t) = e^{ih(t-t_0)}H'(t)e^{-ih(t-t_0)}$  (the subscript *h* denotes a time evolution due to the non-interacting Hamiltonian). This equation has an equivalent form to the Schrödinger equation for a time-dependent Hamiltonian, and thus  $S(t, t_0)$  can be found to be

$$S(t,t_0) = T\left\{e^{-i\int_{t_0}^t dt' H'_h(t')}\right\}.$$
(2.41)

As a result, the full time evolution operator can be expressed as

$$U(t,t_0) = e^{-ih(t-t_0)}T\left\{e^{-i\int_{t_0}^t dt' H_h'(t')}\right\}.$$
(2.42)

### 2.3.3.2 Time evolution along the contour

Now let's consider an operator A in the Heisenberg representation acting at some arbitrary time t and relate this back to our contour. The full time-evolved operator is given by

$$A_{H}(t) = U^{\dagger}(t, t_{0})AU(t, t_{0})$$
  
=  $S^{\dagger}(t, t_{0})e^{-ih(t-t_{0})}Ae^{-ih(t-t_{0})}S(t, t_{0})$   
=  $S^{\dagger}(t, t_{0})A_{h}(t)S(t, t_{0}).$  (2.43)

We will now prove the following theorem:

# Theorem

$$A_{H}(t) = T_{c} \left[ e^{-i \int_{c} d\tau H_{h}'(\tau)} A_{h}(t) \right], \qquad (2.44)$$

where  $T_c$  is the contour time ordering operator along the contour *c*, which we define to range from  $-\infty$  to *t*, and back again.

# Proof

We begin with the right hand side of (2.44) and solve this to find  $A_H(t)$ . First, we partition the contour into two separate sections; the forwards section  $c_{\rightarrow}$  from  $-\infty \rightarrow t$  and the backwards section  $c_{\leftarrow}$  from  $t \rightarrow -\infty$  such that



Figure 2.6: The Keldysh contour along the time axis.

Now we can utilise the commutativity of terms under the time ordering to find

$$A_{H}(t) = T_{c} \left[ e^{-i \int_{c} d\tau H'_{h}(\tau)} A_{h}(t) \right]$$
(2.46)

$$=T_{c}\left[e^{-i\int_{c_{\rightarrow}}d\tau H_{h}'(\tau)-i\int_{c_{\leftarrow}}d\tau H_{h}'(\tau)}A_{h}(t)\right]$$
(2.47)

$$=T_{c}\left[e^{-i\int_{c_{\leftarrow}}d\tau H_{h}'(\tau)}A_{h}(t)e^{-i\int_{c_{\rightarrow}}d\tau H_{h}'(\tau)}\right]$$
(2.48)

$$= T_{\leftarrow} \left[ e^{-i \int_{c_{\leftarrow}} d\tau H'_h(\tau)} \right] A_h(t) T_{\rightarrow} \left[ e^{-i \int_{c_{\rightarrow}} d\tau H'_h(\tau)} \right]$$
(2.49)

$$= S^{\dagger}(t, t_0) A_h(t) S(t, t_0), \qquad (2.50)$$

where  $T_{\rightarrow}$  denotes a contour ordering along the forwards part of the contour, and vice versa. We have arrived at (2.43) and thus the theorem is proved. Additionally, it is clear that we can safely extend the contour up to  $+\infty$  since the components of the integrals when  $\tau > t$  will cancel out. In this case, the contour *c* then becomes the Keldysh contour.

# 2.3.3.3 Interaction picture for the Green's functions

Using (2.44), we can re-express our creation/annihilation operators in the Heisenberg picture as

$$a_{H}(x_{1}t_{1}) = T_{c}\left[e^{-i\int_{c}d\tau H_{h}'(\tau)}a_{h}(x_{1}t_{1})\right],$$
(2.51)

$$a_{H}^{\dagger}(x_{2}t_{2}) = T_{c} \left[ e^{-i \int_{c} d\tau H_{h}'(\tau)} a_{h}^{\dagger}(x_{2}t_{2}) \right].$$
(2.52)

It is then trivial to show that

$$T_{c}\left(a_{H}(1)a_{H}^{\dagger}(2)\right) = T_{c}\left[e^{-i\int_{c}d\tau H_{h}'(\tau)}a_{h}(1)a_{h}^{\dagger}(2)\right] = T_{c}\left[\zeta_{c}a_{h}(1)a_{h}^{\dagger}(2)\right],$$
(2.53)

where

$$\zeta_c = e^{-i\int_c d\tau H_h'(\tau)}.$$
(2.54)

 $\zeta_c$  is called the scattering matrix on the Keldysh contour as it is the evolution which accounts for any interactions within the system.

# 2.3.4 Perturbative expansion of the Green's functions

We can now begin our quest to derive workable equations of motion for the Green's functions. Let's consider the generic Hamiltonian in the position basis,

$$H(t) = h + H'(t),$$
 (2.55)

where

$$H'(t) = \int dx V(x,t) a^{\dagger}(x) a(x).$$
(2.56)

We have partitioned the Hamiltonian in such a way that *V* will later contain information about the leads-system coupling as well as any time-dependent external potentials. However, at this point we need not assign any explicit physical meaning to *V*. For brevity, we can choose to represent the indices  $(x_1\tau_1, x_2\tau_2, ...)$  as (1, 2, ...). Consider the definition for the Green's function while utilizing (2.53);

$$G(1,1') = -i\left\langle T_c\left(\zeta_c a_h(1)a_h^{\dagger}(1')\right)\right\rangle = -i\left\langle T_c\left(e^{-i\int_c d\tau H_h'(\tau)}a_h(1)a_h^{\dagger}(1')\right)\right\rangle.$$
(2.57)

We take the Mclaurin series expansion of the exponential and truncate after the 1st order to find

$$\approx G_0(1,1') + (-i)^2 \left\langle T_c \left( \int_c d\tau H'_h(\tau) a_h(1) a_h^{\dagger}(1') \right) \right\rangle.$$
(2.58)

Here we have defined  $G_0$  to be the *free-field* Green's function, given by

$$G_0(1,1') = -i \left\langle T_c \left( a_h(1) a_h^{\dagger}(1') \right) \right\rangle.$$
(2.59)

It depends only on the non-interacting component of the Hamiltonian and does not take into account the external field. The free-field Green's function forms the basis for our perturbation. Using (2.56), we obtain the following expression for G(1, 1'). Note that  $\int_c d2 = \int_c dx_2 d\tau_2$ ;

$$= G_0(1,1') + (-i)^2 \int_c d2V(2) \left\langle T_c \left( a_h^{\dagger}(2) a_h(2) a_h(1) a_h^{\dagger}(1') \right) \right\rangle.$$
(2.60)

By applying Wick's theorem to decompose the string of operators and retaining only the non-zero terms, we arrive at the following

$$= G_0(1,1') - (-i)^2 \int_c d2V(2) \left\langle T_c \left( a_h^{\dagger}(2) a_h(1) \right) \right\rangle \left\langle T_c \left( a_h(2) a_h^{\dagger}(1') \right) \right\rangle$$
(2.61)

$$= G_0(1,1') + \int_c d2G_0(1,2)V(2)G_0(2,1').$$
(2.62)

Thus, we see that we have been able to decompose the first order component of the Green's function in terms of the free-field Green's functions. An equivalent process can be applied to the second order term in the expansion, such that the full Green's function up to the 2nd

order approximation can be given by,

$$\therefore G(1,1') = G_0(1,1') + \int_c d2G_0(1,2)V(2)G_0(2,1') + \int_c d2d3G_0(1,2)V(2)G_0(2,3)V(3)G_0(3,1').$$
(2.63)

It is clear that there is a pattern emerging and we can in fact write the entire exact Green's function as

$$G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + G_0 V G_0 V G_0 + \dots$$
(2.64)

Here we have omitted the  $\int_c d2d3$  and any indices for brevity. By realising that this expression for *G* contains itself, we observe that

$$G = G_0 + G_0 V G = G_0 + G V G_0. (2.65)$$

Here, we have an integral equation for *G* in terms of the free-field Green's functions. We now aim to transform this to a differential equation.

# 2.3.5 Time derivative on the Keldysh contour

Consider an arbitrary function of  $\tau$  on the Keldysh contour,  $f(\tau)$ . The derivative can be defined in the standard way:

$$\frac{df(\tau)}{d\tau} = \lim_{\tau' \to \tau} \frac{f(\tau') - f(\tau)}{\tau' - \tau}.$$
(2.66)

If  $\tau$  is on the upper branch, then  $\tau = t$  and we can say that  $\tau' = t + \epsilon$ ,

$$\therefore \frac{df(\tau)}{d\tau} = \lim_{\epsilon \to 0} \frac{f(t+\epsilon) - f(t)}{\epsilon} = \frac{df}{dt}.$$
(2.67)

If  $\tau$  is on the lower branch, then  $\tau = t$  and we say that  $\tau' = t - \epsilon$ ,

$$\therefore \frac{df(\tau)}{d\tau} = \lim_{\epsilon \to 0} \frac{f(t-\epsilon) - f(t)}{-\epsilon} = \lim_{\epsilon \to 0} \frac{f(t) - f(t-\epsilon)}{\epsilon} = \frac{df}{dt}.$$
 (2.68)

$$\therefore \frac{df(\tau)}{d\tau} = \frac{df}{dt}.$$
(2.69)

Therefore, it is the clear that the contour time derivative is irrespective of which segment of the contour it is taken on. Consider a contour ordered pair of operators

$$T_c(A(\tau_1)B(\tau_2)) = \theta_c(\tau_1 - \tau_2)A(\tau_1)B(\tau_2) \pm \theta_c(\tau_2 - \tau_1)B(\tau_2)A(\tau_1),$$
(2.70)

where  $\theta_c$  is the Heaviside step function along the contour and the  $\pm$  refers to bosonic and fermionic operators, respectively. Let's express  $\theta_c$  in terms of our Keldysh-Schwinger space;

$$\theta_c(\tau_1 - \tau_2) = \begin{pmatrix} \theta(t_1 - t_2) & 0\\ 1 & \theta(t_2 - t_1) \end{pmatrix},$$
(2.71)

$$\frac{d\theta_c(\tau_1 - \tau_2)}{d\tau_1} = \begin{pmatrix} \delta(t_1 - t_2) & 0\\ 0 & -\delta(t_1 - t_2) \end{pmatrix} = \delta_c(\tau_1 - \tau_2),$$
(2.72)

and similarly,

$$\frac{d\theta_c(\tau_2 - \tau_1)}{d\tau_1} = -\delta_c(\tau_1 - \tau_2).$$
(2.73)

Now we utilize (2.73) to solve,

$$\frac{d}{d\tau_1} \left( T_c \left( A(\tau_1) B(\tau_2) \right) \right) = \frac{d}{d\tau_1} \left[ \theta_c(\tau_1 - \tau_2) A(\tau_1) B(\tau_2) \pm \theta_c(\tau_2 - \tau_1) B(\tau_2) A(\tau_1) \right] \\
= \delta_c(\tau_1 - \tau_2) \left[ A(\tau_1), B(\tau_2) \right]_{\mp} + T_c \left( \frac{dA(\tau_1)}{d\tau_1} B(\tau_2) \right).$$
(2.74)

Likewise,

$$\frac{d}{d\tau_2}\left(T_c(A(\tau_1)B(\tau_2))\right) = -\delta_c(\tau_1 - \tau_2)\left[A(\tau_1), B(\tau_2)\right]_{\mp} + T_c\left(A(\tau_1)\frac{dB(\tau_2)}{d\tau_2}\right),$$
(2.75)

where we have the commutator  $[A, B]_{\mp} = AB \mp BA$ . Using these identities, we can now begin to construct differential equations for the Green's functions.

# 2.3.6 Equation of motion for the non-equilibrium Green's function

Continuing with our full many-body Hamiltonian in second quantization:

$$H = \int dx a^{\dagger}(x) (h(x) + V(x, t)) a(x).$$
(2.76)

Here we use  $x = \{r, \sigma, ...\}$  to denote the appropriate quantum numbers for the system we are dealing with. Begin by taking the contour time derivative of our definition for the Green's function,

$$\frac{d}{d\tau_1}G(1,1') = \frac{d}{d\tau_1} \left( -i \left\langle T_c(a_H(1)a_H^{\dagger}(1')) \right\rangle \right).$$
(2.77)

Using (2.74),

$$i\frac{d}{d\tau_{1}}G(1,1') = \delta_{c}(\tau_{1}-\tau_{2})\left\langle \left[a_{H}(1),a_{H}^{\dagger}(1')\right]_{\mp}\right\rangle + \left\langle T_{c}\left(\frac{da_{H}(1)}{d\tau_{1}}a_{H}^{\dagger}(1')\right)\right\rangle\right\rangle$$
$$= \delta_{c}(\tau_{1}-\tau_{2})\delta(x_{1}-x_{1'}) + \left\langle T_{c}\left(\frac{da_{H}(1)}{d\tau_{1}}a_{H}^{\dagger}(1')\right)\right\rangle$$
$$= \delta_{c}(1-1') + \left\langle T_{c}\left(\frac{da_{H}(1)}{d\tau_{1}}a_{H}^{\dagger}(1')\right)\right\rangle.$$
(2.78)

Here we have utilized the second quantization commutator relation  $[a^{\dagger}(x_1), a(x_{1'})]_{\mp} = \delta(x_1 - x_{1'})$ . Now we compute  $\frac{da_H(1)}{d\tau_1} = \frac{da_H(1)}{dt_1}$  through the use of the Heisenberg Equation of Motion which is defined as:

$$\frac{d}{dt}a_{H}(x,t) = -i\left[a_{H}(x,t), H_{H}(t)\right].$$
(2.79)

Substituting in (2.76) and utilizing the commutation relation: [A, BC] = [A, B]C + B[A, C], we find

$$\frac{d}{dt}a_H(x,t) = -i\int dx_1 \left[a_H(x,t), a_H^{\dagger}(x_1,t)\right]_{\mp} (h(x_1) + V(x_1,t))a_H(x_1,t),$$
(2.80)

$$= -i(h(x) + V(x,t))a_H(x,t).$$
(2.81)

Once again in terms of contour time, we have

$$\frac{d}{d\tau_1}a_H(1) = -i(h(1) + V(1))a_H(1).$$
(2.82)

Substitute (2.82) back into (2.78) to find

$$\therefore \left(i\frac{d}{d\tau_1} - h(1) - V(1)\right) G(1, 1') = \delta_c(1 - 1').$$
(2.83)

This is the Keldysh-Kadanoff-Baym (KKB) equation. Thus, we have derived a differential equation for G along our abstract contour construction. We must now consider the real-time formulation of this equation.

# 2.3.7 From Keldysh contour to real time

We recall that the real-time representations of the Green's function are given by

$$G(1,1') = G(x_1\tau_1, x_1'\tau_1') = \begin{pmatrix} G_{++}(x_1t_1, x_1't_1') & G_{+-}(x_1t_1, x_1't_1') \\ G_{-+}(x_1t_1, x_1't_1') & G_{--}(x_1t_1, x_1't_1') \end{pmatrix}.$$
(2.84)

Thus, if we consider (2.65) as a matrix equation, a specific real-time matrix element of *G* is then found according to

$$G_{\alpha\beta} = G_{0,\alpha\beta} + \int_{-\infty}^{\infty} d2G_{0,\alpha1}VG_{1\beta} + \int_{\infty}^{-\infty} d2G_{0,\alpha2}VG_{2\beta}.$$
 (2.85)

Note that our notation is now in terms of *real* time (i.e.  $d2 = dx_2dt_2$ ). Now, putting the equation back into matrix form (here we use a hat to represent a matrix in the Schwinger-Keldysh space);

$$\hat{G} = \hat{G}_0 + \int_{-\infty}^{\infty} d2 \hat{G}_0 \begin{pmatrix} V & 0 \\ 0 & -V \end{pmatrix} \hat{G}, \qquad (2.86)$$

$$= \hat{G}_0 + \int_{-\infty}^{\infty} d2 \hat{G}_0 V \hat{\sigma}_3 \hat{G}.$$
 (2.87)

Here we have found it useful to utilise the  $\hat{\sigma}_3$  Pauli matrix. To simplify the equation further, we choose to eliminate one component of our Green's function matrices. We begin by proving the following relation;

$$G_{++} + G_{--} = G_{+-} + G_{-+}.$$
(2.88)

Beginning with the left hand side:

$$G_{++}(1,2) + G_{--}(1,2) = -i \left\langle T(a(1)a^{\dagger}(2)) \right\rangle - i \left\langle \tilde{T}(a(1)a^{\dagger}(2)) \right\rangle$$
(2.89)

$$= -i\theta(t_1 - t_2) \left\langle a(1)a^{\dagger}(2) \right\rangle + i\theta(t_2 - t_1) \left\langle a^{\dagger}(2)a(1) \right\rangle$$
(2.90)

$$+i\theta(t_1 - t_2)\left\langle a^{\dagger}(2)a(1)\right\rangle - i\theta(t_2 - t_1)\left\langle a(1)a^{\dagger}(2)\right\rangle$$
(2.91)

$$= -i \left\langle a(1)a^{\dagger}(2) \right\rangle + i \left\langle a^{\dagger}(2)a(1) \right\rangle, \qquad (2.92)$$

$$\therefore G_{++}(1,2) + G_{--}(1,2) = G_{-+}(1,2) + G_{+-}(1,2),$$
(2.93)

$$\therefore G_{--}(1,2) = G_{-+}(1,2) + G_{+-}(1,2) - G_{++}(1,2).$$
(2.94)

We now perform a rotation of the Green's function matrix in the Schwinger-Keldysh space using the rotation matrix  $\hat{L}$ , which will allow us to begin to cancel terms using (2.94),

$$\hat{L} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}, \qquad \qquad \hat{L}^{\dagger} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}.$$
 (2.95)

Note that

$$\hat{L}\hat{L}^{\dagger} = \hat{L}^{\dagger}\hat{L} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{I}.$$
 (2.96)

Applying this transformation to (2.87) (we neglect the integral notation for brevity) and utilizing (2.96), we obtain

$$\hat{L}\hat{G}\hat{L}^{\dagger} = \hat{L}\hat{G}_{0}\hat{L}^{\dagger} + \hat{L}\hat{G}_{0}\hat{L}^{\dagger}\hat{L}\hat{\sigma}_{3}V\hat{L}^{\dagger}\hat{L}\hat{G}\hat{L}^{\dagger}.$$
(2.97)

First we focus on the left hand side, whose results will also apply to the terms on the right hand side.

$$\hat{L}\hat{G}\hat{L}^{\dagger} = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} G_{++} & G_{+-} \\ G_{-+} & G_{--} \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$
(2.98)

$$=\frac{1}{2}\left(\begin{array}{ccc}G_{++}+G_{--}-G_{+-}-G_{-+}&G_{++}-G_{--}+G_{+-}-G_{-+}\\G_{++}-G_{--}-G_{+-}+G_{+-}&G_{++}+G_{--}+G_{+-}+G_{-+}\end{array}\right).$$
 (2.99)

Now, utilizing (2.94);

$$= \frac{1}{2} \begin{pmatrix} 0 & G_{++} - G_{--} + G_{+-} + G_{+-} - G_{-+} + G_{+-} - G_{-+} \\ G_{++} - G_{+-} - G_{-+} + G_{+-} \\ G_{++} - G_{+-} - G_{+-} - G_{+-} + G_{-+} \end{pmatrix} = \begin{pmatrix} 0 & G^{A} \\ G^{R} & G^{K} \end{pmatrix}.$$
(2.100)

Here we have introduced the advanced, the retarded, and the Keldysh Green's functions. The same derivation can be applied to the terms on the right hand side. In doing so, the Kadanoff-Baym equation becomes

$$\begin{pmatrix} 0 & G^{A} \\ G^{R} & G^{K} \end{pmatrix} = \begin{pmatrix} 0 & G_{0}^{A} \\ G_{0}^{R} & G_{0}^{K} \end{pmatrix} + \begin{pmatrix} 0 & G_{0}^{A} \\ G_{0}^{R} & G_{0}^{K} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} V \begin{pmatrix} 0 & G^{A} \\ G^{R} & G^{K} \end{pmatrix}.$$
 (2.101)

Here we have used the relation

$$\hat{L}\hat{\sigma}_{3}\hat{L}^{\dagger} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad (2.102)$$

$$\therefore \begin{pmatrix} 0 & G^A \\ G^R & G^K \end{pmatrix} = \begin{pmatrix} 0 & G^A_0 \\ G^R_0 & G^K_0 \end{pmatrix} + \begin{pmatrix} G^A_0 & 0 \\ G^K_0 & G^R_0 \end{pmatrix} V \begin{pmatrix} 0 & G^A \\ G^R & G^K \end{pmatrix}.$$
(2.103)

We compute the components on the right hand side to find

$$\begin{pmatrix} 0 & G^{A} \\ G^{R} & G^{K} \end{pmatrix} = \begin{pmatrix} 0 & G_{0}^{A} \\ G_{0}^{R} & G_{0}^{K} \end{pmatrix} + \begin{pmatrix} 0 & G_{0}^{A}VG^{A} \\ G_{0}^{R}VG^{R} & G_{0}^{K}VG^{A} + G_{0}^{R}VG^{K} \end{pmatrix}.$$
 (2.104)

Thus, this matrix equation yields the three Kadanoff-Baym equations for the advanced, retarded and Keldysh Green's functions. Explicitly including all integrals and functional dependence, these are given by

$$G^{A/R}(xt, x't') = G_0^{A/R}(xt, x't') + \int_{-\infty}^{\infty} dx_1 dt_1 G_0^{A/R}(xt, x_1t_1) V(x_1t_1) G^{A/R}(x_1t_1, x't'), \quad (2.105)$$

$$G^{K}(xt, x't') = G^{K}_{0}(xt, x't') + \int_{-\infty}^{\infty} dx_{1} dt_{1} G^{K}_{0}(xt, x_{1}t_{1}) V(x_{1}t_{1}) G^{A}(x_{1}t_{1}, x't') + G^{R}_{0}(xt, x_{1}t_{1}) V(x_{1}t_{1}) G^{K}(x_{1}t_{1}, x't').$$
(2.106)

Here we have expressed the advanced/retarded equations collectively, as we will often find it convenient to do. It is often desirable to express equations in terms of  $G^{<}$  rather than  $G^{K}$  due to its relevance to physical observables. In doing so, we utilise the following relations:

$$G^{K} = G_{+-} + G_{-+} = G^{<} + G^{>}, (2.107)$$

$$G^{A} - G^{R} = G_{+-} - G_{-+} = G^{<} - G^{>}.$$
 (2.108)

It is then straight forward to show that

$$G^{<} = \frac{1}{2}(G^{K} + G^{A} - G^{R}), \qquad (2.109)$$

and some tedious manipulation yields

$$G^{<}(xt, x't') = G_{0}^{<}(xt, x't') + \int_{-\infty}^{\infty} dx_{1} dt_{1} G_{0}^{<}(xt, x_{1}t_{1}) V(x_{1}t_{1}) G^{A}(x_{1}t_{1}, x't') + G_{0}^{R}(xt, x_{1}t_{1}) V(x_{1}t_{1}) G^{<}(x_{1}t_{1}, x't').$$
(2.110)

Note that due to the symmetry in (2.65), we are able to make the term on the right the freefield Green's function and the term on the left the full Green's function in our Dyson equations without repercussion.

# 2.3.8 Kadanoff-Baym equations in real time

An equivalent process can be applied to take the KKB equation from contour time to real time. Begin by writing (2.83) in the Schwinger-Keldysh space by utilising (2.72),

$$\left(i\frac{d}{dt_1} - h(1) - V(1)\right)\hat{G}(1, 1') = \hat{\sigma}_3\delta(1 - 1').$$
(2.111)

As in the previous section, we perform a rotation in the Schwinger-Keldysh space by appling  $\hat{L}$  and  $\hat{L}^{\dagger}$  from the left and right, respectively. This results in

$$\left(i\frac{d}{dt_1} - h - V\right) \left(\begin{array}{cc} 0 & G^A\\ G^R & G^K \end{array}\right) = \left(\begin{array}{cc} 0 & 1\\ 1 & 0 \end{array}\right) \delta(1 - 1'), \tag{2.112}$$
Again, we make the transition from  $G^K$  to  $G^<$ , such that our real-time KKB equations take the form

$$\left(i\frac{d}{dt_1} - h(1) - V(1)\right)G^{A/R}(1, 1') = \delta(1 - 1'),$$
(2.113)

$$\left(i\frac{d}{dt_1} - h(1) - V(1)\right)G^<(1,1') = 0.$$
(2.114)

# 2.4 Application of Green's functions to the tunnelling junction

In this section, we forge the connection between the integro-differential equations which describe the Green's functions and our tunnelling junction model. We will now reformulate our Dyson and Kadanoff-Baym equations in terms of our chosen Hamiltonian.

#### 2.4.1 Dyson equations in a discrete basis

Given our choice to express our tunnelling junction Hamiltonian in Section 2.1 in terms of a discrete position basis, we must now transform our Dyson equations from the continuous basis in (2.105) and (2.110) to a discrete basis. We start by introducing an arbitrary discrete basis  $\lambda$  such that

$$|x\rangle = \sum_{\lambda} |\lambda\rangle \langle \lambda | x\rangle.$$
(2.115)

Now we can define the creation and annihilation operators of our old continuous basis in terms of a projection onto the new discrete basis,

$$\Psi^{\dagger}(x) = \sum_{\lambda} \langle \lambda | x \rangle a_{\lambda}^{\dagger} = \sum_{\lambda} \phi(x) a_{\lambda}^{\dagger}, \qquad (2.116)$$

$$\Psi(x) = \sum_{\lambda} \langle x | \lambda \rangle a_{\lambda} = \sum_{\lambda} \phi^*(x) a_{\lambda}.$$
(2.117)

Thus, the free-field Green's function can be expressed in the discrete basis as

$$G_0(x_1\tau_1, x_2\tau_2) = -i\left\langle T_C\left\{\Psi_h(x_1\tau_1)\Psi_h^{\dagger}(x_2\tau_2)\right\}\right\rangle$$
(2.118)

$$= -i \left\langle T_C \left\{ \sum_{\lambda\lambda'} \phi_{\lambda}^*(x_1) \phi_{\lambda'}(x_2) a_h(\lambda\tau_1) a_h^{\dagger}(\lambda'\tau_2) \right\} \right\rangle$$
(2.119)

$$=\sum_{\lambda\lambda'}\phi_{\lambda}^{*}(x_{1})\phi_{\lambda'}(x_{2})G_{0,\lambda\lambda'}(\tau_{1},\tau_{2}).$$
(2.120)

Similarly, the full Green's function is given by

$$G(x_1\tau_1, x_2\tau_2) = -i\left\langle T_C\left\{e^{-i\int_C d\tau H_h'(\tau)}\Psi_h(x_1\tau_1)\Psi_h^{\dagger}(x_2\tau_2)\right\}\right\rangle$$
(2.121)

$$=\sum_{\lambda\lambda'}\phi_{\lambda}^{*}(x_{1})\phi_{\lambda'}(x_{2})G_{\lambda\lambda'}(\tau_{1},\tau_{2}), \qquad (2.122)$$

where the interaction Hamiltonian in the discrete basis becomes

$$H'_{h}(\tau) = \sum_{\lambda\lambda'} \int_{-\infty}^{\infty} dx a^{\dagger}_{\lambda}(\tau) \phi_{\lambda}(x) V(x,\tau) \phi^{*}_{\lambda'}(x) a_{\lambda'}(\tau)$$
(2.123)

$$=\sum_{\lambda\lambda'}a_{\lambda}^{\dagger}(\tau)\langle\lambda|\hat{V}(\hat{x},\tau)|\lambda'\rangle a_{\lambda'}(\tau)$$
(2.124)

$$=\sum_{\lambda\lambda'}a^{\dagger}_{\lambda}(\tau)V_{\lambda\lambda'}(\tau)a_{\lambda'}(\tau).$$
(2.125)

Any real-time element of the Green's function matrix in the Keldysh-Schwinger space can be expressed in the discrete basis as

$$G_{ij}(x_1t_1, x_2t_2) = \sum_{\lambda\lambda'} \phi_{\lambda}^*(x_1) \phi_{\lambda'}(x_2) G_{ij,\lambda\lambda'}(t_1, t_2).$$
(2.126)

Now, given that  $G^{A/R/<}$  are each just linear combinations of the above matrix elements, this basis change relation will also to apply to  $G^{A/R/<}$  such that

$$G^{A/R/<}(x_1t_1, x_2t_2) = \sum_{\lambda\lambda'} \phi_{\lambda}^*(x_1)\phi_{\lambda'}(x_2)G^{A/R/<}_{\lambda\lambda'}(t_1, t_2),$$
(2.127)

and this same process also applies for the free-field Green's functions. Now, we consider the advanced/retarded Dyson equation as given by (2.105) and utilise (2.127) and (2.125) to solve for

$$\sum_{\lambda\lambda'} \phi_{\lambda'}^*(x_1) \phi_{\lambda}(x_2) G_{\lambda'\lambda}^{A/R}(t_1, t_2) = \sum_{\lambda\lambda'} \phi_{\lambda'}^*(x_1) \phi_{\lambda}(x_2) G_{0,\lambda'\lambda}^{A/R}(t_1, t_2) + \int_{-\infty}^{\infty} dt' \sum_{\lambda\lambda'} \sum_{\lambda_1\lambda_2} \phi_{\lambda'}^*(x_1) \phi_{\lambda_2}(x_2) G_{0,\lambda'\lambda}^{A/R}(t_1, t') V_{\lambda\lambda_1}(t') G_{\lambda_1\lambda_2}^{A/R}(t', t_2).$$
(2.128)

By acting  $\int dx_1 \phi_{\lambda_i}(x_1)$  on each side of the equation, we can pull out the identity operator  $\int dx_1 |x_1\rangle \langle x_1|$ . Then using  $\langle \lambda_i | \lambda' \rangle = \delta_{\lambda_i \lambda'}$ , we can simplify to

$$\sum_{\lambda} \phi_{\lambda}(x_2) G_{\lambda_i \lambda}^{A/R}(t_1, t_2) = \sum_{\lambda} \phi_{\lambda}(x_2) G_{0, \lambda_i \lambda}^{A/R}(t_1, t_2) + \int_{-\infty}^{\infty} dt' \sum_{\lambda \lambda_1 \lambda_2} \phi_{\lambda}(x_2) G_{0, \lambda_i \lambda_2}^{A/R}(t_1, t') V_{\lambda_2 \lambda_1}(t') G_{\lambda_1 \lambda}^{A/R}(t', t_2).$$
(2.129)

Act  $\int dx_2 \phi^*_{\lambda_i}(x_2)$  and repeat the above step to find

$$G_{\lambda_{i}\lambda_{j}}^{A/R}(t_{1},t_{2}) = G_{0,\lambda_{i}\lambda_{j}}^{A/R}(t_{1},t_{2}) + \int_{-\infty}^{\infty} dt' \sum_{\lambda_{1}\lambda_{2}} G_{0,\lambda_{i}\lambda_{2}}^{A/R}(t_{1},t') V_{\lambda_{2}\lambda_{1}}(t') G_{\lambda_{1}\lambda_{j}}^{A/R}(t',t_{2}).$$
(2.130)

We have obtained the advanced/retarded Kadanoff-Baym equations in terms of our arbitrary discrete basis. The exact same process can be applied to the lesser Dyson equation to find

$$G_{\lambda_{i}\lambda_{j}}^{<}(t_{1},t_{2}) = G_{0,\lambda_{i}\lambda_{j}}^{<}(t_{1},t_{2}) + \int_{-\infty}^{\infty} dt' \sum_{\lambda_{1}\lambda_{2}} \left[ G_{0,\lambda_{i}\lambda_{2}}^{<}(t_{1},t') V_{\lambda_{2}\lambda_{1}}(t') G_{\lambda_{1}\lambda_{j}}^{A}(t',t_{2}) + G_{0,\lambda_{i}\lambda_{2}}^{R}(t_{1},t') V_{\lambda_{2}\lambda_{1}}(t') G_{\lambda_{1}\lambda_{j}}^{<}(t',t_{2}) \right].$$
(2.131)

#### 2.4.2 Free-field Green's functions in the leads

Here we will derive useful expressions for the free-field Green's functions in the leads, denoted  $G_{0,kk'}^{A/R/<}$  where *k* and *k'* are each states in the same lead since we neglect any interactions between separate leads. The free-field Green's function then evolves according to the leads Hamiltonian

$$H(t) = \sum_{k'} \epsilon_{k'}(t) a_{k'}^{\dagger} a_{k'}, \qquad (2.132)$$

where we have assumed a time-dependence on the electronic states in the leads for generality. This time-dependence will become important for us in Section 5 when we consider an AC driving on the leads. We prove three lemmas on the road to our final expressions.

Lemma 1:

$$U^{\dagger}(t,t_0)a_k U(t,t_0) = e^{-i\int_{t_0}^t dt_1 \epsilon_k(t_1)} a_k,$$
(2.133)

**Proof:** 

$$[a_k, H(t)] = \sum_{k'} \epsilon_k(t) [a_k, a_{k'}^{\dagger} a_{k'}]$$
(2.134)

$$=\sum_{k'}\epsilon_{k'}(t)\left([a_{k},a_{k'}^{\dagger}]a_{k'}+a_{k'}^{\dagger}[a_{k},a_{k'}]\right)$$
(2.135)

$$=\sum_{k'}\epsilon_{k'}\delta_{kk'}(t)a_{k'}$$
(2.136)

$$=\epsilon_k(t)a_k,\tag{2.137}$$

$$\therefore a_k H(t) = \epsilon_k(t)a_k + H(t)a_{k,t} = (\epsilon_k(t) + H(t))a_k.$$
(2.138)

Now consider the following,

$$a_k U(t, t_0) = a_k e^{-i \int_{t_0}^t dt_1 H(t_1)}$$
(2.139)

$$=a_k \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \left( \int_{t_0}^t dt_1 H(t_1) \right) \left( \int_{t_0}^t dt_2 H(t_2) \right) \dots$$
(2.140)

$$=\sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \left( \int_{t_0}^t dt_1(\epsilon_k(t_2) + H(t_1)) \right) \left( \int_{t_0}^t dt_2(\epsilon_k(t_2) + H(t_2)) \right) \dots a_k$$
(2.141)

$$=e^{-i\int_{t_0}^t dt_1(\epsilon_k(t_1)+H(t_1))}a_k,$$
(2.142)

where we have used (2.138).

$$\therefore U^{\dagger}(t,t_0)a_k U(t,t_0) = e^{i\int_{t_0}^t dt_1 H(t_1)} e^{-i\int_{t_0}^t dt_2(\epsilon_k(t_2) + H(t_2))} a_k,$$
(2.143)

$$=e^{-i\int_{t_0}^t dt_1\epsilon_k(t_1)}a_k.$$
 (2.144)

Lemma 2:

$$G^{A}_{0,kk'}(t,t') = i\theta(t'-t)\langle \{a_k(t), a^{\dagger}_{k'}(t')\}\rangle,$$
(2.145)

where  $\theta(t - t')$  is the Heaviside step function and the creation/annihilation operators are in the Heisenberg picture. {, } denotes the anti-commutator.

**Proof:** 

$$G_{0,kk'}^{A}(t,t') = G_{11,kk'}(t,t') - G_{21,kk'}(t,t')$$
(2.146)

$$= -i\langle T(a_k(t)a_{k'}^{\dagger}(t'))\rangle + i\langle a_{k'}(t')a_k^{\dagger}(t)\rangle$$
(2.147)

$$= -i\theta(t-t')\langle a_k(t)a_{k'}^{\dagger}(t')\rangle + i\theta(t'-t)\langle a_{k'}^{\dagger}(t')a_k(t)\rangle$$

$$+ i(\theta(t - t') + \theta(t' - t)) \langle a_k(t) a_{k'}^{\dagger}(t') \rangle$$
(2.148)

$$=i\theta(t'-t)\langle\{a_k(t)a_{k'}^{\dagger}(t')\}\rangle.$$
(2.149)

## A similar approach can be applied to the retarded and the lesser which yields

$$G^{R}_{0,kk'}(t,t') = -i\theta(t-t')\langle \{a_k(t), a^{\dagger}_{k'}(t')\}\rangle,$$
(2.150)

$$G_{0,kk'}^{<}(t,t') = i\langle a_{k'}^{\dagger}(t'), a_{k}(t) \rangle.$$
(2.151)

Lemma 3:

$$\{a_k(t), a_{k'}^{\dagger}(t')\} = e^{-i\int_{t'}^{t} dt_1 \epsilon_k(t_1)} \delta_{kk'}, \qquad (2.152)$$

**Proof:** 

$$\{a_{k}(t), a_{k'}^{\dagger}(t')\} = a_{k}(t)a_{k'}^{\dagger}(t') + a_{k'}^{\dagger}(t')a_{k}(t)$$

$$= U^{\dagger}(t, t_{0})a_{k}U(t, t_{0})U^{\dagger}(t', t_{0})a_{k'}^{\dagger}U(t', t_{0})$$
(2.153)

$$+ U^{\dagger}(t',t_0)a^{\dagger}_{k'}U(t',t_0)U^{\dagger}(t,t_0)a_kU(t,t_0)$$
(2.154)

$$=e^{-i\int_{t_0}^t dt_1\epsilon_k(t_1)}e^{i\int_{t_0}^{t'} dt_2\epsilon_{k'}(t_2)}\{a_k, a_{k'}^{\dagger}\}$$
(2.155)

$$=e^{-i\int_{t'}^{t}\epsilon_{k}(t_{1})}\delta_{kk'},$$
(2.156)

where we have utilized (2.133) as well as  $\{a_k, a_{k'}^{\dagger}\} = \delta_{kk'}$ .

#### **Final Result**

As a result, we can substitute (2.156) into (2.149), (2.150) and (2.151) to find the following expressions for our adiabatic Green's functions:

$$G^{A}_{0,kk'}(t,t') = i\theta(t'-t)e^{-i\int_{t'}^{t}dt_{1}\epsilon_{k}(t_{1})}\delta_{kk'},$$
(2.157)

$$G_{0,kk'}^{R}(t,t') = -i\theta(t-t')e^{-i\int_{t'}^{t}dt_{1}\epsilon_{k}(t_{1})}\delta_{kk'},$$
(2.158)

$$G_{0,kk'}^{<}(t,t') = ie^{-i\int_{t'}^{t} dt_{1}\epsilon_{k}(t_{1})} f_{k}\delta_{kk'}.$$
(2.159)

Here we have introduced the occupation number  $f_k$  for state k in the leads, defined as

$$f_k = \langle a_k^{\dagger} a_k \rangle. \tag{2.160}$$

The electronic occupations in the leads will be modelled according to a Fermi-Dirac distribution.

#### 2.4.3 Dyson equations in the central region

Now we shrink our system space down such that it encompasses only the molecular bridge in the central region, while the leads act as the external environment. We then define V to account for the non-local interaction between the central region and leads states. Thus, V corresponds to the coupling elements of  $H_{ML}$  and  $H_{MR}$  as in (2.15).

#### 2.4.3.1 Advanced/Retarded Dyson equations for the central region

We use (2.130) and take  $\lambda_i$  and  $\lambda_j$  to be the arbitrary states *c* and *c'* in the central region:

$$G_{cc'}^{A/R}(t_1, t_2) = G_{0,cc'}^{A/R}(t_1, t_2) + \int_{-\infty}^{\infty} dt' \sum_{\lambda_1 \lambda_2} G_{0,c\lambda_2}^{A/R}(t_1, t') t_{\lambda_2 \lambda_1}(t') G_{\lambda_1 c'}^{A/R}(t', t_2).$$
(2.161)

In order to obtain a solution beyond the free-field solution, we require that  $\lambda_2$  is also a state in the central region. This is clear if we recall (2.59), which does not contain any interaction between the central region and the leads. Then we find that  $\lambda_1$  must be a state in the leads for the  $t_{\lambda_1\lambda_2}$  element to be non-zero. Thus, we obtain

$$G_{cc'}^{A/R}(t_1, t_2) = G_{0,cc'}^{A/R}(t_1, t_2) + \int_{-\infty}^{\infty} dt' \sum_{k\alpha c_1} G_{0,cc_1}^{A/R}(t_1, t') t_{c_1k\alpha}(t') G_{k\alpha c'}^{A/R}(t', t_2),$$
(2.162)

where  $c_1$  denotes a central region state and as usual,  $k\alpha$  denotes a state k in the  $\alpha$  lead. Consider the  $G_{k\alpha c'}^{A/R}$  term on the right hand side; we can apply the Dyson equation on this term to find

$$G_{k\alpha c'}^{A/R}(t',t_2) = G_{0,k\alpha c'}^{A/R}(t',t_2) + \int_{-\infty}^{\infty} dt_3 \sum_{\lambda_1 \lambda_2} G_{0,k\alpha \lambda_2}^{A/R}(t',t_3) t_{\lambda_2 \lambda_1}(t_3) G_{\lambda_1 c'}^{A/R}(t_3,t_2)$$
(2.163)

$$= \int_{-\infty}^{\infty} dt_3 \sum_{c_2k'\alpha} G_{0,k\alpha k'\alpha}^{A/R}(t',t_3) t_{k'\alpha c_2}(t_3) G_{c_2c'}^{A/R}(t_3,t_2)$$
(2.164)

$$= \int_{-\infty}^{\infty} dt_3 \sum_{c_2} G_{0,k\alpha k\alpha}^{A/R}(t',t_3) t_{k\alpha c_2}(t_3) G_{c_2 c'}^{A/R}(t_3,t_2),$$
(2.165)

where we have utilised the fact that  $G_{0,k\alpha k'\alpha}^{A/R} \sim \delta_{k\alpha k'\alpha}$  in accordance with (2.157) and (2.158). Let's substitute this back into (2.162) to find

$$G_{cc'}^{A/R}(t_1, t_2) = G_{0,cc'}^{A/R}(t_1, t_2) + \int_{-\infty}^{\infty} dt' dt'' \sum_{k\alpha c_1 c_2} G_{0,cc_1}^{A/R}(t_1, t') t_{c_1 k\alpha}(t') G_{0,k\alpha k\alpha}^{A/R}(t', t'') t_{k\alpha c_2}(t'') G_{c_2 c'}^{A/R}(t'', t_2),$$
(2.166)

$$=G_{0,cc'}^{A/R}(t_1,t_2) + \int_{-\infty}^{\infty} dt' dt'' \sum_{c_1c_2} G_{0,cc_1}^{A/R}(t_1,t') \Sigma_{c_1c_2}^{A/R}(t',t'') G_{c_2c'}^{A/R}(t'',t_2),$$
(2.167)

where we have introduced the self-energy for the leads as defined by

$$\Sigma_{c_1 c_2}^{A/R}(t',t'') = \sum_{k\alpha} t_{c_1 k\alpha}(t') G_{0,k\alpha k\alpha}^{A/R}(t',t'') t_{k\alpha c_2}(t'').$$
(2.168)

It is instead convenient for us to represent (2.167) as the matrix equation in the central region:

$$G^{A/R}(t_1, t_2) = G_0^{A/R}(t_1, t_2) + \int_{-\infty}^{\infty} dt' dt'' G_0^{A/R}(t_1, t') \Sigma^{A/R}(t', t'') G^{A/R}(t'', t_2),$$
(2.169)

where the lack of indices make it clear that each term is now a matrix in the space of central region states. Thus, we have obtained the Dyson equation for the central region in which any interaction with the surrounding environment is encapsulated through the self-energy term.

#### 2.4.3.2 Lesser Dyson equation for the central region

An entirely equivalent derivation can be performed for the lesser Green's function case, whereby we obtain

$$G_{cc'}^{<}(t_{1},t_{2}) = G_{0,cc'}^{<}(t_{1},t_{2}) + \int_{-\infty}^{\infty} dt' dt'' \sum_{c_{1}c_{2}} \left[ G_{0,cc_{1}}^{<}(t_{1},t') \Sigma_{c_{1}c_{2}}^{<}(t',t'') G_{c_{2}c'}^{A}(t'',t_{2}) + G_{0,cc_{1}}^{R}(t_{1},t') \Sigma_{c_{1}c_{2}}^{<}(t',t'') G_{c_{2}c'}^{<}(t'',t_{2}) + G_{0,cc_{1}}^{R}(t_{1},t') \Sigma_{c_{1}c_{2}}^{<}(t',t'') G_{c_{2}c'}^{<}(t'',t_{2}) \right].$$
(2.170)

The lesser self-energy is similarly defined according to

$$\Sigma_{c_1c_2}^{<}(t',t'') = \sum_{k\alpha} t_{c_1k\alpha}(t') G_{0,k\alpha k\alpha}^{<}(t',t'') t_{k\alpha c_2}(t'').$$
(2.171)

When expressed as a matrix equation in the central region, it becomes

$$G^{<}(t_{1},t_{2}) = G_{0}^{<}(t_{1},t_{2}) + \int_{-\infty}^{\infty} dt' dt'' \Big[ G_{0}^{<}(t_{1},t') \Sigma^{<}(t',t'') G^{A}(t'',t_{2}) + G_{0}^{R}(t_{1},t') \Sigma^{<}(t',t'') G^{A}(t'',t_{2}) + G_{0}^{R}(t_{1},t') \Sigma^{R}(t',t'') G^{<}(t'',t_{2}) \Big].$$
(2.172)

#### 2.4.4 Kadanoff-Baym equations for the central region

Using the results of the previous section, we can now derive the Keldysh-Kadanoff-Baym equations for the central region. These will be the final equations we need to perturbatively solve for the Green's functions. To begin, we take (2.113) and (2.114) and consider the free-field case. Thus, V = 0 and  $G = G_0$  and our equations become

$$\left(i\frac{d}{dt_1} - h(x_1, t_1)\right) G_0^{A/R}(x_1t_1, x_2t_2) = \delta(x_1 - x_2)\delta(t_1 - t_2),$$
(2.173)

$$\left(i\frac{d}{dt_1} - h(x_1, t_1)\right) G_0^<(x_1t_1, x_2t_2) = 0.$$
(2.174)

We can now make the transformation from the continuous position basis to a discrete basis via an equivalent process as performed in Section 2.4.1. This yields

$$\sum_{\lambda} \left( i \frac{\partial}{\partial t_1} I_{\lambda_i \lambda} - h_{\lambda_i \lambda}(t_1) \right) G_{0, \lambda \lambda_j}^{A/R}(t_1, t_2) = \delta_{\lambda_i \lambda_j} \delta(t_1 - t_2),$$
(2.175)

$$\sum_{\lambda} \left( i \frac{\partial}{\partial t_1} I_{\lambda_i \lambda} - h_{\lambda_i \lambda}(t_1) \right) G_{0, \lambda \lambda_j}^{<}(t_1, t_2) = 0.$$
(2.176)

Once again, we shrink our system down to consider only the central region. As such,  $\lambda_i$  and  $\lambda_j$  become states in the central region. In order to find non-trivial solutions, the free-field Green's function forces  $\lambda$  to also be a central region state. Now we can express (2.175) and (2.176) as matrix equations in the space of central region states according to

$$\left(i\frac{\partial}{\partial t_1}I - h(t_1)\right)G_0^{A/R}(t_1, t_2) = I\delta(t_1 - t_2),$$
(2.177)

$$\left(i\frac{\partial}{\partial t_1}I - h(t_1)\right)G_0^<(t_1, t_2) = 0.$$
(2.178)

To find the Kadanoff-Baym equations in the central region, we now have to apply the  $(i\frac{\partial}{\partial t_1}I - h(t_1))$  operator to both (2.169) and (2.172) while making use of (2.177) and (2.178). This results in our final equations:

$$\left(i\frac{\partial}{\partial t_1}I - h(t_1)\right)G^{A/R}(t_1, t_2) = I\delta(t_1 - t_2) + \int_{-\infty}^{\infty} dt' \Sigma^{A/R}(t_1, t')G^{A/R}(t', t_2),$$
(2.179)

$$\left(i\frac{\partial}{\partial t_1}I - h(t_1)\right)G^{<}(t_1, t_2) = \int_{-\infty}^{\infty} dt' \Big[\Sigma^{<}(t_1, t')G^{A}(t', t_2) + \Sigma^{R}(t_1, t')G^{<}(t', t_2)\Big].$$
(2.180)

# Non-adiabatic corrections to observables

The scaffolding established in the previous chapter now allows us derive the theory which forms the basis for our own novel research. This chapter covers the theory common to all following chapters and subsequent published results. Any expansions on the theory required by a specific chapter will then be derived as needed later on. We begin by solving for explicit adiabatic expressions for the Green's functions along with dynamical corrections which account for the motion of nuclei in Section 3.1. We liberally refer to these corrections as non-adiabatic. This then allows us to calculate non-adiabatic expansions to the Meir-Wingreen formula for the electric current through the tunnelling junction in Section 3.2. Finally, Section 3.3 sees us cast the nuclear motion in terms of a Langevin equation, in which the Langevin coefficients are calculated self-consistently using the perturbatively solved-for Green's functions.

# 3.1 Solution of the Green's functions in the Wigner space

#### 3.1.1 The Wigner transform

Unfortunately, (2.179) and (2.180) are generally insoluble beyond intensive numerical schemes. Useful analytical solutions to the Green's functions are found only via perturbative approximations. In our case, a perturbative solution is enabled by the introduction of Wigner coordinates in the time domain:

$$T = \frac{t+t'}{2}, \qquad \tau = t-t'.$$
 (3.1)

The relative time  $\tau$  is associated with the microscopic properties of the system on short timescales, whereas the central time *T* describes the macroscopic features of the system. As we will soon see, these Wigner coordinates are conducive to a perturbative approximation as the separation of time-scales between the fast quantum electrons and slow classical nuclear coordinate is easily observed and abused. In terms of the Wigner coordinates, an arbitrary Green's function becomes

$$G(t,t') = G(T + \tau/2, T - \tau/2).$$
(3.2)

We now introduce the Wigner transform. In a similar vein to the Fourier transform, the Wigner transform is a transformation from the relative time domain to the frequency domain. It is defined according to

$$\tilde{G}(T,\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G(t,t'), \qquad G(t,t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega\tau} \tilde{G}(T,\omega), \tag{3.3}$$

where we use  $\tilde{G}$  to denote a Green's function in the Wigner space. We will also make frequent use of the following Wigner convolution identity:

$$\int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \int dt_1 A(t,t_1) B(t_1,t') = e^{\frac{1}{2i}(\partial_T^A \partial_\omega^B - \partial_\omega^A \partial_T^B)} \tilde{A}(\omega,T) \tilde{B}(\omega,T).$$
(3.4)

Here we have used  $\partial_T^A$  to denote a derivative of the *A* term with respect to *T*, while  $\partial_{\omega}^B$  denotes a derivative of the *B* term with respect to  $\omega$ , and so on. We will frequently make use of this notation from this point forwards.

#### 3.1.2 Free-field Green's functions in the Wigner space

#### 3.1.2.1 Advanced/Retarded Green's function

Our task is now to start calculating the Green's functions in the Wigner space. The first step is to derive expressions for the self-energies in the Wigner space, which depend on the free-field Green's functions. We will disregard the time dependence of the leads energy levels in this section. The derivation for the time dependent case is more involved and will be treated in Section 5. We will first consider the advanced case. To begin, we take the Wigner transform of an element of  $G_0^A$  by utilizing the expression derived in (2.157):

$$\tilde{G}^{A}_{0,kk'}(\omega,T) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G^{A}_{0,kk'}(T,\tau), \qquad (3.5)$$

$$= \int_{-\infty}^{\infty} d\tau e^{i\omega(t-t')} i\theta(t'-t) e^{-i\epsilon_k(t-t')} \delta_{kk'}.$$
(3.6)

We note that the free-field Green's functions are dependent only on  $\tau$  and as such, the Wigner transform becomes a Fourier transform. Noting that this expression is zero when  $\tau$  is positive,

we can redefine our integral limits to be

$$= \int_{-\infty}^{0} d\tau e^{i\omega(t-t')} i e^{-i\epsilon_k(t-t')} \delta_{kk'}, \qquad (3.7)$$

$$= \int_{-\infty}^{0} d\tau e^{i(\omega - \epsilon_k)(t - t')} i\delta_{kk'}.$$
(3.8)

This integral is not well-defined at the limit  $-\infty$  due to the complex exponential. In order to counteract this, we introduce a new term  $-i\eta$  into the exponential where  $\eta > 0$  and take the limit as  $\eta$  goes to zero so that we have

$$=\lim_{\eta\to 0}\int_{-\infty}^{0}d\tau e^{i(\omega-\epsilon_k-i\eta)(t-t')}i\delta_{kk'}$$
(3.9)

$$= \lim_{\eta \to 0} \frac{i\delta_{kk'}}{i(\omega - \epsilon_k - i\eta)} e^{i(\omega - \epsilon_k - i\eta)(t - t')} \mid_{-\infty}^{0}$$
(3.10)

$$= \lim_{\eta \to 0} \frac{\delta_{kk'}}{(\omega - \epsilon_k - i\eta)} - \frac{\delta_{kk'}}{(\omega - \epsilon_k - i\eta)} e^{i(\omega - \epsilon_k)(-\infty)} e^{\eta(-\infty)}.$$
(3.11)

Clearly  $e^{\eta(-\infty)} \rightarrow 0$  and so the entire second term will go to zero, leaving us with

$$\tilde{G}^{A}_{0,kk'}(\omega,T) = \lim_{\eta \to 0} \frac{\delta_{kk'}}{(\omega - \epsilon_k - i\eta)}.$$
(3.12)

In the retarded case, we instead introduce  $+i\eta$  into the exponential and perform an equivalent derivation to find

$$\tilde{G}^{R}_{0,kk'}(\omega,T) = \lim_{\eta \to 0} \frac{\delta_{kk'}}{(\omega - \epsilon_k + i\eta)}.$$
(3.13)

#### 3.1.2.2 Lesser Green's Function

Beginning with (2.159), take the Wigner transform:

$$\tilde{G}_{0,kk'}^{<}(\omega,T) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G_{0,kk'}^{<}(T,\tau)$$
(3.14)

$$= \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} i e^{-i\epsilon_k(t-t')} f_k \delta_{kk'}$$
(3.15)

$$= \int_{-\infty}^{\infty} d\tau e^{i(\omega - \epsilon_k)\tau} i f_k \delta_{kk'}$$
(3.16)

$$=2\pi i f_k \delta_{kk'} \delta(\omega - \epsilon_k), \qquad (3.17)$$

where we have utilized the definition of the Dirac-Delta function as given by

$$\delta(\omega - \epsilon_k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{i(\omega - \epsilon_k)\tau}.$$
(3.18)

#### 3.1.3 Self-energies in the Wigner space

#### 3.1.3.1 Generalised self-energy

Rather than considering the expression for the self-energy as in (2.168), we will instead consider the following more general expression

$$\Xi_{\alpha,cc'}^{A/R/<} = \sum_{k} A_{ck\alpha}(t) G_{k\alpha k\alpha}^{A/R/<}(t,t') B_{k\alpha c'}(t'), \qquad (3.19)$$

where *A* and *B* are arbitrary functions of time. Obviously, when A = B = t where *t* is our Hamiltonian element, then we obtain  $\Sigma^{A/R/<}$ . The need for this generality will only become clear in Section 3.3. We will neglect the A/R/< notation in the following. Apply the Wigner transform to the above to obtain

$$\tilde{\Xi}_{\alpha,cc'} = \sum_{k} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} A_{ck\alpha} (T + \tau/2) G_{k\alpha k\alpha} (t,t') B_{k\alpha c'} (T - \tau/2)$$
(3.20)

$$=\sum_{k}\int_{-\infty}^{\infty}d\tau e^{i\omega\tau}e^{\frac{\tau}{2}d_{T}^{A}}A_{ck\alpha}(T)G_{k\alpha k\alpha}(t,t')e^{\frac{-\tau}{2}d_{T}^{B}}B_{k\alpha c'}(T)$$
(3.21)

$$=\sum_{k}\int_{-\infty}^{\infty}d\tau e^{i\omega\tau}e^{\frac{\tau}{2}(d_{T}^{A}-d_{T}^{B})}A_{ck\alpha}(T)G_{k\alpha k\alpha}(t,t')B_{k\alpha c'}(T)$$
(3.22)

$$=\sum_{k}\int_{-\infty}^{\infty}d\tau e^{i\omega\tau}e^{\frac{1}{2i}\overleftarrow{\phi_{\omega}}^{t}(d_{T}^{A}-d_{T}^{B})}A_{ck\alpha}(T)G_{k\alpha k\alpha}(t,t')B_{k\alpha c'}(T).$$
(3.23)

(3.24)

Here we have applied the Lagrange shift operator to *A* and *B*. The  $\overleftarrow{\partial_{\omega}^{e}}$  notation denotes the derivative operator acting to the left on the exponential. Now we take all the terms that are independent of  $\tau$  outside of the integral, leaving us with

$$\tilde{\Xi}_{\alpha,cc'} = \sum_{k} e^{\frac{1}{2i} \overline{\partial_{\omega}^{e'}} (d_T^A - d_T^B)} A_{ck\alpha}(T) B_{k\alpha c'}(T) \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G_{k\alpha k\alpha}(t,t')$$
(3.25)

$$=\sum_{k}e^{\frac{1}{2i}\overrightarrow{\partial_{\omega}^{G}}(d_{T}^{A}-d_{T}^{B})}A_{ck\alpha}(T)B_{k\alpha c'}(T)\widetilde{G}_{k\alpha k\alpha}(T,\omega).$$
(3.26)

(3.27)

Finally, we take a Mclaurin series expansion of the exponential to find

$$\tilde{\Xi}_{\alpha,cc'} = \sum_{k} A_{ck\alpha} \tilde{G}_{k\alpha k\alpha} B_{k\alpha c'} + \frac{1}{2i} \sum_{k} \frac{\partial \tilde{G}_{k\alpha k\alpha}}{\partial \omega} \left( \frac{dA_{ck\alpha}}{dT} B_{k\alpha c'} - A_{ck\alpha} \frac{dB_{k\alpha c'}}{dT} \right) + \dots$$
(3.28)

$$=\tilde{\Xi}_{(0),\alpha,cc'}+\tilde{\Xi}_{(1),\alpha,cc'}+...,$$
(3.29)

where the functional dependencies are clear from the context. We will find that the higher order terms in the expansion become important when considering motion on the leads interface in which a time dependence emerges in the  $t_{ck\alpha}$  element due to classical motion. This will be considered in Section 4.

#### 3.1.3.2 Advanced/Retarded self-energy

Our main aim is still to calculate expressions for the self-energies in the Wigner space. For now we will consider only the 0<sup>th</sup> order term from the expansion in (3.28) and let A = B = t. Let's first consider the advanced case whereby we substitute (3.12) to find

$$\tilde{\Sigma}^{A}_{(0),\alpha,cc'} = \lim_{\eta \to 0} \sum_{k} \frac{t^*_{k\alpha c} t_{k\alpha c'}}{(\omega - \epsilon_{k\alpha} - i\eta)}$$
(3.30)

$$= \lim_{\eta \to 0} \sum_{k} \frac{t_{k\alpha c}^* t_{k\alpha c'}}{(\omega - \epsilon_{k\alpha})^2 + \eta^2} (\omega - \epsilon_{k\alpha} + i\eta)$$
(3.31)

$$= \lim_{\eta \to 0} \left( \sum_{k} \frac{t_{k\alpha c'}^* t_{k\alpha c'}(\omega - \epsilon_{k\alpha})}{(\omega - \epsilon_{k\alpha})^2 + \eta^2} + i \sum_{k} \frac{t_{k\alpha c}^* t_{k\alpha c'} \eta}{(\omega - \epsilon_{k\alpha})^2 + \eta^2} \right),$$
(3.32)

where we have noted that  $t_{ck\alpha} = t^*_{k\alpha c}$  since the Hamiltonian is hermitian. We now make use of the following Dirac-delta function identity in order to simplify the second term:

$$\lim_{\eta \to 0} \frac{\eta}{x^2 + \eta^2} = \pi \delta(x).$$
(3.33)

As a result, we find

$$\tilde{\Sigma}^{A}_{(0),\alpha,cc'} = \lim_{\eta \to 0} \sum_{k} \frac{t^{*}_{k\alpha c} t_{k\alpha c'}(\omega - \epsilon_{k\alpha})}{(\omega - \epsilon_{k\alpha})^{2} + \eta^{2}} + i\pi \sum_{k} t^{*}_{k\alpha c} t_{k\alpha c'} \delta(\omega - \epsilon_{k\alpha})$$
(3.34)

$$=\Lambda_{\alpha,cc'}+\frac{i}{2}\Gamma_{\alpha,cc'},\tag{3.35}$$

where we have introduced

$$\Lambda_{\alpha,cc'} = \lim_{\eta \to 0} \sum_{k} \frac{t_{k\alpha c}^* t_{k\alpha c'} (\omega - \epsilon_{k\alpha})}{(\omega - \epsilon_{k\alpha})^2 + \eta^2},$$
(3.36)

$$\Gamma_{\alpha,cc'} = 2\pi \sum_{k} t^*_{k\alpha c} t_{k\alpha c'} \delta(\omega - \epsilon_{k\alpha}).$$
(3.37)

The expression for  $\Gamma$  can be further simplified. First we let the terms under the summation equal to a function  $n(\epsilon_k)$ ;

$$\therefore \Gamma_{\alpha,cc'} = 2\pi \sum_{k} n(\epsilon_k).$$
(3.38)

Now by introducing an arbitrary variable  $\chi$ , we can rewrite  $\sum_k n(\epsilon_k)$  as the following:

$$\sum_{k} n(\epsilon_{k}) = \int_{-\infty}^{\infty} d\chi \sum_{k} n(\chi) \delta(\epsilon_{k} - \chi)$$
(3.39)

$$= \int_{-\infty}^{\infty} d\chi n(\chi) \sum_{k} \delta(\epsilon_{k} - \chi)$$
(3.40)

$$= \int_{-\infty}^{\infty} d\chi n(\chi) \rho_{\alpha}(\chi), \qquad (3.41)$$

where  $\rho(\chi)$  is the density of states:

$$\rho_{\alpha}(\chi) = \sum_{k} \delta(\epsilon_{k} - \chi). \tag{3.42}$$

As one would expect, when the density of states is integrated over some region it provides the number of states within the limits of that integration. Now utilizing (3.41), we can rewrite  $\Gamma$  as

$$\Gamma_{\alpha,cc'} = 2\pi \int_{-\infty}^{\infty} d\chi f(\chi) \rho_{\alpha}(\chi)$$
(3.43)

$$=2\pi \int_{-\infty}^{\infty} d\chi t_{\alpha c}^* t_{\alpha c'} \delta(\omega-\chi) \rho_{\alpha}(\chi)$$
(3.44)

$$=2\pi t_{k\alpha c}^* t_{k\alpha c'} \rho_{\alpha}(\omega). \tag{3.45}$$

In doing so, we have assumed that  $t_{k\alpha c}$  is independent of the leads state k under consideration, such that  $t_{k\alpha c} = t_{\alpha c}$ . Naturally, an equivalent derivation can be performed for the retarded self-energy in which we obtain

$$\tilde{\Sigma}^{R}_{(0),\alpha,cc'} = \Lambda_{\alpha,cc'} - \frac{i}{2} \Gamma_{\alpha,cc'}.$$
(3.46)

The  $\Gamma$  term accounts for the energy broadening of the central state due to interactions with the leads while the  $\Lambda$  term accounts for a shift in the energy level.

#### 3.1.3.3 Lesser Self-Energy

Again, we take the 0<sup>th</sup> order term from the expansion in (3.28) and let A = B = t while we now consider the lesser case. We utilise (3.17) to find

$$\tilde{\Sigma}^{<}_{(0),\alpha,cc'} = 2\pi i \sum_{k} t^*_{k\alpha c'} f_k \delta(\omega - \epsilon_k).$$
(3.47)

If we assume that the electronic populations in the leads as denoted by  $f_k$  can be described by a Fermi-Dirac distribution, then we can further simplify the above to

$$\tilde{\Sigma}^{<}_{(0),\alpha,cc'}(\omega,T) = if_{\alpha}(\omega)\Gamma_{\alpha,cc'}(\omega,T), \qquad (3.48)$$

where

$$f_{\alpha}(\omega) = \frac{1}{e^{\frac{\omega-\mu_{\alpha}}{k_B T_{\alpha}}} + 1}.$$
(3.49)

Here,  $\mu_{\alpha}$  is the chemical potential for the  $\alpha$  lead while  $T_{\alpha}$  is the macroscopic temperature and  $k_B$  is Boltzmann's constant.

#### 3.1.3.4 Wide-Band Approximation

To simplify the self-energy equations, we implement the wide-band approximation. Consider the equation for  $\Lambda$  as given in (3.36):

$$\Lambda_{\alpha,cc'} = \lim_{\eta \to 0} \sum_{k} \frac{t^*_{\alpha c} t_{\alpha c'}(\omega - \epsilon_{k\alpha})}{(\omega - \epsilon_{k\alpha})^2 + \eta^2}$$
(3.50)

$$= \lim_{\eta \to 0} t^*_{\alpha c} t_{\alpha c'} \sum_k \int_{-\infty}^{\infty} d\omega' \delta(\omega' - \epsilon_{k\alpha}) \frac{(\omega - \omega')}{(\omega - \omega')^2 + \eta^2}$$
(3.51)

$$= \lim_{\eta \to 0} t^*_{\alpha c} t_{\alpha c'} \int_{-\infty}^{\infty} d\omega' \rho(\omega') \frac{(\omega - \omega')}{(\omega - \omega')^2 + \eta^2}.$$
(3.52)

Now we assume that the density of states in the leads is a constant such that

$$\rho(\omega) = \begin{cases}
\rho & \omega_{min} \le \omega \le \omega_{max} \\
0 & otherwise
\end{cases},$$
(3.53)

where  $\omega_{min}$  and  $\omega_{max}$  denote the edges of the leads conduction band. As a result,  $\rho$  can be pulled out of the integral in (3.52) and we can truncate the integral limits to find

$$\Lambda_{\alpha,cc'} = t^*_{\alpha c} t_{\alpha c'} \rho \int_{\omega_{min}}^{\omega_{max}} d\omega' \frac{1}{(\omega - \omega')}$$
(3.54)

$$= t_{\alpha c}^* t_{\alpha c'} \rho \ln \left| \frac{\omega_{min} - \omega}{\omega_{max} - \omega} \right|.$$
(3.55)

where we have allowed the  $\eta$  term to go to zero as it will no longer affect our calculations. We now introduce the wide-band approximation which assumes that the conducting band for the electrons within the leads is wide such that we can approximate  $\omega_{max} \to \infty$  and  $\omega_{min} \to -\infty$ . Under this approximation, it can be seen that  $\Lambda$  will go to zero.

#### 3.1.3.5 Summary

Here we summarise the main equations derived in this section. Under the wide-band approximation, our adiabatic self-energies simplify to:

$$\tilde{\Sigma}^{A}_{(0),\alpha,cc'}(T) = \frac{i}{2} \Gamma_{\alpha,cc'}(T), \qquad (3.56)$$

$$\tilde{\Sigma}^{R}_{(0),\alpha,cc'}(T) = -\frac{i}{2}\Gamma_{\alpha,cc'}(T), \qquad (3.57)$$

$$\tilde{\Sigma}^{<}_{(0),\alpha,cc'}(\omega,T) = if_{\alpha}(\omega)\Gamma_{\alpha,cc'}(T), \qquad (3.58)$$

given that

$$\Gamma_{\alpha,cc'} = 2\pi t^*_{\alpha c}(T) t_{\alpha c'}(T) \rho_{\alpha}.$$
(3.59)

We take  $\Gamma$  as a parameter input for our model and thus, we are now able to calculate the self-energies.

#### 3.1.4 Kadanoff-Baym equations in the Wigner space

#### 3.1.4.1 Left-hand side

We seek to transform our Kadanoff-Baym equations presented in (2.179) and (2.180) into the Wigner space. We begin by considering the left-hand side (LHS) individually, which is equivalent for each of the advanced, retarded and lesser case. Application of the Wigner transform yields

$$LHS = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \left( i\frac{\partial}{\partial\tau} I + \frac{i}{2}\frac{\partial}{\partial\tau} I - h(T+\tau/2) \right) G(T+\tau/2, T+\tau/2),$$
(3.60)

where we have expressed the real-time derivative in terms of the Wigner coordinates according to

$$\frac{\partial}{\partial t} = \frac{\partial \tau}{\partial t} \frac{\partial}{\partial \tau} + \frac{\partial T}{\partial t} \frac{\partial}{\partial T}$$
(3.61)

$$=\frac{\partial}{\partial\tau}+\frac{1}{2}\frac{\partial}{\partial T}.$$
(3.62)

Let us now consider each term in this equation individually, starting with the  $i\frac{\partial}{\partial \tau}$  term.

$$=\int_{-\infty}^{\infty} d\tau e^{i\omega\tau} i\frac{\partial}{\partial\tau} IG \tag{3.63}$$

$$=i\int_{-\infty}^{\infty} d\tau \frac{\partial}{\partial \tau} \left[ e^{i\omega\tau} G \right] - \frac{\partial}{\partial \tau} \left[ e^{i\omega\tau} \right] G$$
(3.64)

$$= -i \int_{-\infty}^{\infty} d\tau \frac{\partial}{\partial \tau} \left[ e^{i\omega\tau} \right] G \tag{3.65}$$

$$=\omega I\tilde{G}.$$
(3.66)

We have used the fact that

$$\int_{-\infty}^{\infty} d\tau \frac{\partial}{\partial \tau} \left[ e^{i\omega\tau} G \right] = 0, \qquad (3.67)$$

since  $G(T + \tau/2, T - \tau/2) \rightarrow 0$  as  $|\tau| \rightarrow \infty$ . The second term in (3.60) is trivial; we thus consider the third term. By utilising the Lagrange shift operator, we find

$$= -\int_{-\infty}^{\infty} d\tau e^{i\omega\tau} e^{\frac{\tau}{2}\partial_T^h} h(T) G(T+\tau/2, T-\tau/2)$$
(3.68)

$$= -e^{\frac{1}{2i}\overrightarrow{\partial_{\omega}^{o}}\partial_{T}^{h}}h(T)\int_{-\infty}^{\infty}d\tau e^{i\omega\tau}G(T+\tau/2,T-\tau/2)$$
(3.69)

$$= -e^{\frac{1}{2i}\partial_{\omega}^{G}\partial_{T}^{h}}h(T)\tilde{G}(T,\omega).$$
(3.70)

The entire left-hand side can now be written as

$$LHS = \left(\omega I + \frac{i}{2} \frac{\partial}{\partial T} I - e^{\frac{1}{2i} \partial_{\omega}^{G} \partial_{T}^{h}} h(T)\right) \tilde{G}(T, \omega).$$

#### 3.1.4.2 Right-Hand Side

We now consider the Wigner transform of the right-hand side of (3.60). We will explicitly show the advanced/retarded case. We find

$$RHS = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} I\delta(t-t') + \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \int_{-\infty}^{\infty} dt' \Sigma^{A/R}(t_1,t') G^{A/R}(t',t_2)$$
(3.71)

$$= I + e^{\frac{1}{2i} \left\{ \partial_T^{\Sigma} \partial_{\omega}^{G} - \partial_{\omega}^{\Sigma} \partial_T^{G} \right\}} \tilde{\Sigma}^{A/R}(T, \omega) \tilde{G}^{A/R}(T, \omega),$$
(3.72)

where we have utilized the Wigner convolution theorem as introduced in (3.4).

#### 3.1.4.3 Summary

Our Kadanoff-Baym equations for the Green's functions in the Wigner space are given by

$$\left(\omega I + \frac{i}{2}\frac{\partial}{\partial T}I - e^{\frac{1}{2i}\partial_{\omega}^{G}\partial_{T}^{h}}h(T)\right)\tilde{G}^{A/R}(T,\omega) = I + e^{\frac{1}{2i}\left\{\partial_{T}^{\Sigma}\partial_{\omega}^{G} - \partial_{\omega}^{\Sigma}\partial_{T}^{G}\right\}}\tilde{\Sigma}^{A/R}(T,\omega)\tilde{G}^{A/R}(T,\omega), \quad (3.73)$$

$$\left(\omega I + \frac{i}{2}\frac{\partial}{\partial T}I - e^{\frac{1}{2i}\partial_{\omega}^{G}\partial_{T}^{h}}h(T)\right)\tilde{G}^{<}(T,\omega) = e^{\frac{1}{2i}\left\{\partial_{T}^{\Sigma}\partial_{\omega}^{G} - \partial_{\omega}^{\Sigma}\partial_{T}^{G}\right\}}\left[\tilde{\Sigma}^{<}(T,\omega)\tilde{G}^{A}(T,\omega) + \tilde{\Sigma}^{R}(T,\omega)\tilde{G}^{<}(T,\omega)\right]$$
(3.74)

#### 3.1.5 System energy-scales and the small parameter

We are now at the point where we can solve (3.73) and (3.74) perturbatively for the Green's functions via leveraging our small parameter introduced in Section 2.2. In the absence of an AC driving in the leads, the central time dependence of each term in these equations arises implicitly via the influence of the classical coordinate on our Hamiltonian elements. Then we have

$$h(T) = h(\mathbf{x}[T]), \qquad t(T) = t(\mathbf{x}[T]),$$
(3.75)

where **x** is the vector of classical degrees of freedom. The base-case for our perturbation is the adiabatic case in which the nuclear geometry evolves adiabatically such that the tunnelling electrons view the nuclei as entirely stationary. In this regime, any  $\partial_T$  terms will become negligible since the classical coordinates are unchanging relative to the electrons. Corrections due to the nuclear motion are then included by allowing for  $\partial_T$  terms to be non-zero. As will be observed, the pairing of  $\partial_{\omega}$  and  $\partial_T$  terms in (3.73) and (3.74) result in our small parameter,  $\Omega/\Gamma$ , naturally emerging from the higher order terms in the expansions of the exponentials. This then allows us to truncate the expansion at a chosen point. We will make the following ansatzes:

$$\tilde{G} = \tilde{G}_{(0)} + \tilde{G}_{(1)} + \dots, \tag{3.76}$$

$$\tilde{\Sigma} = \tilde{\Sigma}_{(0)} + \tilde{\Sigma}_{(1)} + \dots, \tag{3.77}$$

where  $\tilde{G}_{(n)}$  and  $\tilde{\Sigma}_{(n)}$  are each  $n^{\text{th}}$  order in  $\Omega/\Gamma$ . We will solve for the 0<sup>th</sup> and 1<sup>st</sup> order Green's functions via (3.73) and (3.74). As it happens, we have already solved for the self-energies; the adiabatic component given in (3.56)-(3.58), while the first order correction can be found from (3.28) which also contains a  $\partial_T \partial_\omega$  pair. We choose to neglect terms higher than first order in our small parameter.

#### 3.1.6 Perturbatively solving for the Green's functions

#### 3.1.6.1 Adiabatic case

We will consider the advanced/retarded case explicitly. We begin by substituting (3.76) and (3.77) into (3.73) to obtain

$$\left(\omega I + \frac{i}{2}\frac{\partial}{\partial T}I - e^{\frac{1}{2i}\partial_{\omega}^{G}\partial_{T}^{h}}h\right)\left(\tilde{G}_{(0)}^{A/R} + ...\right) = I + e^{\frac{1}{2i}\left\{\partial_{T}^{\Sigma}\partial_{\omega}^{G} - \partial_{\omega}^{\Sigma}\partial_{T}^{G}\right\}}\left(\tilde{\Sigma}_{(0)}^{A/R} + ...\right)\left(\tilde{G}_{(0)}^{A/R} + ...\right).$$
(3.78)

We will also take a Maclaurin series expansion of the exponentials on both sides of the equation. In the adiabatic case, we retain only the  $0^{th}$  order term in each expansion such that we find

$$(\omega I - h) \,\tilde{G}_{(0)}^{A/R} = I + \tilde{\Sigma}_{(0)}^{A/R} \tilde{G}_{(0)}^{A/R},\tag{3.79}$$

$$\tilde{G}_{(0)}^{A/R} = \left(\omega I - h - \tilde{\Sigma}_{(0)}^{A/R}\right)^{-1}.$$
(3.80)

As usual, an equivalent method is applied in the lesser case to find the adiabatic form of the Keldysh equation,

$$\tilde{G}_{(0)}^{<} = \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{(0)}^{<} \tilde{G}_{(0)}^{A}.$$
(3.81)

#### 3.1.6.2 First-order correction

Solving for the first-order corrections to the Green's functions is much the same process as in the adiabatic case, except we now truncate all expansions after the first order. In the advanced/retarded case, we find

$$\tilde{G}_{(1)}^{A/R} = \tilde{G}_{(0)}^{A/R} \tilde{\Sigma}_{(1)}^{A/R} \tilde{G}_{(0)}^{A/R} + \frac{1}{2i} \tilde{G}_{(0)}^{A/R} \left( \mathcal{A}^{A/R} \partial_T \tilde{G}_{(0)}^{A/R} + \mathcal{B}^{A/R} \partial_\omega \tilde{G}_{(0)}^{A/R} \right),$$
(3.82)

where we have introduced the convenient quantities, A and B, given by

$$\mathcal{A}^{A/R} = 1 - \partial_{\omega} \tilde{\Sigma}^{A/R}_{(0)}, \qquad \mathcal{B}^{A/R} = \partial_T h + \partial_T \tilde{\Sigma}^{A/R}_{(0)}. \tag{3.83}$$

The first order expression can be further simplified by explicitly calculating the Green's function derivatives as per

$$\partial_T \tilde{G}_{(0)}^{A/R} = \tilde{G}_{(0)}^{A/R} \mathcal{B}^{A/R} \tilde{G}_{(0)}^{A/R}, \qquad \partial_\omega \tilde{G}_{(0)}^{A/R} = -\tilde{G}_{(0)}^{A/R} \mathcal{A}^{A/R} \tilde{G}_{(0)}^{A/R}.$$
(3.84)

Substituting these in, we now find

$$\tilde{G}_{(1)}^{A/R} = \tilde{G}_{(0)}^{A/R} \tilde{\Sigma}_{(1)}^{A/R} \tilde{G}_{(0)}^{A/R} + \frac{1}{2i} \tilde{G}_{(0)}^{A/R} \left( \mathcal{A}^{A/R} \tilde{G}_{(0)}^{A/R} \mathcal{B}^{A/R} \tilde{G}_{(0)}^{A/R} - \mathcal{B}^{A/R} \tilde{G}_{(0)}^{A/R} \mathcal{A}^{A/R} \tilde{G}_{(0)}^{A/R} \right), \quad (3.85)$$

$$= \tilde{G}_{(0)}^{A/R} \tilde{\Sigma}_{(1)}^{A/R} \tilde{G}_{(0)}^{A/R} + \frac{1}{2i} \tilde{G}_{(0)}^{A/R} \left[ \mathcal{A}^{A/R} \tilde{G}_{(0)}^{A/R}, \mathcal{B}^{A/R} \tilde{G}_{(0)}^{A/R} \right]_{-}.$$
(3.86)

We note that the commutator will go to zero in the case of a single electronic level. The same procedure is applied in the lesser case, in which we utilise the following derivatives:

$$\partial_{\omega}\tilde{G}_{(0)}^{<} = -\tilde{G}_{(0)}^{R}\mathcal{A}^{R}\tilde{G}_{(0)}^{<} - \tilde{G}_{(0)}^{<}\mathcal{A}^{A}\tilde{G}_{(0)}^{A} + \tilde{G}_{(0)}^{R}\partial_{\omega}\tilde{\Sigma}^{<}\tilde{G}_{(0)}^{A},$$
(3.87)

$$\partial_T \tilde{G}^{<}_{(0)} = \tilde{G}^R_{(0)} \mathcal{B}^R \tilde{G}^{<}_{(0)} + \tilde{G}^{<}_{(0)} \mathcal{B}^A \tilde{G}^A_{(0)} + \tilde{G}^R_{(0)} \partial_T \tilde{\Sigma}^{<} \tilde{G}^A_{(0)}.$$
(3.88)

This then yields the final expression,

$$\begin{split} \tilde{G}_{(1)}^{<} &= \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{(1)}^{<} \tilde{G}_{(0)}^{A} + \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{(0)}^{<} \tilde{G}_{(1)}^{A} + \tilde{G}_{(1)}^{R} \tilde{\Sigma}_{(0)}^{<} \tilde{G}_{(0)}^{A} \\ &+ \frac{1}{2i} \tilde{G}_{(0)}^{R} \left[ \mathcal{B}^{R} \tilde{G}_{(0)}^{R} \partial_{\omega} \tilde{\Sigma}_{(0)}^{<} + \mathcal{A}^{R} \tilde{G}_{(0)}^{<} \mathcal{B}^{A} + \mathcal{A}^{R} \tilde{G}_{(0)}^{R} \partial_{T} \tilde{\Sigma}_{(0)}^{<} + h.c. \right] \tilde{G}_{(0)}^{A}. \end{split}$$
(3.89)

There is generally little need to simplify this further into the base components and so we leave it in this form.

#### 3.1.6.3 A note on the conjugate transpose

By applying our original Green's function definitions in the Schwinger-Keldysh space according to (2.30)-(2.33), along with utilising (2.88), it is reasonably simple to show that the full Green's functions obey the following conjugate transpose relations:

$$\left[G^{A}\right]^{\dagger} = G^{R}, \qquad \left[G^{}\right]^{\dagger} = -G^{}.$$
 (3.90)

These properties are also carried into the Wigner space. In the advanced/retarded case this is demonstrated by

$$\tilde{G}^{A}(\omega,T) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G^{A}(T+\tau/2,T-\tau/2), \qquad (3.91)$$

$$\left[\tilde{G}^{A}(\omega,T)\right]^{\dagger} = \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} G^{R}(T-\tau/2,T+\tau/2).$$
(3.92)

(3.93)

Now introduce the new dummy variable  $\tau_0 = -\tau$  and manipulate the integration limits to find

$$\left[\tilde{G}^{A}(\omega,T)\right]^{\dagger} = -\int_{\infty}^{-\infty} d\tau e^{i\omega\tau} G^{R}(T+\tau/2,T-\tau/2), \qquad (3.94)$$

$$= \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G^{R}(T + \tau/2, T - \tau/2), \qquad (3.95)$$

$$=\tilde{G}^{R}(\omega,T). \tag{3.96}$$

A similar approach is applied in the lesser/greater case. It is also clear that upon taking our ansatz as in (3.76), the Green's function of any arbitrary order n in our small parameter will also satisfy the relations. The argument is as follows:

$$\tilde{G}^A\Big]^\dagger = \tilde{G}^R, \tag{3.97}$$

$$\left[\tilde{G}_{(0)}^{A} + \lambda \tilde{G}_{(1)}^{A} + \dots + \lambda^{n} \tilde{G}_{(n)}^{A} + \dots\right]^{\dagger} = \tilde{G}_{(0)}^{R} + \lambda \tilde{G}_{(1)}^{R} + \dots + \lambda^{n} \tilde{G}_{(n)}^{R} + \dots,$$
(3.98)

(3.99)

where we have introduced the book-keeping parameter  $\lambda$  which tells us that a term with  $\lambda^n$  is of order *n* in our small parameter. Simple rearrangement leads to

$$\left(\left[\tilde{G}_{(0)}^{A}\right]^{\dagger} - \tilde{G}_{(0)}^{R}\right) + \lambda \left(\left[\tilde{G}_{(1)}^{A}\right]^{\dagger} - \tilde{G}_{(1)}^{R}\right) + \dots + \lambda^{n} \left(\left[\tilde{G}_{(n)}^{A}\right]^{\dagger} - \tilde{G}_{(n)}^{R}\right) + \dots = 0.$$
(3.100)

Given that we have free rein over the choice of size of our small parameter and that we require the above equation to always be satisfied, we find that

$$\left[\tilde{G}^{A}_{(n)}\right]^{\dagger} = \tilde{G}^{R}_{(n)}, \qquad (3.101)$$

for any order n. An equivalent argument can be applied for the lesser/great relation. The argument also applies to our self-energy expansion as in (3.77).

# 3.2 Meir-Wingreen formula for the electric current with non-adiabatic corrections

In this section we derive a Meir-Wingreen type formula for the electric current through the molecular junction following the ideas of Yigal Meir and Ned Wingreen in their seminal paper [175]. Our derivation differs in that we allow nuclei within the junction to move through our choice of classical coordinates, which produces non-adiabatic dynamical corrections to the current due to the nuclear motion. Additionally, we allow for the coupling element between the central region and the leads to be implicitly time dependent through the motion of the

classical coordinate; this is explored thoroughly in Section 4.

To begin, we define the current leaving the  $\alpha$  lead, denoted  $I_{\alpha}$ , according to:

$$I_{\alpha} = -e \left\langle \frac{d\hat{N}_{\alpha}}{dt} \right\rangle = -\left\langle \frac{d\hat{N}_{\alpha}}{dt} \right\rangle, \qquad (3.102)$$

where  $\hat{N}_{\alpha}$  is the total electronic occupation operator of the  $\alpha$  lead and e is the charge of an electron. In atomic units e = 1. To avoid ambiguity in the following derivation, we will explicitly consider the left current while an equivalent derivation will also apply for the right current. Utilising the Heisenberg equation of motion for  $\frac{dN}{dt}$  yields

$$I_L(t) = -ie\left\langle \left[ \hat{H}(t), \hat{N}_L(t) \right] \right\rangle, \qquad (3.103)$$

where H is the Hamiltonian for the system. All operators here are time-dependent under the Heisenberg representation. The Hamiltonian for our system is given by

$$\hat{H}(t) = \sum_{k\alpha} \epsilon_{k\alpha} a_{k\alpha}^{\dagger} a_{k\alpha} + \sum_{ij} h_{ij}(\mathbf{x}[t]) a_i^{\dagger} a_j + \sum_{k\alpha i} \left[ t_{k\alpha i}(\mathbf{x}[t]) a_{k\alpha}^{\dagger} a_i + t_{ik\alpha}(\mathbf{x}[t]) a_i^{\dagger} a_{k\alpha} \right] + K(t) + U(\mathbf{x}[t]),$$
(3.104)

while the total occupation operator for the left-lead is given by

$$\hat{N}_L(t) = \sum_{kL} a_{kL}^{\dagger} a_{kL}.$$
(3.105)

Note that the creation and annihilation operators here are also in the Heisenberg picture; we have only neglected to show the time dependence explicitly for brevity. With some manipulation, it is clear that the only non-zero terms arising from the commutator in (3.103) are going to be from the leads coupling terms of the Hamiltonian. Our expression for the current then becomes

$$I_L(t) = -i \left\langle \left[ \sum_{k\alpha i} \left[ t_{k\alpha i} a_{k\alpha}^{\dagger} a_i + t_{ik\alpha} a_i^{\dagger} a_{k\alpha} \right], \sum_{kL'} a_{kL'}^{\dagger} a_{kL'} \right] \right\rangle$$
(3.106)

$$= -i \left\langle \left[ \sum_{k\alpha i} \sum_{kL'} \left( t_{k\alpha i} \left[ a_{k\alpha}^{\dagger} a_{i}, a_{kL'}^{\dagger} a_{kL'} \right] + t_{ik\alpha} \left[ a_{i}^{\dagger} a_{k\alpha}, a_{kL'}^{\dagger} a_{kL'} \right] \right) \right] \right\rangle$$
(3.107)

$$= -i\sum_{k\alpha i}\sum_{kL'} \left( t_{k\alpha i} \left\langle \left[ a_{k\alpha}^{\dagger} a_{i}, a_{kL'}^{\dagger} a_{kL'} \right] \right\rangle + t_{ik\alpha} \left\langle \left[ a_{i}^{\dagger} a_{k\alpha}, a_{kL'}^{\dagger} a_{kL'} \right] \right\rangle \right)$$
(3.108)

$$= -i\sum_{k\alpha i}\sum_{kL'} \left( t_{k\alpha i} \left\langle \delta_{k\alpha kL'} a_{kL'}^{\dagger} a_i \right\rangle - t_{ik\alpha} \left\langle \delta_{k\alpha kL'} a_i^{\dagger} a_{kL'} \right\rangle \right)$$
(3.109)

$$= -i\sum_{kLi} \left( t_{kLi} \left\langle a_{kL}^{\dagger} a_i \right\rangle - t_{ikL} \left\langle a_i^{\dagger} a_{kL} \right\rangle \right)$$
(3.110)

$$=\sum_{kLi} \left( t_{kLi}(t) G_{ikL}^{<}(t,t) - t_{ikL}(t) G_{kLi}^{<}(t,t) \right).$$
(3.111)

Here we have used the standard second quantization commutator relations as well as the

general commutator identity:

$$[AB, CD] = A [B, C] D + [A, C] BD + CA [B, D] + C [A, D] B.$$
(3.112)

In order to facilitate a transformation to the Wigner space where we can easily identify the different system time-scales, it necessary to introduce an auxiliary function,  $\mathcal{I}(t, t')$ , which satisfies the property,  $\mathcal{I}(t, t) = I(t)$  when t = t'. This will allow us to perform manipulations on  $\mathcal{I}$  in the Wigner space before letting t = t' upon which we find the expression for the current. We define

$$\mathcal{I}(t,t') = \sum_{k\alpha i} \left( t_{k\alpha i}(t) G_{ik\alpha}^{<}(t,t') - t_{ik\alpha}(t) G_{k\alpha i}^{<}(t,t') \right).$$
(3.113)

The Green's functions here span both the central region and left lead. We make use of the Dyson equation found in (2.131) to re-express this in terms of Green's functions for the central region where the influence of the leads is contained within the leads self-energies. Inputting the Dyson expansion yields

$$\mathcal{I}(t,t') = \int_{-\infty}^{\infty} dt_1 \sum_{k\alpha i j} \left( t_{k\alpha i}(t) G_{ij}^{<}(t,t_1) t_{jk\alpha}(t_1) G_{k\alpha k\alpha}^{A}(t_1,t') + t_{k\alpha i}(t) G_{ij}^{R}(t,t_1) t_{jk\alpha}(t_1) G_{k\alpha k\alpha}^{<}(t_1,t') - t_{ik\alpha}(t) G_{k\alpha k\alpha}^{R}(t,t_1) t_{k\alpha j}(t_1) G_{ji}^{<}(t_1,t') - t_{ik\alpha}(t) G_{k\alpha k\alpha}^{R}(t,t_1) t_{k\alpha j}(t_1) G_{ji}^{<}(t_1,t') \right).$$
(3.114)

The free-field Green's functions here are given by  $G_{k\alpha k\alpha} = G_{0,k\alpha k\alpha}$ . This is made clear through the indices since the leads are always non-interacting. Now we introduce the self-energies according to (2.168) and (2.171) to obtain

$$\mathcal{I}(t,t') = \int_{-\infty}^{\infty} dt_1 \text{Tr} \Big\{ G^{<}(t,t_1) \Sigma_{\alpha}^{A}(t_1,t') + G^{R}(t,t_1) \Sigma_{\alpha}^{<}(t_1,t')$$
(3.115)

$$-\Sigma_{\alpha}^{<}(t,t_{1})G^{A}(t_{1},t')-\Sigma_{\alpha}^{R}(t,t_{1})G^{<}(t_{1},t')\Big\},$$
(3.116)

where the summation over matrix elements has been simplified to a trace over matrices. We now find the equation in a form consisting of familiar quantities and are now in a position to transition to the Wigner space. Apply the Wigner transform and use (3.4) to find

$$\int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \mathcal{I}_{\alpha}(t,t') = \operatorname{Tr}\left\{ e^{\frac{1}{2i}(\partial_{T}^{G}\partial_{\omega}^{\Sigma} - \partial_{\omega}^{G}\partial_{T}^{\Sigma})} \left( \tilde{G}^{<} \tilde{\Sigma}_{\alpha}^{A} + \tilde{G}^{R} \tilde{\Sigma}_{\alpha}^{<} \right) - e^{\frac{1}{2i}(\partial_{T}^{\Sigma}\partial_{\omega}^{G} - \partial_{\omega}^{\Sigma}\partial_{T}^{G})} \left( \tilde{\Sigma}_{\alpha}^{<} \tilde{G}^{A} + \tilde{\Sigma}_{\alpha}^{R} \tilde{G}^{<} \right) \right\},$$
(3.117)

where we have subdued the functional dependencies. Finally, we apply the inverse Wigner transform and let t = t' such that  $\mathcal{I}(t, t) = I(t)$  which yields the final expression:

$$I_{\alpha}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} \left\{ e^{\frac{1}{2i} (\partial_T^G \partial_{\omega}^{\Sigma} - \partial_{\omega}^G \partial_T^{\Sigma})} \left( \tilde{G}^{<} \tilde{\Sigma}^A_{\alpha} + \tilde{G}^R \tilde{\Sigma}^{<}_{\alpha} \right) - e^{\frac{1}{2i} (\partial_T^{\Sigma} \partial_{\omega}^G - \partial_{\omega}^{\Sigma} \partial_T^G)} \left( \tilde{\Sigma}^{<}_{\alpha} \tilde{G}^A + \tilde{\Sigma}^R_{\alpha} \tilde{G}^{<} \right) \right\}.$$
(3.118)

We are now poised to find a perturbative solution to the current in a similar manner to the Green's functions in Section 3.1.6.

### 3.2.1 Adiabatic Case

The adiabatic component of the electric current depends only on the instantaneous geometry of the molecular bridge but disregards its motion. To solve for it, we once again input our ansatzes according to (3.76) and (3.77) while considering the 0<sup>th</sup> order term in the expansion of the exponentials. In doing so, we obtain

$$I_{\alpha}^{(0)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} \left\{ \tilde{G}_{(0)}^{<} \tilde{\Sigma}_{\alpha(0)}^{A} + \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{\alpha(0)}^{<} - \tilde{\Sigma}_{\alpha(0)}^{<} \tilde{G}_{(0)}^{A} - \tilde{\Sigma}_{\alpha(0)}^{R} \tilde{G}_{(0)}^{<} \right\}$$
(3.119)

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \operatorname{ReTr} \left\{ \tilde{G}_{(0)}^{<} \tilde{\Sigma}_{\alpha(0)}^{A} + \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{\alpha(0)}^{<} \right\}.$$
(3.120)

#### 3.2.2 First Order Correction

The first order correction to the current will contain terms linear in  $\partial_T$ . A simple application of the chain rule tells us that each term is then proportional to the velocities of the classical coordinates. Thus, the first order correction accounts for the effects of the slow *but non-zero* nuclear motion on the electronic environment. We once again input our ansatzes and expand the exponentials to the 1<sup>st</sup> order, and retain only the first order terms to find

$$I_{\alpha}^{(1)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} \left\{ \tilde{G}_{(1)}^{<} \tilde{\Sigma}_{\alpha(0)}^{A} + \tilde{G}_{(1)}^{R} \tilde{\Sigma}_{\alpha(0)}^{<} - \tilde{\Sigma}_{\alpha(0)}^{<} \tilde{G}_{(1)}^{A} - \tilde{\Sigma}_{\alpha(0)}^{R} \tilde{G}_{(1)}^{<} \right\}$$
(3.121)

$$+ \tilde{G}_{(0)}^{<} \tilde{\Sigma}_{\alpha(1)}^{A} + \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{\alpha(1)}^{<} - \tilde{\Sigma}_{\alpha(1)}^{<} \tilde{G}_{(0)}^{A} - \tilde{\Sigma}_{\alpha(1)}^{R} \tilde{G}_{(0)}^{<}$$
(3.122)

$$+\frac{1}{2i}\partial_{T}\tilde{G}^{<}_{(0)}\partial_{\omega}\tilde{\Sigma}^{A}_{\alpha(0)}-\frac{1}{2i}\partial_{\omega}\tilde{G}^{<}_{(0)}\partial_{T}\tilde{\Sigma}^{A}_{\alpha(0)}+\frac{1}{2i}\partial_{T}\tilde{G}^{R}_{(0)}\partial_{\omega}\tilde{\Sigma}^{<}_{\alpha(0)}-\frac{1}{2i}\partial_{\omega}\tilde{G}^{R}_{(0)}\partial_{T}\tilde{\Sigma}^{<}_{\alpha(0)}$$
(3.123)

$$+\frac{1}{2i}\partial_{T}\tilde{\Sigma}^{<}_{\alpha(0)}\partial_{\omega}\tilde{G}^{A}_{(0)}-\frac{1}{2i}\partial_{\omega}\tilde{\Sigma}^{<}_{\alpha(0)}\partial_{T}\tilde{G}^{A}_{(0)}+\frac{1}{2i}\partial_{T}\tilde{\Sigma}^{R}_{\alpha(0)}\partial_{\omega}\tilde{G}^{<}_{(0)}-\frac{1}{2i}\partial_{\omega}\tilde{\Sigma}^{R}_{\alpha(0)}\partial_{T}\tilde{G}^{<}_{(0)}\bigg\}.$$
 (3.124)

The previously discussed conjugate transpose relations then allow us to simplify to

$$I_{\alpha}^{(1)} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \operatorname{ReTr} \left\{ \tilde{G}_{(1)}^{<} \tilde{\Sigma}_{\alpha(0)}^{A} + \tilde{G}_{(1)}^{R} \tilde{\Sigma}_{\alpha(0)}^{<} + \tilde{G}_{(0)}^{<} \tilde{\Sigma}_{\alpha(1)}^{A} + \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{\alpha(1)}^{<} \right\}$$
(3.125)

$$+\frac{1}{2i}\left(\partial_{T}\tilde{G}_{(0)}^{<}\partial_{\omega}\tilde{\Sigma}_{\alpha(0)}^{A}-\partial_{\omega}\tilde{G}_{(0)}^{<}\partial_{T}\tilde{\Sigma}_{\alpha(0)}^{A}+\partial_{T}\tilde{G}_{(0)}^{R}\partial_{\omega}\tilde{\Sigma}_{\alpha(0)}^{<}-\partial_{\omega}\tilde{G}_{(0)}^{R}\partial_{T}\tilde{\Sigma}_{\alpha(0)}^{<}\right)\right\}.$$
(3.126)

We now have these equations for the current in the form of an integral over terms with known expressions. We will generally take the integral numerically.

# 3.3 A Langevin description in terms of Green's functions

So far, we have derived perturbative solutions to the Green's functions which have allowed us to calculate the adiabatic current along with dynamical corrections due to the nuclear motion. However, we do not yet know *how* to calculate the nuclear motion self-consistently due to interactions with the electronic environment. To this end, we follow the ideas of Bode, Kusminskiy, Egger and Von Oppen in Reference [152], in which they derive a Langevin description for the classical motion whereby the Langevin coefficients are calculated via the electronic Green's functions. Our derivation expands on this by allowing for a position dependency in the coupling element between the leads and central region.

#### 3.3.1 Force due to the quantum environment

For generality, we will consider an arbitrary number of classical degrees of freedom describing the nuclear motion. Our vector classical coordinates is then given by

$$\mathbf{x} = \left[\nu_1, \nu_2, \dots, \nu_n\right]^T. \tag{3.127}$$

The force operator for the force acting on the classical coordinates due to the quantum environment is given by

$$\hat{\mathbf{f}} = -\nabla \hat{H},\tag{3.128}$$

where  $\nabla = [\partial_{\nu_1}, \partial_{\nu_2}, ...]^T$  and  $\partial_{\nu_1}$  is the partial derivative with respect to the classical coordinate  $\nu_1$ , and so on. For our purposes, it is simpler to consider each nuclear degree of freedom separately as each will have its own respective Langevin equation to describe its motion. The force on an arbitrary degree of freedom  $\nu$  is given by

$$\hat{f}_{\nu} = -\partial_{\nu}\hat{H}.\tag{3.129}$$

Let's now substitute in our expression for the full Hamiltonian  $\hat{H}$  and retain only the terms which are non-zero under the derivative:

$$\hat{f}_{\nu} = -\partial_{\nu} U(\mathbf{x}) - \partial_{\nu} \hat{H}_{M}(\mathbf{x}) - \partial_{\nu} \hat{H}_{LM}(\mathbf{x}) - \partial_{\nu} \hat{H}_{RM}(\mathbf{x}), \qquad (3.130)$$

This then leads to

$$\hat{f}_{\nu} = -\partial_{\nu}U - \sum_{ij} \partial_{\nu}h_{ij}(\mathbf{x})a_{i}^{\dagger}a_{j} - \sum_{k\alpha i} \left[\Lambda_{k\alpha i}^{\nu}(\mathbf{x})a_{k\alpha}^{\dagger}a_{i} + \Lambda_{ik\alpha}^{\nu}(\mathbf{x})a_{i}^{\dagger}a_{k\alpha}\right], \qquad (3.131)$$

where we have introduced the quantity  $\Lambda_{k\alpha i}^{\nu} = \partial_{\nu} t_{k\alpha i}$ . Expressed in the Heisenberg picture, the force operator becomes

$$\hat{f}_{\nu}(t) = -\partial_{\nu}U - \sum_{ij}\partial_{\nu}h_{ij}(\mathbf{x}[t])a_{i}^{\dagger}(t)a_{j}(t) - \sum_{k\alpha i} \left[\Lambda_{k\alpha i}^{\nu}(\mathbf{x}[t])a_{k\alpha}^{\dagger}(t)a_{i}(t) + \Lambda_{ik\alpha}^{\nu}(\mathbf{x}[t])a_{i}^{\dagger}(t)a_{k\alpha}(t)\right].$$
(3.132)

#### 3.3.2 Partitioning of the force

We now partition the quantum force operator into two separate contributions; a mean component and a component which captures the quantum fluctuations about the mean:

$$\hat{f}_{\nu}(t) = f_{\nu}(t) + \delta \hat{f}_{\nu}(t),$$
 (3.133)

where  $f(t) = \langle \hat{f}(t) \rangle$ . The mean force is also known as the Ehrenfest force and it will be discussed in detail in chapter 7. So far, we have not yet made any assumptions beyond our classical nuclei assumption.

#### 3.3.3 Priming the mean force for a perturbative solution

The mean force is obtained by taking a quantum average of (3.132) which yields

$$f_{\nu}(t) = -\partial_{\nu}U - \sum_{ij} \partial_{\nu}h_{ij}(t) \left\langle a_{i}^{\dagger}a_{j} \right\rangle - \sum_{k\alpha i} \left[ \Lambda_{k\alpha i}^{\nu} \left\langle a_{k\alpha}^{\dagger}a_{i} \right\rangle + \Lambda_{ik\alpha}^{\nu} \left\langle a_{i}^{\dagger}a_{k\alpha} \right\rangle \right]$$
  
$$= -\partial_{\nu}U + i\sum_{ij} \partial_{\nu}h_{ij}(t)G_{ji}^{<}(t,t) + i\sum_{k\alpha i} \left[ \Lambda_{k\alpha i}^{\nu}(t)G_{ik\alpha}^{<}(t,t) + \Lambda_{ik\alpha}^{\nu}(t)G_{k\alpha i}^{<}(t,t) \right], \quad (3.134)$$

where we have introduced our non-equilibrium Green's functions. The approach now is clear, we transform the mean force to the Wigner space where we can implement a perturbative solution. To do so, we introduce an auxilliary two-time function  $\mathcal{F}_{\nu}(t,t')$  that satisfies  $\mathcal{F}_{\nu}(t,t) = f_{\nu}(t)$ . We then have

$$\mathcal{F}_{\nu}(t,t') = -\partial_{\nu}U + i\sum_{ij}\partial_{\nu}h_{ij}(t)G_{ji}^{<}(t,t') + i\sum_{k\alpha i} \left[\Lambda_{k\alpha i}^{\nu}(t')G_{ik\alpha}^{<}(t,t') + \Lambda_{ik\alpha}^{\nu}(t)G_{k\alpha i}^{<}(t,t')\right].$$
(3.135)

The choices of t and t' here are not arbitrary, this becomes important upon introducing the leads self-energies. The system-leads coupling component introduces Green's functions which span the space of central region and leads. As performed similarly when deriving the current,

we can decompose these troublesome Green's functions via (2.131) to find

$$\begin{aligned} \mathcal{F}_{\nu}(t,t') &= -\partial_{\nu} U + i \sum_{ij} \partial_{\nu} h_{ij}(t) G_{ji}^{<}(t,t') \\ &+ i \sum_{k\alpha ij} \int_{-\infty}^{\infty} dt_1 \Big[ \Lambda_{k\alpha i}^{\nu}(t') G_{ij}^{<}(t,t_1) t_{jk\alpha}(t_1) G_{k\alpha}^{A}(t_1,t') + \Lambda_{k\alpha i}^{\nu}(t') G_{ij}^{R}(t,t_1) t_{jk\alpha}(t_1) G_{k\alpha}^{<}(t_1,t') \\ &+ \Lambda_{ik\alpha}^{\nu}(t) G_{k\alpha}^{<}(t,t_1) t_{k\alpha j}(t_1) G_{ji}^{A}(t_1,t') + \Lambda_{ik\alpha}^{\nu}(t) G_{k\alpha}^{R}(t,t_1) t_{k\alpha j}(t_1) G_{ji}^{<}(t_1,t') \Big]. \end{aligned}$$
(3.136)

Cyclical permutation of the matrix elements is allowed here so that we can encompass the influence of the leads in self-energy terms, yielding

$$\mathcal{F}_{\nu}(t,t') = -\partial_{\nu}U + i\sum_{ij}\partial_{\nu}h_{ij}(t)G_{ji}^{<}(t,t') + i\sum_{ij}\int_{-\infty}^{\infty}dt_{1}\Big[G_{ij}^{<}(t,t_{1})\Phi_{\nu,ji}^{A}(t_{1},t') + G_{ij}^{R}(t,t_{1})\Phi_{\nu,ji}^{<}(t_{1},t') + \Psi_{\nu,ij}^{R}(t,t_{1})G_{ji}^{<}(t_{1},t') + \Psi_{\nu,ij}^{R}(t,t_{1})G_{ji}^{<}(t_{1},t')\Big].$$
(3.137)

Here we have introduced the self-energy like terms,  $\Psi$  and  $\Phi$ , such that

$$\Psi_{\nu,ij}^{A/R/<}(t,t') = \sum_{k\alpha} \Lambda_{ik\alpha}^{\nu}(t) G_{k\alpha k\alpha}^{A/R/<}(t,t') t_{k\alpha j}(t'), \qquad (3.138)$$

$$\Phi_{\nu,ij}^{A/R/<}(t,t') = \sum_{k\alpha} t_{ik\alpha}(t) G_{k\alpha k\alpha}^{A/R/<}(t,t') \Lambda_{k\alpha j}(t').$$
(3.139)

This then explains our insistence on considering the expansion to the generalised self-energy as in (3.28). Indeed, we will also have to consider a perturbative expansion to  $\Psi$  and  $\Phi$ . Let's first simplify the sum over matrix elements to a trace over matrices:

$$\mathcal{F}_{\nu}(t,t') = \operatorname{Tr}\left\{i\partial_{\nu}h(t)G^{<}(t,t') + i\int_{-\infty}^{\infty} dt_{1}\left[G^{<}(t,t_{1})\Phi_{\nu}^{A}(t_{1},t') + G^{R}(t,t_{1})\Phi_{\nu}^{<}(t_{1},t') + \Psi_{\nu}^{<}(t,t_{1})G^{<}(t_{1},t') + \Psi_{\nu}^{R}(t,t_{1})G^{<}(t_{1},t')\right]\right\}.$$
 (3.140)

We are now in a position to apply the Wigner transform to both sides, where we find

$$\int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \mathcal{F}_{\nu}(t,t') = Tr \Big\{ i e^{\frac{1}{2i} d_T^h \partial_{\omega}^G} \partial_{\nu} h \tilde{G}^{<} + i e^{\frac{1}{2i} (\partial_T^{\Psi} \partial_{\omega}^G - \partial_{\omega}^{\Psi} \partial_T^G)} \left( \tilde{\Psi}_{\nu}^{<} \tilde{G}^A + \tilde{\Psi}_{\nu}^R \tilde{G}^{<} \right) \\ + i e^{\frac{1}{2i} (\partial_T^G \partial_{\omega}^\Phi - \partial_{\omega}^G \partial_T^\Phi)} \left( \tilde{G}^{<} \tilde{\Phi}_{\nu}^A + \tilde{G}^R \tilde{\Phi}_{\nu}^{<} \right) \Big\}. \quad (3.141)$$

In solving for the first term on the right side, we have applied a method equivalent as in solving for (3.70) while we have again applied (3.4) for the remaining terms. Finally, we apply the inverse Wigner transform and let t = t' to find our final equation:

$$f_{\nu}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega Tr \Big\{ i e^{\frac{1}{2i} d_T^h \partial_{\omega}^G} \partial_{\nu} h \tilde{G}^{<} + i e^{\frac{1}{2i} (\partial_T^\Psi \partial_{\omega}^G - \partial_{\omega}^\Psi \partial_T^G)} \left( \tilde{\Psi}_{\nu}^{<} \tilde{G}^A + \tilde{\Psi}_{\nu}^R \tilde{G}^{<} \right) \\ + i e^{\frac{1}{2i} (\partial_T^G \partial_{\omega}^\Phi - \partial_{\omega}^G \partial_T^\Phi)} \left( \tilde{G}^{<} \tilde{\Phi}_{\nu}^A + \tilde{G}^R \tilde{\Phi}_{\nu}^{<} \right) \Big\}.$$
(3.142)

#### 3.3.4 Perturbative solution to the mean force

We apply our usual approach for the calculation of a perturbative solution. We consider our previous ansatz for the Green's functions as in (3.76) while we must now also apply equivalent ansatzes for  $\Psi$  and  $\Phi$  such that

$$\tilde{\Psi} = \tilde{\Psi}_{(0)} + \tilde{\Psi}_{(1)} + ...,$$
 (3.143)

$$\tilde{\Phi} = \tilde{\Phi}_{(0)} + \tilde{\Phi}_{(1)} + \dots \tag{3.144}$$

We will once again truncate our expansions after the first order, such that we solve for an adiabatic contribution to the force as well as a first order correction due to the nuclear motion.

#### 3.3.4.1 Adiabatic force

Retaining only the 0<sup>th</sup> order terms in the exponential expansions as well as our ansatzes yields the adiabatic force which depends only on the instantaneous nuclear geometry. It is given by

$$f_{(0),\nu} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} \left\{ i \partial_{\nu} h \tilde{G}_{(0)}^{<} \right\} - \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Im} \operatorname{Tr} \left\{ \tilde{\Psi}_{\nu,(0)}^{<} \tilde{G}_{(0)}^{A} + \tilde{\Psi}_{\nu,(0)}^{R} \tilde{G}_{(0)}^{<} \right\},$$
(3.145)

where  $\Psi_{(0)}$  and  $\Phi_{(0)}$  can be solved for via (3.28). We use ImTr to denote taking the imaginary part of the trace. The adiabatic force can be thought of as a renormalisation to the classical potential due to the presence of the electronic environment.

#### 3.3.4.2 First order force

The first order force is obtained by substituting in our ansatzes and retaining only the first order terms. Some simplification leads to

$$f_{(1),\nu} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} \left\{ i \partial_{\nu} h \tilde{G}_{(1)}^{<} \right\} - \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Im} \operatorname{Tr} \left\{ \tilde{\Psi}_{\nu(0)}^{R} \tilde{G}_{(1)}^{<} + \tilde{\Psi}_{\nu(1)}^{<} \tilde{G}_{(0)}^{A} + \tilde{\Psi}_{\nu(1)}^{R} \tilde{G}_{(0)}^{<} + \tilde{\Psi}_{\nu(0)}^{<} \tilde{G}_{(1)}^{A} \right\} \\ + \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Re} \operatorname{Tr} \left\{ \partial_{T} \tilde{\Psi}_{\nu(0)}^{<} \partial_{\omega} \tilde{G}_{(0)}^{A} + \partial_{T} \tilde{\Psi}_{\nu(0)}^{R} \partial_{\omega} \tilde{G}_{(0)}^{<} - \partial_{\omega} \tilde{\Psi}_{\nu(0)}^{<} \partial_{T} \tilde{G}_{(0)}^{A} - \partial_{\omega} \tilde{\Psi}_{\nu(0)}^{R} \partial_{T} \tilde{G}_{(0)}^{<} \right\}.$$

$$(3.146)$$

#### 3.3.5 Viscosity coefficient tensor

Through some manipulation, we find that this first order force is the very frictional force which we desire for our Langevin description! This is observed by utilising the chain rule for the time derivatives in both the above expression and the expressions for the first order Green's function corrections in (3.86) and (3.89) where we see that

$$\frac{\partial}{\partial T} = v_{\nu_1} \frac{\partial}{\partial \nu_1} + v_{\nu_2} \frac{\partial}{\partial \nu_2} + \dots v_{\nu_n} \frac{\partial}{\partial \nu_n}.$$
(3.147)

Here,  $v_{\nu_1}$  is the velocity of the  $\nu_1$  classical coordinate and so on. It then becomes clear that the total mean force acting on an arbitrary classical coordinate  $\nu$  can be decomposed into a sum of forces due to the motion in each individual classical coordinate, according to

$$f_{(1),\nu} = f_{(1),\nu\nu_1} + f_{(1),\nu\nu_2} + \dots + f_{(1),\nu\nu_n}.$$
(3.148)

Here,  $f_{(1),\nu\nu_1}$  denotes the force acting in the  $\nu$  direction due to motion in the  $\nu_1$  direction. We then define elements of the viscosity coefficient tensor according to

$$\xi_{\nu\nu'} = -\frac{f_{(1),\nu\nu'}}{v_{\nu'}}.$$
(3.149)

We can then express the vector of first order forces acting on each classical coordinate according to

$$\begin{bmatrix} f_{(1),\nu_{1}} \\ f_{(1),\nu_{2}} \\ \vdots \\ f_{(1),\nu_{n}} \end{bmatrix} = -\begin{bmatrix} \tilde{\xi}_{\nu_{1}\nu_{1}} & \tilde{\xi}_{\nu_{2}\nu_{2}} & \dots & \tilde{\xi}_{\nu_{1}\nu_{n}} \\ \tilde{\xi}_{\nu_{2}\nu_{1}} & \tilde{\xi}_{\nu_{2}\nu_{2}} & \dots & \tilde{\xi}_{\nu_{2}\nu_{n}} \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{\xi}_{\nu_{n}\nu_{1}} & \tilde{\xi}_{\nu_{n}\nu_{2}} & \dots & \tilde{\xi}_{\nu_{n}\nu_{n}} \end{bmatrix} \begin{bmatrix} v_{\nu_{1}} \\ v_{\nu_{2}} \\ \vdots \\ v_{\nu_{n}} \end{bmatrix}, \qquad (3.150)$$

$$\mathbf{f}_{(1)} = -\hat{\xi}\mathbf{v}. \qquad (3.151)$$

We use the hat on  $\hat{\xi}$  to denote that it is a tensor in the space of classical coordinates.

#### 3.3.5.1 Symmetric and antisymmetric components

The diagonal components of  $\hat{\zeta}$  act as a conventional viscosity, directly opposing the motion of the given classical coordinate. However, the off-diagonal components introduce non-trivial forces which are not so well behaved. In order to analyse this further, the viscosity coefficient tensor can be split into symmetric and antisymmetric components as

$$\hat{\xi} = \frac{1}{2} \left( \hat{\xi} + \hat{\xi}^T + \hat{\xi} - \hat{\xi}^T \right)$$
 (3.152)

$$=\hat{\xi}_s+\hat{\xi}_a,\tag{3.153}$$

where

$$\hat{\xi}_s = rac{1}{2} \left( \hat{\xi} + \hat{\xi}^T 
ight), \qquad \hat{\xi}_a = rac{1}{2} \left( \hat{\xi} - \hat{\xi}^T 
ight).$$
(3.154)

We observe that the antisymmetric component produces a force which always acts orthogonal to the motion through the space of classical coordinates and is often referred to as a "Lorentz-like" force due to this. This property can be observed by considering the dot product of the antisymmetric force and the velocity vector:

$$\mathbf{f}_{(1),a} \cdot \mathbf{v} = (-\hat{\xi}_a \mathbf{v}) \cdot \mathbf{v} \tag{3.155}$$

$$= \mathbf{v} \cdot (\hat{\xi}_a \mathbf{v}) \tag{3.156}$$

$$= -\mathbf{v} \cdot \mathbf{f}_{(1),a},\tag{3.157}$$

$$\therefore \mathbf{f}_{(1),a} \cdot \mathbf{v} = -\mathbf{f}_{(1),a} \cdot \mathbf{v} \tag{3.158}$$

$$= 0,$$
 (3.159)

where we have used  $\hat{\xi}_a^T = -\hat{\xi}_a$ . Clearly then, the antisymmetric component does no work on the system but can produce interesting dynamics.

#### 3.3.6 Stochastic force

We recall that we chose to partition our force according to

$$\hat{f}_{\nu}(t) = f_{\nu}(t) + \delta \hat{f}_{\nu}(t).$$
 (3.160)

Our perturbative treatment of the mean force was completed in the previous section. We now must consider the quantum fluctuations about the mean. We know from its definition that the mean of  $\delta \hat{f}(t)$  must be zero. In our work, we also assume *a priori* that the stochastic force is a Gaussian process; a result which emerges naturally in the classical limit [162]. Thus, the stochastic force is entirely quantified according to

$$\langle \delta \hat{f}_{\nu}(t) \rangle = 0, \qquad \langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \rangle = D_{\nu\nu'}(t,t'), \qquad (3.161)$$

where we have introduced the exact diffusion coefficient *D*. The expressions on the left hand side of the above are also known as the first and second moments, respectively. The assumption of Gaussianity implies that  $\delta \hat{f}(t)$  is entirely defined by these two moments while any

higher moments go to zero. The above autocorrelation function in general corresponds to coloured noise in the stochastic force.

#### 3.3.6.1 White-noise assumption for the diffusion

Coloured noise is notoriously difficult to simulate computationally, especially in the case of an inhomogeneous environment such as ours. To alleviate this difficulty, the white-noise assumption is often applied. Here, we assume that the exact, coloured-noise diffusion can be replaced by a Markovian, white-noise equivalent:

$$D(t,t') \equiv D^{w}(T)\delta(t-t'), \qquad (3.162)$$

where we have introduced the white-noise diffusion  $D^w$ . The question remains, how do we calculate  $D^w$  to best approximate the dynamics produced by D(t, t')? In an attempt to answer this, we consider a pedagogical example in which we neglect all forces except the stochastic force. The governing equation of motion is then given by

$$m\frac{dv}{dt} = \delta f(t). \tag{3.163}$$

This is solved for the velocity at time t according to

$$v(t) = v(0) + \frac{1}{m} \int_0^t dt' \delta f(t').$$
(3.164)

The change in kinetic energy of the classical coordinate is then found by squaring the above and taking an average over the fluctuations such that we obtain

$$\Delta KE = \frac{1}{2m} \int_0^t dt' \int_0^t dt'' D(t', t'').$$
(3.165)

Now, we implement the white noise approximation according to (3.162) and solve for an equation for  $D^w$  which yields the same change in kinetic energy as produced when using the exact diffusion. Making the transformation from (t', t'') to  $(T, \tau)$  yields

$$\Delta KE = \frac{1}{2m} \int_0^t dT \int_{-t}^t d\tau D^w(T) \delta(\tau)$$
(3.166)

$$= \frac{1}{2m} \int_0^t dT D^w(T).$$
 (3.167)

By enforcing that (3.167) and (3.165) are equal, we find

$$\int_{0}^{t} dT D^{w}(T) = \int_{0}^{t} dT \int_{-t}^{t} d\tau D(T,\tau).$$
(3.168)

Application of  $\frac{d}{dt}$  to both sides and using the symmetry property,  $D(T, \tau) = D(T, -\tau)$  (this property is a consequence of  $\delta f$  being a classical force and is explained in more detail in section 7.3.3), then yields

$$D^{w}(t) = \int_{-t}^{t} d\tau D(t,\tau) + 2 \int_{0}^{t} dT D(T,t).$$
(3.169)

Finally, we assume that time *t* is sufficiently large such that D(T,t) is approximately zero. This amounts to assuming that the correlations in the stochastic force decay to zero over time intervals of *t* or longer. The second term disappears, while we can safely extend the integration region of the first term from  $-\infty \rightarrow \infty$ , leaving us with our final expression for the white-noise diffusion coefficient:

$$D^{w}(t) = \int_{-\infty}^{\infty} d\tau D(t,\tau).$$
(3.170)

Clearly, the white noise approximation in this case will produce the same observable change in kinetic energy over any time-scale. However, the inclusion of a frictional force and an external potential will limit the validity of the approximation to finite time-scales dependent on their respective strengths. This is because these forces may produce an appreciable effect on the dynamics over the time-scales for which the stochastic force is correlated. We will analyse the validity of the white-noise approximation in detail in chapter 7. Our task is now to calculate  $D^w$  in terms of the Green's functions, as given by

$$D^{w}(T) = \int_{-\infty}^{\infty} d\tau \langle \delta \hat{f}(t) \delta \hat{f}(t') \rangle.$$
(3.171)

We will not encounter the exact diffusion coefficient again until chapter 7. Until that point, when referring to the diffusion coefficient we will be talking about the *white-noise diffusion coefficient* which we will denote simply as *D* for brevity.

#### 3.3.6.2 Calculating the white-noise diffusion

We now calculate the diffusion coefficient tensor with which we will have all the required ingredients to simulate the classical dynamics according to a Langevin equation. We need to start by finding an expression for the autocorrelation function. Let's take (3.160) and square it for arbitrary times and classical degrees of freedom:

$$\langle \hat{f}_{\nu}(t)\hat{f}_{\nu'}(t')\rangle = \langle f_{\nu}(t)f_{\nu'}(t')\rangle + \langle \delta\hat{f}_{\nu}(t)\delta\hat{f}_{\nu'}(t')\rangle + f_{\nu}(t)\langle\delta\hat{f}_{\nu'}(t')\rangle + \langle\delta\hat{f}_{\nu}(t)\rangle f_{\nu'}(t')$$
(3.172)

$$= f_{\nu}(t)f_{\nu'}(t') + \langle \delta \hat{f}_{\nu}(t)\delta \hat{f}_{\nu'}(t') \rangle.$$
(3.173)

The autocorrelation function is then given by

$$\langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \rangle = \langle \hat{f}_{\nu}(t) \hat{f}_{\nu'}(t') \rangle - f_{\nu}(t) f_{\nu'}(t').$$
(3.174)

We already have expressions for  $\hat{f}_{\nu}(t)$  and  $f_{\nu}(t)$  given in (3.132) and (3.134), respectively.

The first term on the right hand side of (3.174) will result in quantum averages of creation and annihilation operators of the form

$$\langle a_A^{\dagger} a_B a_C^{\dagger} a_D \rangle = \langle a_A^{\dagger} a_B \rangle \langle a_C^{\dagger} a_D \rangle + \langle a_A^{\dagger} a_D \rangle \langle a_B a_C^{\dagger} \rangle, \qquad (3.175)$$

where the right hand side is obtained via a Wick decomposition. In a serendipitous twist of fate, the terms involving no permutation of the operators will cancel exactly with the terms produced by  $f_{\nu}(t)f_{\nu'}(t')$  and so we only need to consider the terms involving a permutation. As a result, (3.174) takes the form

$$\begin{split} \langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu}(t') \rangle &= \sum_{ij\bar{i}\bar{j}} \partial_{\nu} h_{ij} \partial_{\nu'} h_{\bar{i}\bar{j}} \langle d_{i}^{\dagger} d_{\bar{j}} \rangle \langle d_{j} d_{\bar{i}}^{\dagger} \rangle \\ &+ \sum_{ik\alpha\bar{i}\bar{k}\alpha} \left( \Lambda_{k\alpha i}^{\nu} \Lambda_{\bar{k}\alpha\bar{i}}^{\nu'} \langle d_{k\alpha}^{\dagger} d_{\bar{i}} \rangle \langle d_{i} d_{\bar{k}\alpha}^{\dagger} \rangle + \Lambda_{ik\alpha}^{\nu} \Lambda_{\bar{i}\bar{k}\alpha}^{\nu'} \langle d_{i}^{\dagger} d_{\bar{k}\alpha} \rangle \langle d_{k\alpha} d_{\bar{i}}^{\dagger} \rangle \\ &+ \Lambda_{k\alpha i}^{\nu} \Lambda_{\bar{i}\bar{k}\alpha}^{\nu'} \langle d_{k\alpha}^{\dagger} d_{\bar{k}\alpha} \rangle \langle d_{i} d_{\bar{i}}^{\dagger} \rangle + \Lambda_{ik\alpha}^{\nu} \Lambda_{\bar{k}\alpha\bar{i}}^{\nu'} \langle d_{i}^{\dagger} d_{\bar{i}} \rangle \langle d_{k\alpha} d_{\bar{k}\alpha}^{\dagger} \rangle \right) \\ &+ \sum_{ij\bar{i}\bar{k}\alpha} \left( \partial_{\nu} h_{ij} \Lambda_{\bar{k}\alpha\bar{i}}^{\nu'} \langle d_{i}^{\dagger} d_{\bar{i}} \rangle \langle d_{j} d_{\bar{k}\alpha}^{\dagger} \rangle + \partial_{\nu} h_{ij} \Lambda_{\bar{i}\bar{k}\alpha}^{\nu'} \langle d_{i}^{\dagger} d_{\bar{i}\alpha} \rangle \langle d_{j} d_{\bar{i}}^{\dagger} \rangle \right) \\ &+ \sum_{ij\bar{i}k\alpha} \left( \Lambda_{k\alpha i}^{\nu} \partial_{\nu'} h_{\bar{i}\bar{j}} \langle d_{k\alpha}^{\dagger} d_{\bar{j}} \rangle \langle d_{i} d_{\bar{i}}^{\dagger} \rangle + \Lambda_{ik\alpha}^{\nu} \partial_{\nu'} h_{\bar{i}\bar{j}} \langle d_{i}^{\dagger} d_{\bar{j}} \rangle \langle d_{k\alpha} d_{\bar{i}}^{\dagger} \rangle \right). \tag{3.176}$$

In an attempt to somewhat simplify the notation, an index here also encompasses a time; an index without an overbar denotes time t while an index with an overbar denotes time t' so that we need not show the time dependence explicitly. Note that i and  $\overline{i}$  do not necessarily index the same state, they are entirely different indices. Appropriate letters are hard to come by! We can now substitute in our Green's functions to obtain

$$\begin{split} \langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \rangle &= \sum_{ij\bar{i}\bar{j}} \partial_{\nu} h_{ij} \partial_{\nu'} h_{\bar{i}\bar{j}} G_{\bar{j}\bar{i}}^{\leq} G_{\bar{j}\bar{i}}^{\geq} \\ &+ \sum_{ik\alpha\bar{i}k\bar{\alpha}} \left( \Lambda_{k\alpha i}^{\nu} \Lambda_{\bar{k}\bar{\alpha}\bar{i}}^{\nu'} G_{\bar{i}k\alpha}^{\leq} G_{i\bar{k}\bar{\alpha}}^{\geq} + \Lambda_{ik\alpha}^{\nu} \Lambda_{\bar{i}\bar{k}\bar{\alpha}}^{\nu'} G_{\bar{k}\bar{\alpha}\bar{i}}^{\leq} G_{\bar{k}\bar{\alpha}\bar{i}}^{\geq} \\ &+ \Lambda_{k\alpha i}^{\nu} \Lambda_{\bar{i}\bar{k}\bar{\alpha}}^{\nu'} G_{\bar{k}\bar{\alpha}\bar{k}\alpha}^{\leq} G_{\bar{i}\bar{i}}^{\geq} + \Lambda_{ik\alpha}^{\nu} \Lambda_{\bar{k}\bar{\alpha}\bar{i}}^{\nu'} G_{\bar{i}\bar{i}}^{\leq} G_{\bar{k}\bar{\alpha}\bar{i}}^{\geq} \right) \\ &+ \sum_{ij\bar{i}\bar{k}\bar{\alpha}} \left( \partial_{\nu} h_{ij} \Lambda_{\bar{k}\bar{\alpha}\bar{i}}^{\nu'} G_{\bar{j}\bar{k}\bar{\alpha}}^{\leq} G_{\bar{j}\bar{k}\bar{\alpha}}^{\geq} + \partial_{\nu} h_{ij} \Lambda_{\bar{i}\bar{k}\bar{\alpha}}^{\nu'} G_{\bar{k}\bar{\alpha}\bar{i}}^{\leq} G_{\bar{j}\bar{i}}^{\geq} \right) \\ &+ \sum_{ij\bar{i}\bar{k}\bar{\alpha}} \left( \Lambda_{k\alpha i}^{\nu} \partial_{\nu'} h_{\bar{i}\bar{j}} G_{\bar{j}\bar{k}\alpha}^{\leq} G_{\bar{i}\bar{i}}^{\geq} + \Lambda_{ik\alpha}^{\nu} \partial_{\nu'} h_{\bar{i}\bar{j}} G_{\bar{j}\bar{i}}^{\leq} G_{\bar{k}\bar{\alpha}\bar{i}}^{\geq} \right). \end{split}$$
(3.177)

Once again, we have Green's functions spanning the system space and the leads. Also note

that we have Green's functions  $G_{k\alpha k\bar{\alpha}}$  which will contain terms which span over *both* leads. These can all be decomposed according to the Dyson equation in (2.131). Doing so is arduous and requires significant attention to detail. However, after doing this and subsequently introducing our self-energy terms, we find

$$\begin{split} \langle \delta \hat{f}_{\nu}'(t) \delta \hat{f}_{\nu'}'(t') \rangle &= \mathrm{Tr} \Big\{ \partial_{\nu} h(t) G^{>}(t,t') \partial_{\nu'} h(t') G^{<}(t',t) \\ &+ \int_{-\infty}^{\infty} dt_{1} dt_{2} \Big( G^{>}(t,t_{2}) \Phi_{\nu'}^{\lambda}(t_{2},t') G^{<}(t',t_{1}) \Phi_{\nu}^{\lambda}(t_{1},t) \\ &+ G^{R}(t,t_{2}) \Phi_{\nu'}^{\lambda}(t_{2},t') G^{<}(t',t_{1}) \Phi_{\nu}^{\lambda}(t_{1},t) \\ &+ G^{>}(t,t_{2}) \Phi_{\nu'}^{\lambda}(t_{2},t') G^{R}(t',t_{1}) \Phi_{\nu'}^{<}(t_{1},t) + G^{R}(t,t_{2}) \Phi_{\nu'}^{>}(t_{2},t') G^{R}(t',t_{1}) \Phi_{\nu'}^{<}(t_{1},t) \\ &+ \Psi_{\nu}^{>}(t,t_{2}) G^{A}(t_{2},t') \Psi_{\nu'}^{<}(t',t_{1}) G^{A}(t_{1},t) + \Psi_{\nu}^{R}(t,t_{2}) G^{>}(t_{2},t') \Psi_{\nu'}^{<}(t',t_{1}) G^{A}(t_{1},t) \\ &+ \Psi_{\nu}^{>}(t,t_{2}) G^{A}(t_{2},t') \Psi_{\nu'}^{R}(t',t_{1}) G^{<}(t_{1},t) + \Psi_{\nu}^{R}(t,t_{2}) G^{>}(t_{2},t') \Psi_{\nu'}^{<}(t',t_{1}) G^{A}(t_{1},t) \\ &+ \Psi_{\nu}^{>}(t,t_{2}) G^{A}(t_{2},t') \Psi_{\nu'}^{<}(t',t_{1}) G^{<}(t_{1},t) + \Psi_{\nu}^{N}(t,t_{2}) G^{>}(t_{2},t') \Psi_{\nu'}^{A}(t',t_{1}) G^{<}(t_{1},t) \\ &+ \Psi_{\nu}^{>}(t,t_{2}) G^{A}(t_{2},t') \Psi_{\nu'}^{>}(t',t_{1}) G^{<}(t_{1},t) + \Psi_{\nu}^{R}(t,t_{1}) G^{A}(t_{1},t_{2}) \Phi_{\nu'}^{A}(t_{2},t') G^{<}(t',t) \\ &+ G^{>}(t,t') \xi_{\nu'\nu}^{<}(t',t) + \xi_{\nu\nu'}^{>}(t,t') G^{<}(t',t) \\ &+ G^{>}(t,t') \Psi_{\nu'}^{R}(t',t_{1}) G^{A}(t_{1},t_{2}) \Phi_{\nu}^{A}(t_{2},t) + \Psi_{\nu}^{R}(t,t_{1}) G^{>}(t_{1},t_{2}) \Phi_{\nu'}^{A}(t_{2},t') G^{<}(t',t) \\ &+ G^{>}(t,t') \Psi_{\nu'}^{<}(t',t_{1}) G^{R}(t_{1},t_{2}) \Phi_{\nu}^{<}(t_{2},t) + \Psi_{\nu}^{R}(t,t_{1}) G^{R}(t_{1},t_{2}) \Phi_{\nu'}^{>}(t_{2},t') G^{<}(t',t) \\ &+ G^{>}(t,t') \Psi_{\nu'}^{<}(t',t_{1}) G^{R}(t_{1},t_{2}) \Phi_{\nu}^{<}(t_{2},t) + \Psi_{\nu}^{R}(t,t_{1}) G^{R}(t_{1},t_{2}) \Phi_{\nu'}^{>}(t_{2},t') G^{<}(t',t) \\ &+ \int_{-\infty}^{\infty} dt_{1} \Big( G^{>}(t,t_{1}) \Phi_{\nu'}^{A}(t_{1},t') G^{<}(t',t) \partial_{\nu}h(t) + G^{R}(t,t_{1}) \Phi_{\nu'}^{>}(t_{1},t') G^{<}(t',t) \partial_{\nu}h(t) \\ &+ G^{>}(t,t') \partial_{\nu'}h(t') G^{<}(t',t_{1}) \Phi_{\nu}^{A}(t_{1},t) + G^{>}(t,t') \partial_{\nu'}h(t') G^{<}(t',t) \\ &+ \Psi_{\nu}^{>}(t,t_{1}) G^{A}(t_{1},t') \partial_{\nu'}h(t') G^{<}(t',t) + \Psi_{\nu}^{R}(t,t_{1}) G^{>}(t_{1},t') \partial_{\nu'}h(t') G^{<}(t',t) \Big) \Big\}. \end{split}$$

In deriving this rather cumbersome expression, we have collapsed the summations over indices into a trace and cyclically permuted terms such that each group starts and ends at time *t*. Additionally, we have introduced another self-energy quantity  $\zeta$ , whose elements are defined as

$$\zeta_{\nu\nu',ij}(t,t') = \sum_{k\alpha} \Lambda^{\nu}_{ik\alpha}(t) G_{k\alpha k\alpha}(t,t') \Lambda^{\nu'}_{k\alpha j}(t').$$
(3.180)

Let's not forget that we wish to find the diffusion coefficient from this equation:

$$D_{\nu\nu'}(T) = \int_{-\infty}^{\infty} d\tau \left\langle \delta f_{\nu}(t) \delta f_{\nu'}(t') \right\rangle.$$
(3.181)

We would like to be able to calculate D via our Green's functions and self-energies in the Wigner space. The right hand side here is very nearly a Wigner transform and can be coerced into a full Wigner transform with some work. However, the method applied depends on which term in (3.179) we consider. There are three different possibilities; terms with no integrals, terms with one integral over time, and terms with two integrals over time. We consider each case separately. Before we begin, we note that we will consider the diffusion coefficient to

be wholly adiabatic. This means that our perturbative expansions will be truncated after the 0<sup>th</sup> order. This is for pragmatic purposes, since the Langevin equation and its surrounding context assumes the diffusion coefficient to be independent of the motion of the Brownian particle. In any case the inclusion of, for example, a velocity dependent term in the diffusion coefficient would presumably have little effect since the velocity would average to zero over any relevant experimental time scales.

#### **Double Integral:**

Let's consider an arbitrary term from (3.179) with two integrals, which we will denote by a subscript *A*. The same derivation will apply to all other terms with two integrals. We have

$$\left\langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \right\rangle_{A} = \int_{-\infty}^{\infty} dt_{1} dt_{2} G^{>}(t, t_{2}) \Phi_{\nu'}^{A}(t_{2}, t') G^{<}(t', t_{1}) \Phi_{\nu}^{A}(t_{1}, t),$$
(3.182)

and

$$D_{A,\nu\nu'} = \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} dt_1 dt_2 G^>(t,t_2) \Phi_{\nu'}^A(t_2,t') G^<(t',t_1) \Phi_{\nu}^A(t_1,t)$$
(3.183)

$$= \int_{-\infty}^{\infty} d\tau A(t,t') B(t',t)$$
(3.184)

$$= \int_{-\infty}^{\infty} d\tau A(T,\tau) B(T,-\tau), \qquad (3.185)$$

where we have simply grouped together consecutive terms and included their respective integrals. Next, we are free to introduce an integral over a Dirac-delta function so that we obtain

$$D_{A,\nu\nu'} = \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} d\tau_1 \delta(\tau + \tau_1) A(T,\tau) B(T,-\tau)$$
(3.186)

$$= \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} d\tau_1 \delta(\tau + \tau_1) A(T, \tau) B(T, \tau_1)$$
(3.187)

$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\int d\tau\int_{-\infty}^{\infty}d\tau_{1}e^{i\omega(\tau+\tau_{1})}A(T,\tau)B(T,\tau_{1})$$
(3.188)

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} A(T,\tau) \int_{-\infty}^{\infty} d\tau_1 e^{i\omega\tau_1} B(T,\tau_1)$$
(3.189)

$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\tilde{A}(T,\omega)\tilde{B}(T,\omega),$$
(3.190)

where we have used the following Dirac-Delta function identity:

$$\delta(x-a) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega(x-a)}$$
Then the Wigner convolution theorem in (3.4) can be applied to calculate  $\tilde{A}$  and  $\tilde{B}$ . For  $\tilde{A}$ , we find

$$\tilde{A}(T,\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \int_{-\infty}^{\infty} dt_2 G^{>}(t,t_2) \Phi_{\nu'}^{A}(t_2,t')$$
(3.191)

$$=e^{\frac{1}{2i}\left\{\partial_{T}^{G}\partial_{\omega}^{\Phi}-\partial_{\omega}^{G}\partial_{T}^{\Phi}\right\}}\tilde{G}^{>}(T,\omega)\tilde{\Phi}_{\nu'}^{A}(T,\omega)$$
(3.192)

$$= \tilde{G}^{>}_{(0)}(T,\omega)\tilde{\Phi}^{A}_{(0),\nu'}(T,\omega), \qquad (3.193)$$

since we only consider the 0<sup>th</sup> order. Similarly applying this logic to  $\tilde{B}$ , we find the contribution to the diffusion coefficient from this entire term to be

$$D_{A,\nu\nu'} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{G}_{(0)}^{>} \tilde{\Phi}_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} \tilde{\Phi}_{(0),\nu}^{A}.$$
(3.194)

Single Integral:

Consider the single integral term

$$\left\langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \right\rangle_{B} = \int_{-\infty}^{\infty} dt_{1} \partial_{\nu} h(t) G^{>}(t,t_{1}) \Phi_{\nu'}^{A}(t_{1},t') G^{<}(t',t).$$
(3.195)

In this case it is convenient for us to cyclically permute the terms under the trace to arrive at

$$\left\langle \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \right\rangle_{B} = \int_{-\infty}^{\infty} dt_{1} G^{>}(t, t_{1}) \Phi_{\nu'}^{A}(t_{1}, t') G^{<}(t', t) \partial_{\nu} h(t).$$
(3.196)

The corresponding diffusion coefficient is given by

$$D_{B,\nu\nu'} = \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} dt_1 G^>(t,t_1) \Phi_{\nu'}^A(t_1,t') G^<(t',t) \partial_\nu h(t)$$
(3.197)

$$= \int_{-\infty}^{\infty} d\tau A(t,t') B(t',t), \qquad (3.198)$$

where the integral over  $t_1$  has been grouped inside of *A*. Performing an equivalent derivation as in the previous case yields

$$D_{B,\nu\nu'} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{A}(T,\omega) \tilde{B}(T,\omega).$$
(3.199)

We can once again find  $\tilde{A}$  by utilising the Wigner convolution theorem:

$$\tilde{A}(T,\omega) = \int_{-\infty}^{\infty} dt_1 \tilde{G}^{>}_{(0)}(T,\omega) \tilde{\Phi}^{A}_{(0),\nu'}(T,\omega).$$
(3.200)

However, given that  $\tilde{B}$  does not contain an integral, we cannot use our Wigner convolution theorem. We instead revert to the derivation performed in (3.68)-(3.70) to find

$$\tilde{B}(T,\omega) = e^{\frac{1}{2i}\partial_{\omega}^{G}d_{T}^{h}}\tilde{G}^{<}(T,\omega)\partial_{\nu}h(T)$$
(3.201)

$$= \tilde{G}_{(0)}^{<}(T,\omega)\partial_{\nu}h(T), \qquad (3.202)$$

Resultantly, we find

$$D_{B,\nu\nu'} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{G}_{(0)}^{>} \tilde{\Phi}_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} \partial_{\nu} h.$$
(3.203)

No Integral:

The only term of this form in our expression for  $\left< \delta \hat{f}_{\nu}(t) \delta \hat{f}_{\nu'}(t') \right>$  is given by

$$\left\langle \delta f_{\nu}(t) \delta f_{\nu}(t') \right\rangle_{C} = \partial_{\nu} h(t) G^{>}(t,t') \partial_{\nu'} h(t') G^{<}(t',t).$$
(3.204)

Once again, we find

$$D_{C,\nu\nu'} = \int_{-\infty}^{\infty} d\tau \partial_{\nu} h(t) G^{>}(t,t') \partial_{\nu'} h(t') G^{<}(t',t)$$
(3.205)

$$= \int_{-\infty}^{\infty} d\tau A(t,t') B(t',t)$$
(3.206)

$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\tilde{A}(T,\omega)\tilde{B}(T,\omega),$$
(3.207)

A and B each contain no integrals and so we again apply the method of (3.68)-(3.70) to eventually find

$$D_{C,\nu\nu'} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \partial_{\nu} h \tilde{G}^{>}_{(0)} \partial_{\nu'} h \tilde{G}^{<}_{(0)}.$$
(3.208)

#### **Full Expression:**

Applying the derivations outlined above to each term individually, we find the following total expression for  $D_{\nu\nu'}$ :

$$\begin{split} D_{\nu\nu'} &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} \left\{ \partial_{\nu} h \tilde{G}_{(0)}^{<} \partial_{\nu'} h \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \Phi_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{A} + \tilde{G}_{(0)}^{R} \Phi_{(0),\nu'}^{>} \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{A} \right. \\ &+ \tilde{G}_{(0)}^{>} \Phi_{(0),\nu'}^{A} \tilde{G}_{(0)}^{R} \Phi_{(0),\nu}^{<} + \tilde{G}_{(0)}^{R} \Phi_{(0),\nu'}^{>} \tilde{G}_{(0)}^{R} \Phi_{(0),\nu}^{<} \\ &+ \tilde{\Psi}_{(0),\nu}^{>} \tilde{G}_{(0)}^{A} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{A} + \tilde{\Psi}_{(0),\nu}^{R} \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{A} \\ &+ \tilde{\Psi}_{(0),\nu}^{>} \tilde{G}_{(0)}^{A} \Psi_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} + \tilde{\Psi}_{(0),\nu}^{R} \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \tilde{\xi}_{(0),\nu'}^{<} \nu + \tilde{\xi}_{(0),\nu\nu'}^{>} \tilde{G}_{(0)}^{<} \\ &+ \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{A} \Phi_{(0),\nu}^{A} + \tilde{\Psi}_{(0),\nu}^{>} \tilde{G}_{(0)}^{A} \Phi_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{A} \\ &+ \tilde{\Psi}_{(0),\nu}^{R} \tilde{G}_{(0)}^{>} \Phi_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} + \tilde{\Phi}_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &+ \tilde{\Psi}_{(0),\nu}^{R} \tilde{G}_{(0)}^{>} \Phi_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} + \tilde{\Psi}_{(0),\nu'}^{R} \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &+ \tilde{\Psi}_{(0),\nu}^{R} \tilde{G}_{(0)}^{>} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{R} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &+ \partial_{\nu} h \left[ \tilde{G}_{(0)}^{>} \Phi_{(0),\nu'}^{A} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{R} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{<} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{<} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &+ \partial_{\nu} h \left[ \tilde{G}_{(0)}^{<} \Phi_{(0),\nu}^{A} \tilde{G}_{(0)}^{>} + \tilde{G}_{(0)}^{R} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{<} \Psi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &+ \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{*} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &+ \tilde{G}_{(0)}^{<} \Phi_{(0),\nu'}^{<} \tilde{G}_{(0)}^{<} \\ &$$

## 3.3.7 Summary

We have derived an equation for the quantum force operator which acts on an arbitrary classical vibrational coordinate v as

$$\hat{f}_{\nu}(t) = f_{(0),\nu}(t) - \sum_{\nu'} \xi_{\nu\nu'} v_{\nu'} + \delta \hat{f}_{\nu}(t), \qquad (3.210)$$

where we have explicit expressions for  $f_{(0)}$  and  $\xi$  while  $\delta \hat{f}$  is quantified according to a diffusion coefficient *D*. The last step is to map this equation onto a classical equation of motion where the forces are no longer quantum mechanical operators, but physical quantities. Our governing equation of motion for the vibrational dynamics is then, finally, given by

$$f_{\nu}(t) = f_{(0),\nu}(t) - \sum_{\nu'} \xi_{\nu\nu'} v_{\nu'} + \delta f_{\nu}(t).$$
(3.211)

Since the stochastic force is now classical, the diffusion coefficient which quantifies it must be real. This is not an issue for the white-noise diffusion as given by (3.209), but the exact diffusion which we encounter in chapter 7 is not strictly real and special care must be taken.

## Motion on the Leads Interface

This chapter contains material that has been previously published in the following journal article:

*Current-induced atomic motion, structural instabilities, and negative temperatures on molecule-electrode interfaces in electronic junctions,* 

R.J. Preston, V.F. Kershaw, D.S. Kosov, Phys. Rev. B, 101, 155415 (2019)

## 4.1 Motivation

With a handful of exceptions [95, 100, 127, 147, 176, 177], theoretical approaches to dynamics in molecular junctions largely focus on nuclear motion localized in the central region; however, the motion at the molecule-electrode interface is at least equally important. Large amplitude conformational changes such as chemical reactions, switching between different geometries, localized heating, and electromigration of atoms predominantly occur on the interface in molecular electronic junctions.

Our goal is to apply our theory to the dynamics of nuclear motion on molecule-electrode interfaces. In doing so, we observe the emergence of negative viscosity coefficients in the interface region which leads to eventual device breakdown. Additionally, we observe the natural formation of bi-stable nuclear potentials which leads to stochastic switching behaviour in the measured electric current, also known as telegraph noise. The telegraph noise is quantified according to the Fano factor. In bi-stable regimes, we observe strongly super-Poissonian noise where the Fano factor reaches values larger than 300. The Fano factor can be used in experimental systems to probe the otherwise difficult to observe nuclear dynamics.

This chapter is organized as follows: Section 4.2 describes the model and relevant theory, the results of calculations are presented in Section 4.3, and the chapter is summarized in Section 4.4.

## 4.2 Theory

#### 4.2.1 System Hamiltonian and relevant equations of motion

#### 4.2.1.1 System Hamiltonian

We will consider a commonly realised experimental geometry in which the valence state of the molecular bridge which allows for electron transport is near to one lead; in our case the left lead. The single classical degree of freedom present in the model will represent the displacement of the valence state from the left lead whereby a classical dependence will emerge in our Hamiltonian through the coupling to the left lead. Additionally, a classical dependence is present in the energy of the valence state itself due to the electric fields produced by the leads. Our general tunnelling junction Hamiltonian as discussed in Section 2.1 is given by

$$H(t) = H_M + H_L + H_R + H_{ML} + H_{MR} + H_{cl}.$$
(4.1)

The molecular bridge is modelled by a single molecular orbital with energy  $\epsilon(x)$  as

$$H_M = \epsilon(x)a^{\dagger}a, \tag{4.2}$$

where *x* is the classical time-dependent coordinate. This *x*-dependence of the molecular orbital comes from the voltage drop across the junction

$$\epsilon(x) = \epsilon_0 + \mathcal{E}(x - x_0) + V_0, \tag{4.3}$$

where

$$\mathcal{E} = (\mu_L - \mu_R) / (L_L - L_R),$$
 (4.4)

is the electric field across the junction and

$$V_0 = \mu_L - L_L(\mu_L - \mu_R) / (L_L - L_R).$$
(4.5)

is the *x*-independent energy level shift. Here we use  $L_L$  and  $L_R$  to denote the positions of the left and right leads, while  $\mu_L$  and  $\mu_R$  are the left and right lead chemical potentials. The equilibrium bond-length is denoted by  $x_0$ . The applied voltage bias V will be applied symmetrically such that  $\mu_L = V/2$  and  $\mu_R = -V/2$  in all our calculations.

The tunnelling interaction is

$$H_{LM}(t) + H_{RM}(t) = \sum_{k\alpha i} t_{k\alpha i}(t) a_{k\alpha}^{\dagger} a_i + h.c.$$
(4.6)

where the tunneling amplitudes  $t_{k\alpha i}(t)$  are time-dependent tunneling amplitudes. We assume that the coupling to the right electrode is rigid and the coupling to the left depends on the bond-length:

$$t_{k\alpha}(x) = \begin{cases} t_L s(x), \text{ if } \alpha = L \\ t_R, \text{ if } \alpha = R \end{cases}$$
(4.7)

where the function s(x) is taken in the form of the overlap between two 1s orbitals separated by distance *x* as given by

$$s(x) = e^{-x}(1 + x + x^2/3),$$
 (4.8)

and  $t_L$  and  $t_R$  are two constants. This choice of coordinate dependence mimics the behavior of a generic isotropic chemical bond [169].

The left and right leads of the molecular junction are macroscopic reservoirs of non-interacting electrons

$$H_L + H_R = \sum_{k\alpha} \epsilon_{k\alpha} a^{\dagger}_{k\alpha} a_{k\alpha}, \qquad (4.9)$$

where  $a_{k\alpha}^{\dagger}$  creates an electron in the single-particle state *k* of the  $\alpha = L/R$  (left/right) lead with energy  $\epsilon_{k\alpha}$ , and  $a_{k\alpha}$  is the corresponding electron annihilation operator.

Finally, the classical Hamiltonian  $H_{cl}$  is

$$H_{cl}(t) = \frac{p^2}{2m} + U(x), \tag{4.10}$$

where *p* is the classical momentum, *m* is the mass associated with the classical degree of freedom, and U(x) is the potential. The classical potential U(x) is taken to be harmonic

$$U(x) = \frac{1}{2}k(x - x_0)^2,$$
(4.11)

where  $x_0$  is the equilibrium bond-length and k is the spring constant associated with the bond strength.

#### 4.2.1.2 Simplifications to the Green's functions and self-energies

The consideration of only a single electronic level in the central region allows us to greatly simplify the form of the main dynamical quantities since the Green's functions and self-energies become scalars in this case. The simplifications are generally straight forward and so we will merely present the simplified form here rather than showing each step explicitly. The adiabatic self-energy components in the Wigner space are given by

$$\tilde{\Sigma}^{A}_{(0),\alpha}(T) = \frac{i}{2}\Gamma_{\alpha}(T), \qquad \tilde{\Sigma}^{R}_{(0),\alpha}(T) = -\frac{i}{2}\Gamma_{\alpha}(T), \qquad \tilde{\Sigma}^{<}_{(0),\alpha}(\omega,T) = if_{\alpha}(\omega)\Gamma_{\alpha}(T).$$
(4.12)

Meanwhile, the adiabatic self-energy-like terms,  $\tilde{\Psi}_{(0)}$ ,  $\tilde{\Phi}_{(0)}$  and  $\tilde{\zeta}_{(0)}$ , can be found by noting that  $\partial_x t_{kL}(x) = t_L \partial_x s(x)$  as per our definition for the tunnelling amplitude. Then we can say that

$$\partial_x t_{kL}(x) = \frac{\partial_x s(x)}{s(x)} t_{kL}(x).$$
(4.13)

This allows us to express the self-energy-like terms in terms of the self-energies according to

$$\tilde{\Psi}_{(0),\alpha} = \tilde{\Phi}_{(0),\alpha} = \frac{\partial_x s(x)}{s(x)} \tilde{\Sigma}_{(0),\alpha}, \qquad \tilde{\zeta}_{(0),\alpha} = \left(\frac{\partial_x s(x)}{s(x)}\right)^2 \tilde{\Sigma}_{(0),\alpha}, \tag{4.14}$$

when  $\alpha = L$ , while each term goes to zero when  $\alpha = R$ . Evaluating (3.28) for the appropriate choices of *A* and *B* readily allow us to obtain the first order corrections to the self-energy terms due to the motion of the classical coordinate. These are given by

$$\widetilde{\Sigma}_{(1),\alpha} = 0, \qquad \widetilde{\Psi}_{(1),\alpha} = -\widetilde{\Phi}_{(1),\alpha} = \frac{\dot{x}}{2i} \Big( \partial_{x\omega}^2 \widetilde{\Psi}_{(0),\alpha} - 2\partial_{\omega} \widetilde{\zeta}_{(0),\alpha} \Big).$$
(4.15)

The adiabatic Green's functions take the familiar form

$$\tilde{G}_{(0)}^{A/R} = \left(\omega - h - \tilde{\Sigma}_{(0)}^{A/R}\right)^{-1}, \qquad \tilde{G}_{(0)}^{} = \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{(0)}^{} \tilde{G}_{(0)}^{A}, \tag{4.16}$$

where the inverse here is now just a multiplicative inverse. The first order corrections to the Green's functions can be simplified to

$$\tilde{G}_{(1)}^{A/R} = 0, \qquad \tilde{G}_{(1)}^{<} = -i\tilde{G}_{(0)}^{R}\operatorname{Re}\left\{\tilde{G}_{(0)}^{<}\mathcal{B}^{A} + \tilde{G}_{(0)}^{R}\partial_{T}\tilde{\Sigma}_{(0)}^{<} + \mathcal{B}^{R}\tilde{G}_{(0)}^{R}\partial_{\omega}\tilde{\Sigma}_{(0)}^{<}\right\}\tilde{G}_{(0)}^{A}.$$
(4.17)

#### 4.2.1.3 Simplifications to the Langevin Coefficients

The Langevin coefficients which dictate the dynamics of the classical coordinate can also be simplified in the case of a single electronic level. The adiabatic force is given by

$$f_{(0)}(t) = \frac{i\mathcal{E}}{2\pi} \int d\omega \tilde{G}_{(0)}^{<} - \frac{1}{\pi} \int d\omega \operatorname{Im} \left\{ \tilde{\Psi}_{(0)}^{<} \tilde{G}_{(0)}^{A} + \tilde{\Psi}_{(0)}^{R} \tilde{G}_{(0)}^{<} \right\},$$
(4.18)

while the first order force which yields the viscosity coefficient is

$$f_{(1)}(t) = \frac{i\mathcal{E}}{2\pi} \int d\omega \tilde{G}_{(1)}^{<} - \frac{1}{\pi} \int d\omega \operatorname{Im} \left\{ \tilde{\Psi}_{(0)}^{R} \tilde{G}_{(1)}^{<} + \tilde{\Psi}_{(1)}^{<} \tilde{G}_{(0)}^{A} \right\} + \frac{1}{2\pi} \int d\omega \operatorname{Re} \left\{ \partial_{T} \tilde{\Psi}_{(0)}^{<} \partial_{\omega} \tilde{G}_{(0)}^{A} - \partial_{\omega} \tilde{\Psi}_{(0)}^{<} \partial_{T} \tilde{G}_{(0)}^{A} \right\}.$$
(4.19)

Finally, the diffusion coefficient is

$$D(t) = \frac{1}{2\pi} \int d\omega \Big( \mathcal{E}^2 \tilde{G}^{<}_{(0)} \tilde{G}^{<}_{(0)} + \tilde{G}^{>}_{(0)} \tilde{\zeta}^{<}_{(0)} + \tilde{\zeta}^{>}_{(0)} \tilde{G}^{<}_{(0)} \\ + 2 \operatorname{Re} \Big\{ \mathcal{E} \left( \tilde{G}^{<}_{(0)} \tilde{\Psi}^{>}_{(0)} \tilde{G}^A_{(0)} + \tilde{G}^{>}_{(0)} \tilde{\Psi}^{<}_{(0)} \tilde{G}^A_{(0)} + 2 \tilde{G}^{>}_{(0)} \tilde{\Psi}^R_{(0)} \tilde{G}^{<}_{(0)} \right) + \tilde{\Psi}^{>}_{(0)} \tilde{G}^A_{(0)} \tilde{\Psi}^{<}_{(0)} \tilde{G}^A_{(0)} \Big\} \Big).$$
(4.20)

#### 4.2.1.4 Simplifications to the electric current

The adiabatic electric current through the junction is given by

$$I_{\alpha}^{(0)}(t) = \frac{1}{\pi} \int d\omega \operatorname{Re} \Big\{ \tilde{G}_{(0)}^{<} \tilde{\Sigma}_{(0),\alpha}^{A} + \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{(0),\alpha}^{<} \Big\},$$
(4.21)

while the first order correction simplifies to

$$I_{\alpha}^{(1)}(t) = \frac{1}{\pi} \int d\omega \operatorname{Re}\left\{\tilde{G}_{(1)}^{<}\tilde{\Sigma}_{(0),\alpha}^{A}\right\} + \frac{1}{2\pi} \int d\omega \operatorname{Im}\left\{\partial_{T}\tilde{G}_{(0)}^{R}\partial_{\omega}\tilde{\Sigma}_{(0),\alpha}^{<} - \partial_{\omega}\tilde{G}_{(0)}^{R}\partial_{T}\tilde{\Sigma}_{(0),\alpha}^{<}\right\}.$$
 (4.22)

#### 4.2.2 Fluctuation-dissipation theorem

As we saw in Section 1.4.1, the temperature of the Brownian particle emerges through the balance of the excitations due to the stochastic force and the dissipation of energy due to the viscosity coefficient according to

$$T = \frac{D}{2\xi}.$$
(4.23)

In the absence of a voltage bias over the junction, we expect the temperature of the classical coordinate to equilibrate to the temperature of the leads. The first test for the model is to then take our explicit expressions for D and  $\xi$  in equilibrium and observe if (4.23) is satisfied, where T is the temperature of the leads. To do this, we must first simplify our expressions to be in terms of the base parameters of the model; a tedious but simple process which we don't demonstrate explicitly. For the benefit of generality we show the result in the case of an arbitrary number of classical degrees of freedom, which can be easily simplified to the case of

a single classical degree of freedom. The first order force is given by

$$\begin{split} f_{(1),\nu} &= \frac{1}{4\pi} \sum_{\nu'} v_{\nu'} \int d\omega \left( \left[ \left( Y_L^2 + Y_L Y_R \right) \partial_\omega f_L + \left( Y_R^2 + Y_L Y_R \right) \partial_\omega f_R \right] \partial_{\nu'} h \partial_\nu h \right. \\ &+ \left( Y_L^2 + Y_L Y_R \right) \frac{\partial_{\nu'} \Gamma}{\Gamma} \partial_\nu h \left[ \partial_\omega f_L (\omega - h) - f_L \right] + \left( Y_R^2 + Y_L Y_R \right) \frac{\partial_{\nu'} \Gamma}{\Gamma} \partial_\nu h \left[ \partial_\omega f_R (\omega - h) - f_R \right] \\ &+ \frac{Y^2}{\Gamma} \partial_\nu h \left( \partial_{\nu'} \Gamma_L f_L + \partial_{\nu'} \Gamma_R f_R \right) + Y^2 (\omega - h) \partial_{\nu'} h \left( \partial_\omega f_L \frac{\partial_\nu \Gamma_L}{\Gamma} + \partial_\omega f_R \frac{\partial_\nu \Gamma_R}{\Gamma} \right) \\ &+ \frac{Y^2}{2} \left( \frac{1}{Y} \left[ \partial_\omega f_L \frac{\partial_\nu \Gamma_L \partial_{\nu'} \Gamma_L}{\Gamma_L} + \partial_\omega f_R \frac{\partial_\nu \Gamma_R \partial_{\nu'} \Gamma_R}{\Gamma_R} \right] + \frac{\partial_{\nu'} \Gamma}{\Gamma} \left[ \frac{1}{Y} - \frac{1}{2} \Gamma \right] \left[ \partial_\nu \Gamma_L \partial_\omega f_L + \partial_\nu \Gamma_R \partial_\omega f_R \right] \right) \end{split}$$

$$(4.24)$$

where we have defined the quantity

$$Y_{\alpha} = \frac{\Gamma_{\alpha}}{(\omega - h)^2 + \frac{\Gamma^2}{4}}.$$
(4.25)

An element of the viscosity tensor can then be found according to

$$\xi_{\nu\nu'} = -\frac{f_{(1),\nu\nu'}}{v_{\nu'}},\tag{4.26}$$

such that we have

$$\begin{aligned} \xi_{\nu\nu'} &= -\frac{1}{4\pi} \int d\omega \left( \left[ \left( Y_L^2 + Y_L Y_R \right) \partial_\omega f_L + \left( Y_R^2 + Y_L Y_R \right) \partial_\omega f_R \right] \partial_{\nu'} h \partial_\nu h \right. \\ &+ \left( Y_L^2 + Y_L Y_R \right) \frac{\partial_{\nu'} \Gamma}{\Gamma} \partial_\nu h \left[ \partial_\omega f_L (\omega - h) - f_L \right] + \left( Y_R^2 + Y_L Y_R \right) \frac{\partial_{\nu'} \Gamma}{\Gamma} \partial_\nu h \left[ \partial_\omega f_R (\omega - h) - f_R \right] \\ &+ \frac{Y^2}{\Gamma} \partial_\nu h \left( \partial_{\nu'} \Gamma_L f_L + \partial_{\nu'} \Gamma_R f_R \right) + Y^2 (\omega - h) \partial_{\nu'} h \left( \partial_\omega f_L \frac{\partial_\nu \Gamma_L}{\Gamma} + \partial_\omega f_R \frac{\partial_\nu \Gamma_R}{\Gamma} \right) \\ &+ \frac{Y^2}{2} \left( \frac{1}{Y} \left[ \partial_\omega f_L \frac{\partial_\nu \Gamma_L \partial_{\nu'} \Gamma_L}{\Gamma_L} + \partial_\omega f_R \frac{\partial_\nu \Gamma_R \partial_{\nu'} \Gamma_R}{\Gamma_R} \right] + \frac{\partial_{\nu'} \Gamma}{\Gamma} \left[ \frac{1}{Y} - \frac{1}{2} \Gamma \right] \left[ \partial_\nu \Gamma_L \partial_\omega f_L + \partial_\nu \Gamma_R \partial_\omega f_R \right] \right) \end{aligned}$$

$$(4.27)$$

Let's now consider the equilibrium case, such that we let  $f_L = f_R = f_{eq}$ . It then takes the form

$$\xi_{\nu\nu'}^{eq} = -\frac{1}{4\pi} \int d\omega Y^2 \partial_\omega f_{eq} \left( \partial_{\nu'} h \partial_\nu h + (\omega - h) \frac{\partial_{\nu'} \Gamma}{\Gamma} \partial_\nu h + (\omega - h) \partial_{\nu'} h \frac{\partial_\nu \Gamma}{\Gamma} \right. \\ \left. + \frac{1}{2Y} \left[ \frac{\partial_\nu \Gamma_L \partial_{\nu'} \Gamma_L}{\Gamma_L} + \frac{\partial_\nu \Gamma_R \partial_{\nu'} \Gamma_R}{\Gamma_R} + \frac{\partial_{\nu'} \Gamma \partial_\nu \Gamma}{\Gamma} \right] - \frac{1}{4} \partial_{\nu'} \Gamma \partial_\nu \Gamma \right).$$

$$(4.28)$$

An element of the non-equilibrium diffusion coefficient is given by

$$D_{\nu\nu'} = \frac{1}{2\pi} \int d\omega \left( \partial_{\nu} h \partial_{\nu'} h \left[ (1 - f_L) \left( f_L Y_L^2 + f_R Y_L Y_R \right) + (1 - f_R) \left( f_R Y_R^2 + f_L Y_L Y_R \right) \right] \right. \\ \left. + \left( \omega - h \right) \frac{Y^2}{\Gamma^2} \left( f_L \Gamma_L + f_R \Gamma_R \right) \times \left. \left( \partial_{\nu} h \left[ \partial_{\nu'} \Gamma_L (1 - f_L) + \partial_{\nu'} \Gamma_R (1 - f_R) \right] + \partial_{\nu'} h \left[ \partial_{\nu} \Gamma_L (1 - f_L) + \partial_{\nu} \Gamma_R (1 - f_R) \right] \right] \right. \\ \left. - \frac{1}{4} Y^2 \left[ \partial_{\nu'} \Gamma_L (1 - f_L) + \partial_{\nu'} \Gamma_R (1 - f_R) \right] \left[ \partial_{\nu} \Gamma_L f_L + \partial_{\nu} \Gamma_R f_R \right] \right. \\ \left. + \frac{Y^2}{2} \frac{1}{Y\Gamma} \left( 2 \partial_{\nu'} \Gamma_L \partial_{\nu} \Gamma_L f_L (1 - f_L) + 2 \partial_{\nu'} \Gamma_R \partial_{\nu} \Gamma_R f_R (1 - f_R) \right. \\ \left. + \left[ f_R (1 - f_L) \Gamma_R \partial_{\nu'} \Gamma_L + f_L (1 - f_R) \Gamma_L \partial_{\nu'} \Gamma_R \right] \left( \frac{\partial_{\nu} \Gamma_L}{\Gamma_L} + \frac{\partial_{\nu} \Gamma_R}{\Gamma_R} \right) \right).$$

$$(4.29)$$

In equilibrium, this then simplifies to

$$D_{\nu\nu'}^{eq} = \frac{1}{2\pi} \int d\omega Y^2 f_{eq} (1 - f_{eq}) \left( \partial_\nu h \partial_{\nu'} h + (\omega - h) \partial_\nu h \frac{\partial_{\nu'} \Gamma}{\Gamma} + (\omega - h) \partial_{\nu'} h \frac{\partial_\nu \Gamma}{\Gamma} \right)$$
(4.30)

$$+\frac{1}{2Y}\left[\frac{\partial_{\nu'}\Gamma\partial_{\nu}\Gamma}{\Gamma}+\frac{\partial_{\nu}\Gamma_{L}\partial_{\nu'}\Gamma_{L}}{\Gamma_{L}}+\frac{\partial_{\nu}\Gamma_{R}\partial_{\nu'}\Gamma_{R}}{\Gamma_{R}}\right]-\frac{1}{4}\partial_{\nu'}\Gamma\partial_{\nu}\Gamma\right).$$
(4.31)

The derivative of the Fermi-Dirac distributions for the leads can be calculated according to

$$\partial_{\omega} f_{\alpha} = -\frac{1}{T_{\alpha}} f_{\alpha} (1 - f_{\alpha}), \qquad (4.32)$$

where  $T_{\alpha}$  is the temperature of the  $\alpha$  lead. We will take  $T_L = T_R = T_{eq}$  such that the system is in thermal equilibrium. Upon applying the above identity in (4.28), we find that

$$\frac{D_{\nu\nu'}^{eq}}{2\xi_{\nu\nu'}^{eq}} = T_{eq}.$$
(4.33)

Thus, we have shown that in chemical and thermal equilibrium our classical coordinate will equilibrate to the temperature of the leads, as would be expected from a physical standpoint. This also applies for any arbitrary element of the diffusion and viscosity tensors.

#### 4.2.2.1 Anti-symmetric viscosity components in equilibrium

Recall from Section 3.3.5 that an arbitrary element of the anti-symmetric component of the viscosity coefficient can be defined according to

$$\xi_{a,\nu\nu'} = \frac{1}{2} \left( \xi_{\nu\nu'} - \xi_{\nu'\nu} \right). \tag{4.34}$$

By using (4.27) we can show that an arbitrary anti-symmetric element is then given by

$$\frac{1}{2} \left( \xi_{\nu\nu'} - \xi_{\nu'\nu} \right) = \frac{1}{8\pi} \int d\omega \left( \left[ (f_L - f_R) - (\omega - h) \partial_\omega \left( f_L - f_R \right) \right] \times \left( \frac{\left( Y_R^2 + Y_L Y_R \right)}{\Gamma} \left[ \partial_{\nu'} \Gamma_L \partial_\nu h - \partial_\nu \Gamma_L \partial_{\nu'} h \right] - \frac{\left( Y_L^2 + Y_L Y_R \right)}{\Gamma} \left[ \partial_{\nu'} \Gamma_R \partial_\nu h - \partial_\nu \Gamma_R \partial_{\nu'} h \right] \right) \\
+ \partial_\omega \left( f_L - f_R \right) \frac{1}{\Gamma} \left[ \frac{1}{Y} - \frac{1}{2} \Gamma \right] \left[ \partial_{\nu'} \Gamma_R \partial_\nu \Gamma_L - \partial_{\nu'} \Gamma_L \partial_\nu \Gamma_R \right] \right).$$
(4.35)

Let's once again consider the equilibrium case in which we let  $f_L = f_R = f_{eq}$ . It is immediately clear that each term will go to zero and thus, we observe that

$$\hat{\zeta}_a^{eq} = \mathbf{0},\tag{4.36}$$

where **0** is the corresponding matrix of zeroes. Despite this, it has been shown theoretically that the anti-symmetric viscosity can be non-zero in equilibrium if the Hamiltonian is complex such as when the spin-orbit coupling is explicitly accounted for [178], or when a time-dependent driving is present in the leads [179].

#### 4.2.2.2 Positivity of the viscosity coefficient

The diagonal elements of the viscosity tensor are given by (4.27) when  $\nu = \nu'$ . These elements correspond to a frictional force which directly opposes the motion of the  $\nu$  degree of freedom. For pedagogical purposes, let's for now assume that  $\Gamma_{\alpha}$  is a scalar constant such that only the first line of (4.27) survives; we will denote this by  $\xi_{\nu\nu}^h$  since now only *h* depends on the classical coordinate. This can be simplified to the form

$$\xi_{\nu\nu}^{h} = \frac{\Gamma(\partial_{\nu}h)^{2}}{4\pi} \int d\omega \frac{\frac{f_{L}}{T_{L}}(1-f_{L})\Gamma_{L} + \frac{f_{R}}{T_{R}}(1-f_{R})\Gamma_{R}}{\left[(\omega-h)^{2} + \Gamma^{2}/4\right]^{2}}.$$
(4.37)

This quantity is purely positive since  $\Gamma$  must be positive according to its definition. So we see that in the single-level case where only the molecular Hamiltonian is dependent on the classical coordinate, the force due to the viscosity coefficient must be purely dissipative. Allowing  $\Gamma$  to have a classical dependence (motion on the leads interface) then has an important effect; it allows for the viscosity coefficient to become negative in which there are no longer any forces acting to dissipate energy away from the classical vibrations.

## 4.3 Results

#### 4.3.1 Motion on the leads interface

Each of our calculations utilize a common set of unchanging parameters: the bandwidth for numerical integration is set to [-5, 5]; left and right lead temperatures are set to be equal  $(T_L = T_R = 300K)$ ; the reduced mass associated with the chemical bond is m = 1000; the molecule is always strongly coupled to the left lead with  $\Gamma_L = 4$  and  $\Gamma_R = 0.03$ ; and the equilibrium bond-length is  $x_0 = 5$ . All numerical values in the text and figures are given in atomic units.

We note that in a similar approach to previous work [180], we employ a finite bandwidth in numerical calculations to avoid the logarithmic divergence of the adiabatic force (4.18).

#### 4.3.1.1 Electronic friction, diffusion coefficient, and local effective temperature

We first study how the parameters of the model control the three main ingredients of the Langevin equation: the diffusion coefficient, viscosity, and adiabatic force. Figure 4.1a shows the diffusion coefficient D(x) as a function of the bond-length. The amplitude of the random force is the square root of the diffusion coefficient. As seen in Figure 4.1a, the diffusion coefficient has a strong dependence on the bond-length, reaching its maximum at the equilibrium bond-length and then decaying to zero as the bond stretches or contracts. As physically expected, the amplitude of the random force increases as the voltage becomes larger.

The viscosity  $\xi(x)$  is shown in Figure 4.1b. At small voltages the viscosity behavior mirrors the diffusion coefficient's dependence on the bond-length. This is not surprising if one recalls the fluctuation-dissipation theorem which relates the ratio of the diffusion coefficient D(x) and viscosity  $\xi(x)$  to the temperature, and temperature should not deviate significantly from the equilibrium value for small voltages. If the voltage is increased, we start to observe regions of negative viscosity which energize the stretching/contraction of the bond rather than dampening its oscillations as one may expect from the viscous force.

Figure 4.1c shows viscosity as a function of bond-length computed at V = 0.06 of applied voltage. Once the level moves away from the resonance position  $\epsilon_0 = 0$ , the second peak in the viscosity starts to shift closer to the equilibrium bond-length. The second peak occurs when the energy of the level intersects the Fermi level of the right lead, such that electrons are easily able to transition between the lead and the resonance level, while the left lead is essentially disconnected due to the exponential coupling decay.



Figure 4.1: (a) Diffusion coefficient D(x) and (b) viscosity  $\xi(x)$  as functions of nuclear position computed for different values of the applied voltage and with resonant energy level set to zero  $\epsilon_0 = 0$ ; (c) viscosity  $\xi(x)$  as a function of bond-length computed for different resonant-level energies  $\epsilon_0$  at voltage V = 0.06.

In analogy to the fluctuation-dissipation theorem [181], it is instructive to define an effective temperature as

$$T_{\rm eff}(x) = \frac{D(x)}{2\xi(x)}.$$
 (4.38)

Figure 4.2 shows that there is a good agreement between the effective local temperature defined using (4.38) and the local kinetic energy computed directly from simulations of the Langevin equation. Therefore, the effective temperature (4.38) is an intuitively clear physical quantity which reveals information on the steady-state spatial distribution of kinetic energy within the junction and is related to current-induced localized heating or cooling effects.

It is clear from Figure 4.3a that in the equilibrium case (zero applied voltage), the fluctuationdissipation theorem is satisfied as  $T_{\text{eff}}$  is independent of x and equals to 300 K, exactly the temperature of left and right leads. Once the voltage is increased, the current carrying electrons produce significant local heating in the junction leading to the rise of the effective temperature. The coordinate dependence of effective temperature has a small dip at equilibrium bond-length and then reaches its maximum value if the bond is stretched.

In Figure 4.3d, we observe a region of parameters in our junction in which the effective temperature becomes negative, such that the nucleus has no defined steady-state local kinetic energy in this region and as such, the kinetic energy of the nucleus will continue to increase if constrained to this region.

Next, we compute the effective potential as a function of bond-length. By combining the classical potential and integrating our adiabatic force  $f_{(0)}(x)$  computed by (4.18), we obtain the effective potential [182]

$$U_{\rm eff}(x) = U(x) - \int_a^x dx' f_{(0)}(x'). \tag{4.39}$$

Notice that the lower limit in this integral *a* is completely arbitrary and serves as a reference



Figure 4.2: Effective temperature  $T_{\text{eff}}(x)$  computed via (4.38), and computationally measured temperature computed from the local kinetic energy as a function of the bond-length, calculated in the resonance regime. The applied voltage is V = 0.02 and the spring constant is k = 2.

point for the computed potential energy. We use a = 0 in all our calculations. We observe in 4.4a and 4.4b the possibility of different potential regimes in which we may observe two separate stable minima.

These regimes are summarized according to the changing bond spring constant and coupling in Figure 4.4. There is a narrow region of bistability. Once we move away from this region, one minimum starts to dominate until the other minimum disappears completely. As the voltage is increased, the bistable yellow region becomes wider and shifts towards smaller values of the spring constant.

#### 4.3.2 Current noise

In this section, we show results for the current computed along a given trajectory of the bondlength time-evolution obtained from the solution of the Langevin equation. To compute a trajectory x(t), we utilize an m-BAOAB algorithm provided by Sachs et al [183], which enables a numerical solution of the Langevin equation with a coordinate dependent viscosity and diffusion coefficient. The trajectory is used to compute Green's functions, and current with first order dynamical corrections using the equations presented in Section 4.2. We consider three representative scenarios with very distinct nuclear dynamics: rigid chemical bonding (k = 0.136), intermediate chemical bonding (k = 0.131), and soft chemical bonding (k = 0.127). In the case of a rigid chemical bond, the bond-length oscillates around a single minima; this is



Figure 4.3: (a) Effective temperature  $T_{\text{eff}}(x)$  as a function of bond-length computed in the resonance regime  $\epsilon_0 = 0$  at various values of the applied voltage. (b) Effective temperature  $T_{\text{eff}}(x)$  as a function of bond-length computed at applied voltage V = 0.02 for different values of the resonant-level energies. Contour plots of effective temperature  $T_{\text{eff}}(x)$  as a function of voltage and bond-length for (c) low voltages and (d) high voltages; the white region represents negative effective temperatures.



Figure 4.4: Effective potential for (a) varying spring constants (V = 0), and (b) for varying bias voltages (k = 0.12).



Figure 4.5: (a) Different effective potential regimes for varying k and  $\Gamma_L$ , computed at V = 0 and color coded according to (b), (c), (d). Dashed lines show the boundaries of the bistable yellow region for V = 0.2.

reflected in the time dependence of current shown in Figure 4.6a, 4.6b. Both the electric current with dynamical corrections  $I_L(t) = I_L^{(0)}(t) + I_L^{(1)}(t)$  and the first order correction  $I_L^{(1)}(t)$  itself oscillate around single average values. Once the chemical bond becomes softer (k = 0.131), the length of the chemical bond switches between two states, spending roughly equal time in each. This behavior of the bond-length results into telegraphic switching of the current between two values as shown in Figure 4.6c, 4.6d. The first order dynamical correction is more noticeable in the more conducting state. For a soft molecule-lead chemical bond, k = 0.127, the bond-length experiences switching but has a preference for a specific value, as does the current.

#### 4.3.2.1 Quantifying the current noise

The temporal correlations between stochastic fluctuations of the electric current (current noise) have become a very important experimental and theoretical tool in studying transport properties of molecular junctions. Noise spectroscopy enables the study of the special features of a single-molecule junction, which are not accessible by standard current-voltage measurements. The experimental noise measurements provide significantly new information on fundamental mechanisms of electron transport in molecular junctions, such as atomistic details of the local environment and metal-molecule interfaces[71, 184], coupling between electronic and vibrational degrees of freedom[60, 88, 185, 186], identifications of the individual conduction transport channel[61, 187–189], and mechanical stability of the junction[66].

Current noise is formally defined as

$$S_{\alpha}(\tau) = \lim_{T \to +\infty} \frac{1}{T} \int_{0}^{T} dt \langle \left[ \delta \hat{I}_{\alpha}(t), \delta \hat{I}_{\alpha}(t+\tau) \right]_{+} \rangle, \qquad (4.40)$$

where  $\delta \hat{I}(t)$  describes the instantaneous deviation of the electric current at time *t* from its average value and  $[...,..]_+$  is the anti-commutator. Eq.(4.40) involves two averages:  $\langle ... \rangle$  is the quantum expectation value over electronic degrees of freedom and  $\lim_{T \to +\infty} \frac{1}{T} \int_0^T dt...$  is the time average over the classical motion of the nuclei. The time average is equivalent to the ensemble average over many realizations of geometries of the molecular junction. The current noise power spectrum is the Fourier transformation of (4.40)

$$S_{\alpha}(\omega) = \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} S_{\alpha}(\tau).$$
(4.41)

The electric current noise provides valuable information about the system and originates from multiple factors: (a) the quantum nature of electrons, discreteness of charge, Pauli exclusion principle, shot noise, and the finite temperature of electrons; (b) various types of quantum correlations between current-carrying electrons, which are not present in our model; (c) and finally, the "mechanical" noise due to current-induced changes to the molecular junction ge-



Figure 4.6: Current with dynamical corrections  $I_L(t) = I_L^{(0)}(t) + I_L^{(1)}(t)$  and first order correction  $I_L^{(1)}(t)$  to the current as functions of time computed at V = 0.01 for different values of the spring constant (a,b) k = 0.136 (c,d) k = 0.131 (e,f) k = 0.127. The red dashed line denotes the current mean over the displayed time interval.

ometry. Generally the total noise is not simply the addition of (a), (b), and (c) contributions; there is a cross interference between different contributions. However, within our approach the distinctly different time-scales of fast electronic and slow nuclear motion enables the separation of the mechanical noise contribution [190]. The characteristic time scale of shot noise decay is  $1/\Gamma$ , whereas the noise due to nuclear motion appears on much longer times. Hence the noise induced by geometrical fluctuations dominates the noise power spectrum at low frequencies, and can exceed the shot noise contribution by orders of magnitude [190].

In what follows we focus on the "mechanical" noise as

$$S_{\alpha}(\tau) = 2 \lim_{T \to +\infty} \frac{1}{T} \int_0^T dt \delta I_{\alpha}(t) \delta I_{\alpha}(t+\tau), \qquad (4.42)$$

where the current fluctuation at time t is

$$\delta I_{\alpha}(t) = I_{\alpha}(t) - \lim_{T \to +\infty} \frac{1}{T} \int_{0}^{T} dt I_{\alpha}(t).$$
(4.43)

The Fano factor is

$$F_{\alpha} = \frac{S_{\alpha}(\omega=0)}{2I_{\alpha}}.$$
(4.44)

The variance and mean of a Poisson process is equal, therefore the Fano factor can be used to characterize electron transport as either a sub-Poissonian (F < 1), Poissonian (F = 1), or super-Poissonian (F > 1) process. Indeed, super-Poissonian or sub-Poissonian noise is caused by a host of very interesting and often hidden physical effects.

Figures 4.7a and 4.7b show Fano factors computed as a functions of the applied voltage V and spring constant k. The presence of telegraphic switching between two minima in a bi-stable adiabatic potential results in the gigantic enhancement of the Fano factor, indicating that the electron transport is a super-Poissonian process. The behavior of the Fano factor depends on a number of factors relating to the microscopic details of the Langevin dynamics in a locally heated adiabatic potential.

This behavior of the Fano factor can be rationalized based on the following observations. The only negative contributions to the integral over time in the current noise (4.42) are on the boundaries when the current crosses the mean. For the bi-stable case, this generally occurs only when the current switches between stable states. It is an intuitive notion to then conclude that larger switch rates will have an effect on decreasing the Fano factor (however having no switches at all will minimize it).

The size of the positive contribution to the current noise is dependent on two factors: firstly, the size of the fluctuations around the mean which correspond to the difference in current values between two configurations; and secondly, the ratio of time spent in each minimum.



Figure 4.7: (a) Fano factors as functions of the spring constant k. (b) Fano factors as functions of voltage V. Here k = 0.13 yields two minima with approximately equal depth, while k = 0.125 yields a deeper left minimum. (c) Average switch rate between minima in a bi-stable regime, varying k. (d) Average waiting times in a bi-stable regime for V = 0.05. The vertical dashed line denotes the k value for which the two minima have equal depth. All calculations are performed for  $\epsilon_0 = 0$ .



Figure 4.8: Fano factor computed as a function of the spring constant; V = 0.05 and  $\epsilon_0 = 0$ . The background of the figure is color-coded in accordance to the different regimes of effective potential shown in Figure 4.5 (b,c,d).

An increase to the applied voltage results in a larger fluctuation around the mean and as such, one would expect this to have an effect on increasing the Fano factor. However, this effect is counteracted by an increase to the mean current, which stays in the denominator of the Fano factor (4.44). Additionally, the noise should be maximized when the mean current is directly in between our two current states; this occurs when the nucleus spends approximately equal time in each minimum. Therefore, the two key parameters to control the Fano factor are the average switch rate (a single switch being a transition from one minimum to the other) shown in Figure 4.7c, as well as the average waiting time (the average amount of time spent waiting in a minima before switching out) shown in Figure 4.7d. To maximize the Fano factor, one wants to keep the switch rate between conformations as small as possible but at the same the waiting times in both conformations should be comparable. For example, let us consider the case of V = 0.05. As the voltage increases, the difference in effective temperatures between the left and right minima increases as well, such that the left is substantially hotter, which will decrease the time spent waiting in the left minimum. In addition, the large applied voltage will physically deform the adiabatic potential in a manner akin to Figure 4.4b, decreasing the depth of the left minimum relative to the right. These factors each act to decrease the left minimum waiting time relative to the right (see Figure 4.7d). To compensate for this, the Fano factor peaks shifts towards smaller values of k, which act to deepen the left minimum, thus having the opposing effect of increasing the left minimum waiting time.

In Figure 4.8, we observe the Fano factor as the adiabatic potential transitions over the three possible regimes in our system as the spring constant k is altered. The Fano factor demonstrates a strong dependency on instabilities within the system, undergoing a large peak as the bi-stable regime is entered, before decreasing back to sub-Poissonian values in the monostable regimes. The peak is shifted towards lower k values for the reasons outlined regarding Figure 4.7c. The peak decreases slowly into the blue mono-stable regime because the stable minimum is very close to the left lead, which yields a small mean current in this region. As such our Fano factor according to (4.44) is still large despite the adiabatic potential only being mono-stable.

### 4.4 Summary

In this section, we studied current-induced atomic motion on molecule-electrode interfaces in molecular electronic junctions. Structural changes on the interfaces are described in terms of a Langevin equation, which is obtained from the quantum mechanical first principles in which we extract the slow nuclear dynamics from Wigner space Green's functions. The calculations of Green's functions and consequently all molecular junction observables include dynamical velocity-dependent corrections to include non-adiabatic effects of nuclear motion into the

calculation of electronic properties. We illustrate the theory by computing the transport properties of a model molecular junction: a single position-dependent resonant energy level which is coupled to the leads via a flexible (changing in time due to current flow) bond-length. The Langevin equation for the bond-length is integrated numerically and then the Green's functions, electric current, and current noise are computed along the stochastic trajectory. We observe that even if the initial classical potential is harmonic, the effective potential may develop bi-stability depending upon the parameters of the model. We mapped the shapes of the effective potential in the parameter space of the model. The different regimes for bistability depend critically on the interplay between the softness of the linking electrode-molecule bond and the coupling to the corresponding electrode.

We introduce the concept of an effective local temperature using fluctuation-dissipation theorem ideas, which provides a useful insight on localized current-induced heating in molecular electronic junctions. We observe a region of parameters in our junction where the effective temperature becomes negative, which means the kinetic energy of nuclei will continue to increase if constrained to this region. The structural instabilities and localized heating on molecule-electrode interfaces are quantified in terms of the current noise and Fano Factor. These demonstrated the influence of the calculated effective temperatures and adiabatic potentials on the nuclear dynamics, in which super-Poissonian Fano factors on the order of  $\approx 400$ were observed.

# Dynamics Under a Time-Dependent AC Driving

This chapter contains material that has been previously published in the following journal article:

Cooling molecular electronic junctions by AC current,

R.J. Preston, T.D. Honeychurch, D.S. Kosov, J. Chem. Phys., 153, 121102 (2020)

## 5.1 Motivation

The lifetime of molecular devices is notoriously small [41, 191, 192]. The record lifetime achieved in a recent breakthrough experiment is still only 2.7 seconds [193], which is obviously much shorter than what is expected for feasible post-silicon technology. The significant operational voltage bias of a few volts required in molecular junctions along with large electric current densities destroy the molecular device's structural integrity through chemical bond rupture, large scale molecular geometry alteration or electromigration of the lead interfacial atoms.

A practical solution to the sensitivity of structural stability in molecular junctions remains elusive. Subsequently, in this chapter we propose a new strategy to decrease the Joule heating in molecular junctions: the application of a sinusoidal voltage over the large DC voltage bias which acts to reduce the effective vibrational temperature of the molecular junction. The inclusion of an AC driving requires additions to our theory, which will be covered in Section 5.2. In Section 5.3 we analyse the results produced by the theory, in which an AC driving is observed to produce selective heating/cooling to the classical degrees of freedom. The chapter is then summarised in Section 5.5.

## 5.2 Theory

#### 5.2.1 System Hamiltonian

We consider a single-electronic state in the central region coupled to the leads which are each under the influence of a sinusoidal time-dependent driving. As usual, we begin with our general tunnelling Hamiltonian:

$$H = H_M + H_{ML} + H_{MR} + H_L + H_R + H_{cl}.$$
(5.1)

The classical dependence of the system emerges solely through the molecular Hamiltonian as given by

$$H_M = h(x)a^{\dagger}a, \tag{5.2}$$

where h(x) is the energy of a single molecular orbital and x is the classical coordinate. The classical coordinate here can be interpreted as the position of the molecular orbital in the junction where x = 0 is equidistant to the left and right leads. We assume in our calculations that the molecular orbital depends linearly on x

$$h(x) = \epsilon_0 + \lambda x, \tag{5.3}$$

where  $\lambda$  is the coupling strength between the electronic and nuclear degrees of freedom. The molecular Hamiltonian in tandem with the classical Hamiltonian as given by

$$H_{cl} = \frac{p^2}{2m} + U(x),$$
(5.4)

provides a complete description of the nuclear geometry. The classical potential is taken in the harmonic oscillator form

$$U(x) = \frac{1}{2}kx^2,$$
 (5.5)

where k is the spring constant associated with the chemical bonding to the leads. Both leads are modelled as macroscopic reservoirs of noninteracting electrons

$$H_L + H_R = \sum_{k\alpha = L,R} \epsilon_{k\alpha}(t) a^{\dagger}_{k\alpha} a_{k\alpha}.$$
(5.6)

The leads energy levels have a sinusoidal dependence on time due to an external AC driving with frequency  $\zeta$  and amplitude  $\Delta_{\alpha}$ 

$$\epsilon_{k\alpha}(t) = \epsilon_{k\alpha} + \Delta_{\alpha} \cos(\zeta t). \tag{5.7}$$

Additionally, the leads are also held at different static chemical potentials  $\mu_{\alpha}$  at all times, the difference between them corresponds to the applied DC voltage bias  $V = \mu_L - \mu_R$ . Both sinusoidal AC and static DC voltages are applied symmetrically in our calculations:  $\Delta_L = -\Delta_R$  and  $\mu_L = -\mu_R$ .

The coupling between the central region and the left and right leads are given by the tunnelling interaction

$$H_{ML} + H_{MR} = \sum_{k\alpha = L,R} (t_{k\alpha} a_{k\alpha}^{\dagger} d + \text{h.c.}), \qquad (5.8)$$

where  $t_{k\alpha}$  is the tunnelling amplitude between the leads single-particle states and the molecular orbital. In contrast to Section 4,  $t_{k\alpha}$  is treated as a constant independent of the nuclear geometry.

#### 5.2.2 System time-scales

Our model exploits two separate small parameters related to the separation of time-scales within the system. These are

$$\frac{\Omega}{\Gamma} \ll 1, \qquad \frac{\zeta}{\Gamma} \ll 1,$$
 (5.9)

where the first is our usual assumption that the nuclear motion is slow relative to electron tunnelling. Similarly, the second relation characterises the slow time-dependent driving of the leads relative to the time-scale associated with electronic tunnelling. Our perturbative expansions are then taken to the first order in *either* of the above small parameters. For example, this means a term proportional to  $\frac{\Omega \zeta}{\Gamma^2}$  would be treated as second order and is thus neglected.

#### 5.2.3 Calculating the time-dependent self-energies

The presence of a time-dependence in the leads necessitates special care upon calculating explicit expressions for the leads self-energies. The leads self-energies follow the standard definition

$$\Sigma_{\alpha,ij}(t,t') = \sum_{k} t_{ik\alpha}(t) G_{0,k\alpha k\alpha}(t,t') t_{k\alpha j}(t'), \qquad (5.10)$$

where we recall that the free-field Green's functions for the leads are given by (2.157)-(2.159). For the benefit of the reader, these are

$$G^{A}_{k\alpha k'\alpha}(t,t') = i\theta(t'-t)e^{-i\int_{t'}^{t}dt_{1}\epsilon_{k\alpha}(t_{1})}\delta_{k\alpha k'\alpha},$$
(5.11)

$$G^{R}_{k\alpha k'\alpha}(t,t') = -i\theta(t-t')e^{-i\int_{t'}^{t}dt_{1}\epsilon_{k\alpha}(t_{1})}\delta_{k\alpha k'\alpha},$$
(5.12)

$$G^{<}_{k\alpha k'\alpha}(t,t') = i e^{-i \int_{t'}^{t} dt_1 \epsilon_{k\alpha}(t_1)} f_{k\alpha} \delta_{k\alpha k'\alpha}.$$
(5.13)

Due to the absence of any classical dependence on the leads interface in this section, we note that  $\tilde{\Sigma} = \tilde{\Sigma}_{(0)}$ . Let's consider the integrals in the above exponentials. By substituting in (5.7) for  $\epsilon_{k\alpha}$ , we obtain

$$\int_{t'}^{t} dt_1 \epsilon_{k\alpha}(t_1) = \epsilon_{k\alpha}(t - t') + \frac{\Delta_{\alpha}}{\zeta} \left[ \sin(\zeta t) - \sin(\zeta t') \right]$$
(5.14)

$$=\epsilon_{k\alpha}(t-t')+\frac{2\Delta_{\alpha}}{\zeta}\cos(\zeta(t+t')/2)\sin(\zeta(t-t')/2),$$
(5.15)

where we have used the fact that  $sin(x) - sin(y) = 2sin(\frac{x-y}{2})cos(\frac{x+y}{2})$ . The free-field Green's functions then become

$$G^{A}_{k\alpha k'\alpha}(\tau,T) = \underbrace{i\theta(-\tau)e^{-i\epsilon_{k\alpha}\tau}\delta_{k\alpha k'\alpha}}_{(\tau,\tau) = 1 \text{ or } i\theta(-\tau)e^{-i\epsilon_{k\alpha}\tau}\delta_{k\alpha k'\alpha}} e^{-i\frac{2\Delta\alpha}{\zeta}\cos(\zeta T)\sin(\zeta \tau/2)}, \quad (5.16)$$

standard GF for time-independent leads  $G^{A}_{k\alpha k'\alpha}(\tau)$ 

$$G^{R}_{k\alpha k'\alpha}(\tau,T) = \underbrace{-i\theta(\tau)e^{-i\epsilon_{k\alpha}\tau}\delta_{k\alpha k'\alpha}}_{G^{R}_{k\alpha k'\alpha}(\tau)} e^{-i\frac{2\Delta\alpha}{\zeta}\cos(\zeta T)\sin(\zeta \tau/2)}$$
(5.17)

$$G_{k\alpha k'\alpha}^{<}(\tau,T) = \underbrace{if_{k\alpha}e^{-i\epsilon_{k\alpha}\tau}\delta_{k\alpha k'\alpha}}_{G_{k\alpha k'\alpha}^{<}}e^{-i\frac{2\Delta\alpha}{\zeta}\cos(\zeta T)\sin(\zeta \tau/2)},$$
(5.18)

where we have made use of the central and relative times

$$T = \frac{1}{2}(t+t'), \qquad \tau = t - t'.$$
(5.19)

Thus, we see that our time-dependent free-field Green's functions for the leads can be expressed by the time-independent Green's functions under the influence of some phase factor determined by the driving. Making use of the Jacobi-Anger expansion as given by

$$e^{iz\cos\theta} = \sum_{n=-\infty}^{\infty} i^n J_n(z) e^{in\theta},$$
(5.20)

where  $J_n$  is a Bessel function of the first kind, we find that

$$e^{-i\frac{2\Delta\alpha}{\zeta}\cos(\zeta T)\sin(\zeta\tau/2)} = e^{i\frac{2\Delta\alpha}{\zeta}\cos(\zeta T)\cos(\zeta\tau/2+\pi/2)} = \sum_{n=-\infty}^{\infty} i^n J_n\left(\frac{2\Delta_\alpha}{\zeta}\cos(\zeta T)\right) e^{in(\zeta\tau/2+\pi/2)}$$
$$= \sum_{n=-\infty}^{\infty} (-1)^n J_n\left(\frac{2\Delta_\alpha\cos(\zeta T)}{\zeta}\right) e^{\frac{i}{2}n\zeta\tau}.$$
(5.21)

Finally, all components of the leads GFs are written as

$$G_{k\alpha k'\alpha}(\tau,T) = G_{k\alpha k'\alpha}(\tau) \sum_{n=-\infty}^{\infty} (-1)^n J_n\left(\frac{2\Delta_{\alpha}\cos(\zeta T)}{\zeta}\right) e^{\frac{i}{2}n\zeta\tau}.$$
(5.22)

These free-field Green's functions are then substituted into the general expressions for the self-energies to give

$$\Sigma_{\alpha,ij}(t,t') = \sum_{k} t^*_{k\alpha i} G_{k\alpha k\alpha}(t,t') t_{k\alpha j} = \underbrace{\Sigma_{\alpha,ij}(\tau)}_{\text{self-energy of static leads}} \sum_{n=-\infty}^{\infty} (-1)^n J_n\left(\frac{2\Delta_{\alpha} \cos(\zeta T)}{\zeta}\right) e^{\frac{i}{2}n\zeta\tau},$$
(5.23)

while the corresponding self-energy in the Wigner space takes the form

$$\tilde{\Sigma}_{\alpha,ij}(\omega,T) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \Sigma_{\alpha,ij}(\tau) = \sum_{n=-\infty}^{\infty} \underbrace{\tilde{\Sigma}_{\alpha,ij}(\omega+n\zeta/2)}_{\text{self-energy of static leads}} (-1)^n J_n\left(\frac{2\Delta_\alpha \cos(\zeta T)}{\zeta}\right).$$
(5.24)

Now, we apply the wide-band approximation and utilise the following Bessel function properties [194]:

$$\sum_{k=-\infty}^{\infty} J_{n\pm k}(z) = 1, \qquad \sum_{k=-\infty}^{\infty} (-1)^k J_{n\pm k}(z) = (-1)^n, \tag{5.25}$$

allowing us to simplify the self-energy components, now expressed as matrices, to

$$\tilde{\Sigma}_{\alpha}^{<}(\omega,T) = i\Gamma_{\alpha}\sum_{n=-\infty}^{\infty} f_{\alpha}(\omega + n\zeta/2)(-1)^{n}J_{n}\left(\frac{2\Delta_{\alpha}\cos(\zeta T)}{\zeta}\right),$$
(5.26)

$$\tilde{\Sigma}^{>}_{\alpha}(\omega,T) = -i\Gamma_{\alpha} + \tilde{\Sigma}^{<}_{\alpha}(\omega,T), \qquad (5.27)$$

$$\tilde{\Sigma}^{A}_{\alpha} = -\frac{i}{2}\Gamma_{\alpha}, \quad \tilde{\Sigma}^{R}_{\alpha} = \frac{i}{2}\Gamma_{\alpha}.$$
(5.28)

For future use within the Kadanoff-Baym equations, we compute time and energy derivatives of the lesser lead self-energy in Wigner space. Considering the derivative with respect to the central time,

$$\partial_T \tilde{\Sigma}^<_{\alpha}(\omega, T) = i\Gamma_{\alpha} \sum_{n=-\infty}^{\infty} f_{\alpha}(\omega + n\zeta/2)(-1)^n \partial_T \left( J_n\left(\frac{2\Delta_{\alpha}\cos(\zeta T)}{\zeta}\right) \right), \tag{5.29}$$

where only the Bessel functions are dependent on the central time. Using the following property of a Bessel function [194],

$$J_{n-1}(x) - J_{n+1}(x) = 2\frac{dJ_n(x)}{dx},$$
(5.30)

we find that

$$\partial_T \left( J_n \left( \frac{2\Delta_\alpha \cos(\zeta T)}{\zeta} \right) \right) = \Delta_\alpha \sin\left(\zeta T\right) \left( J_{n+1} \left( \frac{2\Delta_\alpha \cos(\zeta T)}{\zeta} \right) - J_{n-1} \left( \frac{2\Delta_\alpha \cos(\zeta T)}{\zeta} \right) \right). \tag{5.31}$$

Substituting this back into our self-energy and making use of the fact that the summation is infinite, we find that

$$\partial_{T} \tilde{\Sigma}_{\alpha}^{<}(\omega, T) = \partial_{T} \tilde{\Sigma}_{\alpha}^{>}(\omega, T) = i \Gamma_{\alpha} \Delta_{\alpha} \sin\left(\zeta_{\alpha} T\right) \sum_{n=-\infty}^{\infty} (-)^{n} f_{\alpha}(\omega + n\zeta_{\alpha}/2) \\ \times \left[ J_{n+1}\left(\frac{2\Delta_{\alpha} \cos(\zeta_{\alpha} T)}{\zeta_{\alpha}}\right) - J_{n-1}\left(\frac{2\Delta_{\alpha} \cos(\zeta_{\alpha} T)}{\zeta_{\alpha}}\right) \right].$$
(5.32)

Considering the derivative with respect to omega,

$$\partial_{\omega}\tilde{\Sigma}_{\alpha}^{<}(\omega,T) = i\Gamma_{\alpha}\sum_{n=-\infty}^{\infty}\partial_{\omega}f_{\alpha}(\omega+n\zeta/2)(-1)^{n}J_{n}\left(\frac{2\Delta_{\alpha}\cos(\zeta T)}{\zeta}\right),$$
(5.33)

where

$$\partial_{\omega} f_{\alpha}(\omega + n\zeta/2) = \partial_{\omega} \left( \frac{1}{1 + e^{(\omega + \frac{1}{2}\zeta n - \mu)/T_{\alpha}^{\text{lead}}}} \right)$$
(5.34)

$$= -\frac{e^{\left(\omega + \frac{1}{2}\zeta n - \mu\right)/T_{\alpha}^{\text{lead}}}/T_{\alpha}^{\text{lead}}}{\left(1 + e^{\left(\omega + \frac{1}{2}\zeta n - \mu\right)/T_{\alpha}^{\text{lead}}}\right)^{2}}$$
(5.35)

$$= -\left(f_{\alpha}(\omega+n\zeta/2)\right)^{2} e^{\left(\omega+\frac{1}{2}\zeta n-\mu\right)/T_{\alpha}^{\text{lead}}}/T_{\alpha}^{\text{lead}},$$
(5.36)

we find that

$$\partial_{\omega}\tilde{\Sigma}_{\alpha}^{<}(\omega,T) = \partial_{\omega}\tilde{\Sigma}_{\alpha}^{>}(\omega,T)$$

$$= -i\frac{\Gamma_{\alpha}}{T_{\alpha}^{\text{lead}}}\sum_{n=-\infty}^{\infty} (-)^{n} \left(f_{\alpha}\left(\omega + \frac{1}{2}n\zeta_{\alpha}\right)\right)^{2} e^{\left(\omega + \frac{1}{2}n\zeta_{\alpha} - \mu_{\alpha}\right)/T_{\alpha}^{\text{lead}}} J_{n}\left(\frac{2\Delta_{\alpha}\cos(\zeta_{\alpha}T)}{\zeta_{\alpha}}\right).$$
(5.38)

For clarity, we emphasise here that *T* is the central time while  $T_{\alpha}^{\text{lead}}$  is the temperature of the  $\alpha$  lead.

## 5.2.4 Simplifications to the Green's functions

The adiabatic Green's functions once again take the familiar form

$$\tilde{G}_{(0)}^{A/R} = \left(\omega - h - \tilde{\Sigma}_{(0)}^{A/R}\right)^{-1}, \qquad \tilde{G}_{(0)}^{} = \tilde{G}_{(0)}^{R} \tilde{\Sigma}_{(0)}^{} \tilde{G}_{(0)}^{A}.$$
(5.39)

Meanwhile, the first order corrections can be simplified significantly as all terms are now scalars in the single level case. They now take the form

$$\tilde{G}_{(1)}^{A/R} = 0, \qquad \tilde{G}_{(1)}^{<} = \frac{i}{2} \tilde{G}_{(0)}^{R} \tilde{G}_{(0)}^{A} (\tilde{G}_{(0)}^{A} - \tilde{G}_{(0)}^{R}) (\partial_{T} \tilde{\Sigma}^{<} + \partial_{T} h \partial_{\omega} \tilde{\Sigma}^{<}).$$
(5.40)

For convenience, we split  $\widetilde{G}_{(1)}^{<}$  into a component which is first-order in nuclear motion, and a component which is first-order in the motion of the leads energies. First, we separate  $\partial_T$  into a nuclear motion component, and a leads-energy motion component;

$$\partial_T = v\partial_x + (\partial_T)_x,\tag{5.41}$$

where the subscript outside brackets denotes the quantity held constant. Note that where a  $v\partial_x$  term is associated with  $\Omega$ ,  $(\partial_T)_x$  is similarly associated with  $\zeta$ . This allows us to partition  $\tilde{G}_{(1)}^<$  into

$$\tilde{G}_{(1)}^{<} = \tilde{G}_{(1),v}^{<} + \tilde{G}_{(1),\epsilon'}^{<}$$
(5.42)

where

$$\tilde{G}_{(1),v}^{<} = \frac{i}{2} v \epsilon'(t) \tilde{G}_{(0)}^{R} \tilde{G}_{(0)}^{A} (\tilde{G}_{(0)}^{A} - \tilde{G}_{(0)}^{R}) \partial_{\omega} \tilde{\Sigma}^{<},$$
(5.43)

and

$$\tilde{G}_{(1),\epsilon}^{<} = \frac{i}{2} \tilde{G}_{(0)}^{R} \tilde{G}_{(0)}^{A} (\tilde{G}_{(0)}^{A} - \tilde{G}_{(0)}^{R}) \partial_{T} \tilde{\Sigma}^{<}.$$
(5.44)

Here we have used the fact that  $(\partial_T)_x h = 0$  and  $\partial_x \tilde{\Sigma}^{<} = 0$  for our model.

### 5.2.5 Langevin coefficients under a time-dependent driving

In the case of a single electronic level in the central region with no classical dependence on the leads interface, the mean force prior to perturbative expansion is given by

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega i e^{\frac{1}{2i} d_T^h \partial_{\omega}^G} \partial_x h \tilde{G}^{<}.$$
 (5.45)

The adiabatic is zeroth order in the nuclear motion; however, this does not additionally constrain it to zeroth order in the motion of the leads energies. In solving for the adiabatic force, the higher order nuclear motion terms are neglected while we retain the first order leads energy terms. As a result, the adiabatic force is given by

$$f_{(0)}(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \left( \partial_x h \tilde{G}_{(0)}^< + \partial_x h \tilde{G}_{(1),\epsilon}^< \right).$$
(5.46)

Here, we have the usual renormalization of the classical potential due to the occupation of the central electronic level along with an additional correction due to the time-dependent driving in the leads. Similarly, the first order force (first order here meaning in terms of nuclear

motion) is given by

$$f_{(1)}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left( i\partial_x h \tilde{G}_{v(1)}^< + \frac{v}{2} \partial_x^2 h \partial_\omega \tilde{G}_{(0)}^< \right).$$
(5.47)

We note that the last term in (5.47) reduces to zero as

$$\int_{-\infty}^{\infty} d\omega \partial_{\omega} G^{<} = 0.$$
 (5.48)

As usual, the diffusion coefficient is computed as a time-correlation of the force variations

$$\langle \delta f(t) \delta f(t') \rangle = D(T) \delta(t - t'), \tag{5.49}$$

where the correlation function is found according to

$$\langle \delta f(t) \delta f(t') \rangle = \partial_x h(t) G^{>}(t, t') \partial_x h(t') G^{<}(t', t).$$
(5.50)

We recall from Section 3.3.6 that (5.50) must now be transformed to the Wigner space where we can perform a perturbative expansion and truncation. We find that in the Wigner space, we have

$$D(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{A}(T,\omega) \tilde{B}(T,\omega), \qquad (5.51)$$

where

$$\tilde{A} = e^{\frac{1}{2i}\partial_{\omega}^{G}\partial_{T}^{h}}\partial_{x}h\tilde{G}^{>}, \qquad \tilde{B} = e^{-\frac{1}{2i}\partial_{\omega}^{G}\partial_{T}^{h}}\partial_{x}h\tilde{G}^{<}.$$
(5.52)

As previously, the  $\partial_T$  terms are split into derivatives with respect to nuclear motion, and derivatives with respect to the motion of the lead-energies. Noting that the central-region Hamiltonian for this model is independent of the leads, the latter terms do not contribute. We enact the adiabatic nucleus assumption, truncating *D* after the zeroth order in nuclear motion which yields

$$D(t) = [\partial_x h(t)]^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left( \tilde{G}_{(0)}^{>} \tilde{G}_{(0)}^{<} + \tilde{G}_{(1),\epsilon}^{>} \tilde{G}_{(0)}^{<} + \tilde{G}_{(0)}^{>} \tilde{G}_{(1),\epsilon}^{<} \right).$$
(5.53)

The diffusion coefficient consists of two contributions: the first term is again the standard expression as used in DC current junctions, while the remaining terms are new and arise from the dynamical corrections to the lesser and greater Green's functions computed using sinusoidally oscillating self-energies.



Figure 5.1: Electronic viscosity (a) and diffusion coefficient (b) computed as functions of the AC driving frequency and the molecular orbital energy. Parameters used in calculations:  $\lambda^2/k = 0.002\Gamma$ ,  $V = 2\Gamma/3$ ,  $\Delta = \Gamma/3$ .  $\Omega$  and  $\epsilon_0$  are given in terms of  $\Gamma$ .

## 5.3 Results

#### 5.3.1 Nonequilibrium viscosity and noise produced by AC driven electrons

Figure 5.1 shows the viscosity and diffusion coefficient (averaged over a period of oscillation and also statistically averaged with respect to possible values of *x*). The viscosity and diffusion coefficients are shown as a ratio to the corresponding DC (static) values for a given average voltage, the DC calculations are performed using (5.47) and (5.53) and setting the amplitude of sinusoidal voltage modulation  $\Delta = 0$  [143]. The leads temperature is set to 0.02 $\Gamma$  in all our calculations. In the centre of the resonance region, application of the AC driving acts to decrease the diffusion coefficient while slightly increasing the viscosity. In our previous work [143] (and in agreement with Subotnik et al. results [148]), peaks in the friction occur when the molecular orbital energy aligns with either the left or right chemical potentials, since the electrons can deposit any amount of energy taken from the nuclear degrees of freedom to the leads via inelastic scattering to the available empty states above the chemical potential. This is in contrast to the diffusion which has contributions from all lead states in the resonant region. Applying this analysis to our system, we observe that the viscosity increase in the resonant region is a result of the lead chemical potentials being allowed to shift closer to the resonant level and inducing increased interaction between the nucleus and the high-energy electrons in the leads. However, the AC voltage has minimal effect on increasing the diffusion near the resonance. The growth of the viscosity relative to the diffusion coefficient results in an optimal transport regime in which the molecular junction is cooled relative to the static case. As we shift our resonant level to the edges of the resonant region, we observe a notable decrease to the viscosity upon application of the AC leads, relative to the DC case. In the static

regime, the viscosity is maximised here due to the alignment between the resonant level and the leads, which is broken upon application of an AC voltage. Resultantly, the AC driving acts to increase the junction temperature in this region.

#### 5.4 Effective temperature

Using  $\xi$  and *D* we define an effective temperature of the molecular junction via analogy with the equilibrium fluctuation-dissipation theorem as given by  $\frac{D}{2\xi}$  for one-dimensional motion. There are two options in defining the effective temperature for a given frequency; we can calculate the instantaneous effective temperature for each given time in a period of AC leads oscillation and then average over the period, given by

$$T_{AC}^{inst} = \frac{\Omega}{2\pi} \int_0^{2\pi/\Omega} dt \frac{D(t)}{2\xi(t)},$$
(5.54)

or alternately, we can first take *D* and  $\xi$  to be time-averaged quantities over a period of AC oscillation, then calculate the effective temperature as

$$T_{AC}^{ave} = \frac{\int_0^{2\pi/\Omega} dt D(t)}{2\int_0^{2\pi/\Omega} dt\xi(t)}.$$
(5.55)

In Figure 5.2, we compare these options with average temperature data obtained from kinetic energy calculated via numerical Langevin simulations for the same parameters. In the interest of computational efficiency,  $\lambda^2/k = \Gamma/6$ , where all other parameters coincide with other results presented in this study. We observe  $T_{AC}^{ave}$  to be a far more accurate measure of the average nuclear temperature within the system for these parameters. Given that  $\xi$  and D are each proportional to  $\lambda^2$ , decreasing  $\lambda^2/k$  (in line with the presented results in this paper) will only further improve the accuracy of the average calculation, since the molecule will react more slowly to temperature variations due to the AC leads oscillations. As such, we choose to use  $T_{AC}^{ave}$  as our measure for the effective temperature.

Figure 5.3 shows the ratio  $T_{AC}/T_{DC}$  computed for various transport regimes. The AC temperature is compared to the static DC temperature  $T_{DC}$  computed again as the ratio between the diffusion and friction coefficients, but now obtained using NEGF calculations for static leads [143]. Both temperatures are again statistically averaged over *x* and over a period of AC driving. As we have already deduced from the behaviour of the viscosity and diffusion coefficient, cooling is observed in the central resonance transport regime, while heating is observed at the edges of resonant transport. The effect of cooling is more significant for slow AC driving (Figure 5.3a) and is amplified if the amplitude of voltage driving is increased (Figure 5.3b). Figure



Figure 5.2: Comparison of methods of effective temperature calculation with Langevinsimulated nuclear temperature results for the same parameters. Parameters used in calculations:  $\lambda^2/k = \Gamma/6$ ,  $\Omega = \Gamma/15$ ,  $V = 2\Gamma/3$  and  $\Delta = \Gamma/3$ .  $\epsilon_0$  is given in terms of  $\Gamma$ .

5.3c shows the case of a large static bias voltage, which also enables the consideration of large AC voltage amplitudes; as one observes, it enables a reduction to the effective temperature by as much as 80% for the chosen parameters, while the corresponding decrease to the average current is less than 20% for the same  $\epsilon_0$ .

Figure 5.4 demonstrates the role of the chemical bond spring constant k and the coupling strength between the electronic population and the nuclear motion. These parameters are interconnected. The term  $\lambda x$  in (5.3) results in the shift of the molecular orbital energy due to deviations away from the equilibrium nuclear position.  $\lambda$  describes the magnitude of this shift whilst k governs the range of variation in the x coordinate. Therefore,  $\lambda^2/k$  is an energy related quantity which encapsulates both effects. As shown in figure 5.4, the cooling effects are observed in the resonance regime when  $\lambda^2/k < 0.2\Gamma$ . This means that this cooling phenomenon can be observed for systems with rigid chemical bonds, or weak electron-nuclear coupling. In any other case, the deviations in the energy level due to nuclear motion may be large enough such that the level leaves this cooling region.

The temperature change *per se* for a given average voltage may not be a complete measure of heating/cooling, since the AC driving may simply produce a smaller current (averaged over the period of oscillation) relative to the corresponding DC voltage, resulting in less power dissipated over the molecule. It is illuminating for us to then consider the heating/cooling effects upon application of an AC driving, relative to the DC case at a given average current (but now a different average voltage). As such, the static lead electric current  $J_{DC}$  is computed using the Landauer formula for static leads, and  $J_{AC}$  is the exact electric current (averaged)



Figure 5.3: Ratio of AC and DC molecular temperatures computed as functions of molecular orbital energy. (a) shows the results for different AC driving frequencies with  $\Delta = \Gamma/3$  and  $V = 2\Gamma/3$  (b) shows the results for different amplitudes of AC voltage oscillations with  $\Omega = \Gamma/15$  and  $V = 2\Gamma/3$ . (c) shows the temperatures ratio, currents ratio, and cooling ratio defined by Eq.(5.56) for a higher DC voltage  $V = 5\Gamma/3$  and  $\Delta = 5\Gamma/6$ .  $\lambda^2/k = 0.002\Gamma$  and  $\epsilon_0$  is given in terms of  $\Gamma$ .



Figure 5.4: Ratio of AC and DC molecular temperatures as function of  $\lambda^2/k$  and  $\epsilon_0$ . Parameters used in calculations:  $\Omega = \Gamma/15$ ,  $V = 2\Gamma/3$  and  $\Delta = \Gamma/3$ . Both  $\lambda^2/k$  and  $\epsilon_0$  are given in terms of  $\Gamma$ .

over a period of oscillation) computed using Jauho, Meir, and Wingreen NEGF theory for AC driven quantum transport [195]. Then we introduce the following quantity called the "cooling ratio"

$$\eta = \frac{T_{AC}(J)}{T_{DC}(J)},$$
(5.56)

which provides a measure of the heating/cooling observed upon application of an AC driving, for a given average current;  $\eta < 1$  means that the AC driving yields a lower temperature while allowing for the same average current. Figure 5.3c shows that the application of an AC driving allows for in excess of 40% cooling of the molecular junction, while maintaining the same average current as in the DC case.

## 5.5 Summary

We have demonstrated that the application of an AC driving in the leads' voltage can result in a significant reduction to the power dissipation in a molecular junction, relative to the case of a large static voltage. The lifetime of a chemical bond is  $\tau_{\text{life}} \sim e^{E_b/kT}$ , where  $E_b$  is the energetic barrier for bond dissociation. One observes that the lifetime depends exponentially on the effective temperature *T*; therefore, even a moderate temperature reduction produces a colossal extension of the device lifetime. The observed effect is quite robust and does not require special fine-tailoring of the model parameters. Moreover, using a master equation derived in the time-averaged Born-Markov approximation and assuming that the driving period
must be shorter than characteristic electron tunneling time  $1/\Gamma$ , Peskin et al. demonstrated that the harmonically driven leads may reduce the vibrational temperature of the molecular junction [196]. The approach of Reference [196] is complementary in all respects to what we consider in this paper regarding transport and AC driving regimes. They additionally treated the nuclear vibrations on a quantum level, in which heating or cooling effects can be more pronounced due to the resonance structure of vibrations. This serves as a strong indication that the proposed effect is very robust, ubiquitous, and may be applicable for various transport scenarios. Although the cooling was the main focus of our paper, it has not escaped our notice that depending upon the parameters, the sinusoidal driving of the leads may result in significant heating of the molecular junction. However, this may also allow for enhanced device functionality as this parameter-controlled heating may be utilized for current-induced selective bond breaking, and energy efficient single-molecule catalysis of chemical reactions.

# First-passage time theory of activated rate chemical processes

This chapter contains material that has been previously published in the following journal article:

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# 6.1 Motivation

Molecular junctions provide an exciting opportunity to explore and produce new chemical reactions by providing a device which traps a single molecule in a confined space of a few nanometers where the electric field and current are applied locally and selectively [74, 197, 198]. In this chapter, we shift the focus to the calculation of chemical reaction rates in molecular junctions.

The adequate and well established theories have been developed for reaction rate calculations in gas and condensed phases [181, 199–205]. However, the development of similar theories for molecules in an electronic junction environment is no simple task and as such, the scope of theoretical work is still very limited. Three types of approaches have been proposed to model current-induced dissociation. The first is based on the rate equation approach where a single harmonic vibration is pumped beyond the dissociation threshold limit [94, 206]. The second is a numerically exact scheme, which uses the hierarchical quantum master equation method in conjunction with a discrete variable representation for the nuclear degrees of freedom to numerically study current-induced dissociation [207]. The third uses Keldysh nonequilibrium Green's functions to obtain a Fokker-Planck equation for the reaction coordinate which is used to compute average escape times and the accompanying reaction rates [172, 182]. The further development of this approach is the subject of this paper. The method has proven successful

in a range of circumstances [141, 143–146, 149–152, 172, 176, 177].

The method further lends itself to the study of current-induced chemical reaction rates [172, 182]. The use of Langevin dynamics to compute reaction rates was first explored by Kramers in his seminal 1940 paper [208], in which the mean first-escape time of a particle trapped in an arbitrary potential well subject to Langevin forces was approximated. The next significant step was made in the 1990s, when Kramers' theory was extended to account for position-dependent friction and generalized Langevin equations describing finite-memory (non-Markovian) fluctuation-dissipation processes [209-212]. The effect of a velocity-dependent friction on Kramers' rates was investigated in Reference [213]. However, these studies were limited to the regime of thermodynamic equilibrium. Beyond this regime, the fluctuationdissipation theorem no longer holds, allowing for the emergence of localized heating effects in analogy to Landauer's proposed blowtorch effect [214, 215], in which specific configurations of the reaction coordinate may experience heightened temperatures, which may have a significant effect on the evolution of the system. Such systems are not limited to the realms of molecular electronics; the most common examples include numerous molecular motors, ratchets, and heat engines [216-218] as well as various confined nanosystems [219-223], notably of biological significance [224, 225]. Several explicit simulations of Landauer's blowtorch effects in double-well potentials have also been performed recently [226–228].

One of the aims of this chapter is to further shed light on this topic. A comprehensive understanding of the effects of localized heating on the stability of molecular geometries is required to ensure the productive development of specific functionalities of molecular-scale electronic systems. In this chapter, we relax the requirement of thermodynamic equilibrium, allowing for the self-consistent study of the mean first-passage times in model molecular electronic junctions in both the underdamped and overdamped regimes. This is calculated through a Fokker-Planck equation, which arises due to our Langevin description of the reaction coordinate within the junction. The work presented here is a continuation of two papers [172, 182], however Reference [182] considered the problem employing the fluctuation-dissipation theorem and Reference [172] focused on the underdamped case only.

The chapter is structured as follows. In Section 6.2, we demonstrate our calculations for the mean first-passage time in the limiting regimes. This involves the calculation of the current-induced forces in the system, from which a Fokker-Planck description then yields an equation for the mean first-passage times. This is then applied to a simple model of the blowtorch effect in Section 6.3.1. In Section 6.3.2, we calculate the reaction rates for a single-level junction model, in which current-induced forces are calculated self-consistently within the model. This is then further applied to a model two-level molecule within the junction in Section 6.3.3.

# 6.2 Theory

Thus far, we have used the Langevin equation to calculate non-deterministic trajectories of the classical coordinate in time. However, the study of reaction rates requires a more general approach whereby the state of the classical coordinate a certain time is described by a probability distribution. The time evolution of the phase-space probability density is described by a specific form of the Fokker-Planck equation generally known as the Klein-Kramers equation and is given by

$$\partial_t \rho(x, p, t) = \left( -\frac{p}{m} \partial_x + U'(x) \partial_p + \xi(x) \left[ \partial_p \frac{p}{m} + \partial_p^2 T(x) \right] \right) \rho(x, p, t).$$
(6.1)

Here,  $\rho(x, p, t)$  is the probability density to find the classical coordinate at position x with momentum p at time t. The Langevin and Fokker-Planck descriptions contain exactly the same information; a Langevin trajectory is merely a specific outcome of the probability distribution solved for via the Fokker-Planck equation [229]. This then explains the appearance of our now all too familiar Langevin coefficients in (6.1), where we have used T to denote the effective temperature and U to denote the effective potential according to their usual definitions. A note on the notation: we will use  $\partial_x$  to denote a derivative acting on all terms to the right, whereas the conventional notation  $\frac{\partial A}{\partial x}$  acts only on the arbitrary term A. In the interest of brevity, we re-express (6.1) as

$$\partial_t \rho(x, p, t) = \left( \Lambda + \xi(x) \left[ \partial_p \frac{p}{m} + \partial_p^2 T(x) \right] \right) \rho(x, p, t), \tag{6.2}$$

where we have introduced the component  $\Lambda$  such that

$$\Lambda = \partial_p \frac{\partial H}{\partial x} - \partial_x \frac{\partial H}{\partial p} = -\partial_x \frac{p}{m} + \partial_p U'(x).$$
(6.3)

 $\Lambda$  describes the time evolution of the probability density in the absence of an external environment. We have defined the classical Hamiltonian as

$$H(x,p) = \frac{p^2}{2m} + U(x).$$
 (6.4)

Our goal is to solve (6.2) for the probability density, from which we can then calculate relevant observables such as the mean first-passage time. However, analytical solutions are generally difficult to obtain; we must then resort to the consideration of two limiting cases. We will separately consider the overdamped and underdamped cases, which concern the strength of the interactions with the environment as governed by  $\xi$  and *T*. The overdamped case emerges when environmental interactions are strong such that  $\Lambda$  is dominated by the second term in (6.2). In contrast, the underdamped case considers when the second term is weak in comparison to  $\Lambda$ . The consideration of these regimes gives us the foothold we require to

approach the problem of solving for the mean first-passage time.

#### 6.2.1 Overdamped limit

The system is considered overdamped when  $\xi/m$  is large; this parameter defines the timescale of thermal relaxation of the classical coordinate. In this case, any inertial effects can be reasonably neglected and our governing Langevin equation can be expressed as

$$\frac{dx}{dt} = \frac{1}{\xi(x)} \left( -\frac{dU}{dx} + \delta f(t) \right).$$
(6.5)

Here we have taken the full Langevin equation and set  $\frac{d^2x}{dt^2} = 0$ ; expressed in the case of a single degree of freedom for clarity. This amounts to assuming that the velocity distribution equilibrates instantaneously to the equilibrium distribution [120]. Following this logic, from (6.5) one can then derive the overdamped form of the Klein-Kramers equation which describes the time evolution of the probability density of the classical coordinate - now independent of the velocity:

$$\partial_t \rho(x,t) = \partial_x \frac{1}{\xi(x)} \left[ U'(x) + \partial_x T(x) \right] \rho(x,t).$$
(6.6)

This is commonly known as the Smoluchowski equation, after it was first applied by the physicist in the description of Brownian motion. The form of (6.6) was derived by Van Kampen in Reference [230], who circumvents the Ito-Stratonovich dilemma which arises upon the consideration of a multiplicative noise [231]. The probability distribution as described by this equation is the foundation for our calculations in the overdamped limit.

#### 6.2.1.1 Stationary solution in the overdamped limit

We can reinterpret (6.6) as a continuity equation according to

$$\partial_t \rho(x,t) = \partial_x S(x,t),$$
 (6.7)

where *S* must be interpreted as a probability current, defined as

$$S(x,t) = \frac{1}{\xi(x)} \left[ U'(x) + \partial_x T(x) \right] \rho(x,t).$$
(6.8)

We require that the probability distribution must maintain its normalisation in time according to

$$\int_{x_{\text{left}}}^{x_{\text{right}}} dx \rho(x, t) = \text{constant},$$
(6.9)

where  $x_{\text{left}}$  and  $x_{\text{right}}$  are the boundaries for our system. This implies that  $S(x_{\text{left}}, t) = S(x_{\text{right}}, t)$ , since there is no source term in (6.7). When applying the natural boundaries of  $x_{\text{left}} = -\infty$ and  $x_{\text{right}} = \infty$ , probability cannot flow out of the system, since the system encompasses the whole universe! Thus, we must have that  $S(-\infty, t) = S(\infty, t) = 0$  [229]. In the stationary case when  $\partial_t \rho = 0$ , this then leads to

$$\partial_x S(x) = 0, \tag{6.10}$$

$$\int_{-\infty}^{x} dx' S(x') = 0, \tag{6.11}$$

$$S(x) - S(-\infty) = 0,$$
 (6.12)

$$\therefore S(x) = 0. \tag{6.13}$$

As is perhaps self-evident, the probability current is zero for all *x* when in the stationary state. Our stationary probability distribution  $\rho_{st}$  can then be calculated from

$$S(x) = 0,$$
 (6.14)

$$\frac{1}{\tilde{\xi}(x)} \left[ U'(x) + \partial_x T(x) \right] \rho_{st}(x) = 0.$$
(6.15)

Note that this is equivalent to integrating (6.6) over *x* when  $\partial_t \rho = 0$ , and setting the integration constant to zero. The process to find an expression for  $\rho_{st}$  is now straight-forward: begin by writing the above in the form of a separable differential equation,

$$-\frac{U'(x) + T'(x)}{T(x)} = \frac{1}{\rho_{st}(x)} \frac{d\rho_{st}}{dx}.$$
(6.16)

Apply a definite integral over *x* to both sides to obtain

$$-\int_{a}^{x'} dx \frac{U'(x) + T'(x)}{T(x)} = \int_{a}^{x'} dx \frac{1}{\rho_{st}(x)} \frac{d\rho_{st}}{dx},$$
(6.17)

$$-\int_{a}^{x'} dx \frac{U'(x)}{T(x)} - \ln\left(\frac{T(x')}{T(a)}\right) = \ln\left(\frac{\rho_{st}(x')}{\rho_{st}(a)}\right).$$
(6.18)

Here, *a* is an arbitrary constant which has no bearing on the final result. Consequently, we find that

$$\rho_{st}(x') = \rho_{st}(a) \frac{T(a)}{T(x')} e^{-\int_a^{x'} dx \frac{U'(x)}{T(x)}}.$$
(6.19)

By applying our normalisation condition, we find that  $\rho_{st}(a)$  is given by

$$\rho_{st}(a) = \frac{1}{T(a) \int_{-\infty}^{\infty} dx' \frac{1}{T(x')} e^{-\int_{a}^{x'} dx \frac{U'(x)}{T(x)}}}.$$
(6.20)

Our final result for the stationary distribution in the overdamped limit is then calculated according to [230]

$$\rho_{st}(x') = \frac{1}{ZT(x')} e^{-\int_a^{x'} dx \frac{U'(x)}{T(x)}},$$
(6.21)

where the partition function, Z, is defined as

$$Z = \frac{1}{\int_{-\infty}^{\infty} dx' \frac{1}{T(x')} e^{-\int_{a}^{x'} dx \frac{U'(x)}{T(x)}}}.$$
(6.22)

#### 6.2.1.2 Alternate form of the Smoluchowski equation

Now that we have knowledge of the stationary distribution, we can re-express (6.6) in a form more tenable for our first-passage time calculations; it is given by

$$\partial_t \rho(x,t) = \partial_x \frac{T(x)}{\xi(x)} \rho_{st}(x) \partial_x \rho_{st}^{-1}(x) \rho(x,t).$$
(6.23)

This is demonstrated as follows; firstly

$$\left(U'(x) + \partial_x T(x)\right) = \left(U'(x) + \partial_x T(x)\right)\rho_{st}(x)\rho_{st}^{-1}(x).$$
(6.24)

It is straight forward to show that

$$\partial_x \rho_{st}(x) = -\frac{1}{T(x)} \left( T'(x) + U'(x) \right) \rho_{st}(x), \tag{6.25}$$

which can be used to find

$$(U'(x) + \partial_x T(x)) \rho_{st}(x) \rho_{st}^{-1}(x) = T(x) \rho_{st}(x) \partial_x \rho_{st}^{-1}(x).$$
(6.26)

Substituting (6.26) back into (6.6) yields our result in (6.23).

#### 6.2.1.3 Calculation of the mean first-passage times

Equation (6.23) describes the evolution of the probability density for an arbitrary classical potential, where the interaction with the environment determines the inhomogeneous Langevin coefficients. In this section, we calculate an explicit expression for the mean first-passage time of the classical coordinate through some boundary,  $x_B$ . The choice of  $x_B$  is again unrestricted; however, in our treatment we will always consider  $x_B$  to correspond to a maximum in the potential, thereby naturally separating the reactant and product states. This is shown diagrammatically in Figure 6.1, where any  $x > x_B$  (corresponding to the dashed line) becomes



Figure 6.1: The reaction potential, where a barrier at  $x_B$  separates the product state from the reactant state.

irrelevant to the calculations. Now, the task is to use (6.23) to find an expression for the mean first-passage time. We begin by applying suitable initial and boundary conditions. We choose the classical coordinate to have value  $x_0$  at time  $t_0$ , so that the initial condition is given by

$$\rho(x, t_0) = \delta(x - x_0), \tag{6.27}$$

where  $x_0 < x_B$ . Additionally, we define an absorbing boundary condition such that the probability density exactly at the barrier is set to zero:

$$\rho(x_b, t) = 0.$$
(6.28)

This ensures that once the reaction coordinate has crossed  $x_B$ , it is unable to re-enter the reactant region. At the initial time  $t_0$ , the probability of finding the classical coordinate within our potential is 1. The proportion of paths that are still within our potential after time t given some initial condition  $x_0$  is given by

$$P(t, x_0) = \int_{-\infty}^{x_b} dx \rho(x, t).$$
(6.29)

The proportion of paths which crossed  $x_B$  in the time period  $t \rightarrow t + dt$  is given by

$$P(t, x_0) - P(t + dt, x_0) = J(t, x_0)dt,$$
(6.30)

where we have defined the distribution of first-passage times (as a function of time)  $J(t, x_0)$  as

$$J(t, x_0) = -\frac{dP(t, x_0)}{dt}.$$
(6.31)

 $J(t, x_0)$  tells us how quickly the proportion of paths inside the potential is changing at any given time *t*. The mean first-passage time is then given by

$$\tau(x_0) = \int_{t_0}^{\infty} dt J(t, x_0) t.$$
(6.32)

Now we need to find a useable form to be able to calculate this quantity. Let's begin by integrating it by parts and use the fact that  $\int dt J(t, x_0) = -P(t, x_0)$ :

$$\tau(x_0) = \left[-P(t, x_0)t\right]_{t_0}^{\infty} + \int_{t_0}^{\infty} dt P(t, x_0)$$
(6.33)

$$= t_0 + \int_{t_0}^{\infty} dt P(t, x_0)$$
(6.34)

$$=\int_0^\infty dt P(t,x_0),\tag{6.35}$$

where we have let  $t_0 = 0$  for simplicity and used the fact that  $P(\infty, x_0) = 0$ , since all paths must eventually escape. Now, recall that our overdamped equation for the probability density is given by

$$\partial_t \rho(x,t) = \partial_x \frac{T(x)}{\xi(x)} \rho_{st}(x) \partial_x \rho_{st}^{-1}(x) \rho(x,t)$$
(6.36)

$$=\mathcal{L}\rho(x,t),\tag{6.37}$$

where the time evolution is determined by the operator  $\mathcal{L}$ . The general solution to the above can be found as

$$\rho(x,t) = e^{t\mathcal{L}}\delta(x-x_0), \tag{6.38}$$

where we have again applied the initial condition. Note that the ordering is important here since  $\mathcal{L}$  acts on the  $\delta$ -function. Thus,  $\tau$  becomes

$$\tau(x_0) = \int_0^\infty dt P(t, x_0)$$
(6.39)

$$=\int_0^\infty dt \int_{0-\infty}^{x_b} dx \rho(x,t)$$
(6.40)

$$= \int_0^\infty dt \int_{-\infty}^{x_b} dx e^{t\mathcal{L}} \delta(x - x_0).$$
(6.41)

Since  $\rho$  must always be real, it must also be self-adjoint. The adjoint of an operator is defined according to  $(A\psi, \phi) = (\psi, A^{\dagger}\phi)$ , where (,) denotes a complex inner product. The adjoint of

 $\rho$  is then found by

$$(\rho(x,t)\psi,\phi) = \left(e^{t\mathcal{L}}\delta(x-x_0)\psi,\phi\right)$$
(6.42)

$$= \left(\delta(x - x_0)\psi, e^{t\mathcal{L}^{\dagger}}\phi\right) \tag{6.43}$$

$$= \left(\psi, \delta(x - x_0)e^{t\mathcal{L}^{\dagger}}\phi\right) \tag{6.44}$$

$$= \left(\psi, \rho^{\dagger}(x, t)\phi\right). \tag{6.45}$$

As a result, (6.41) becomes

$$\tau(x_0) = \int_0^\infty dt \int_{-\infty}^{x_b} dx \delta(x - x_0) e^{t\mathcal{L}^+} 1$$
(6.46)

$$\tau(x) = \int_0^\infty dt e^{t\mathcal{L}^\dagger} 1. \tag{6.47}$$

We can find a differential equation for the mean first-passage time by applying  $\mathcal{L}$  on the left of both sides, yielding

$$\mathcal{L}^{\dagger}\tau(x) = \int_{0}^{\infty} dt \mathcal{L}^{\dagger} e^{t\mathcal{L}^{\dagger}} \mathbf{1}$$
(6.48)

$$= \int_0^\infty dt \frac{\partial \left(e^{tL^*}\right)}{\partial t} 1 \tag{6.49}$$

$$= [e^{t\mathcal{L}^{\dagger}}1]_0^{\infty} \tag{6.50}$$

$$= -1,$$
 (6.51)

where the upper limit vanishes due to the absorbing boundary condition. We must now calculate the form of  $\mathcal{L}^{\dagger}$ . We have

$$(\mathcal{L}f(x),g(x)) = \left(f(x),\mathcal{L}^{\dagger}g(x)\right), \qquad (6.52)$$

$$\int_{a}^{b} dx \mathcal{L} f^{*}(x) g(x) = \int_{a}^{b} dx f^{*}(x) \mathcal{L}^{\dagger} g(x).$$
(6.53)

The strategy to find  $\mathcal{L}^{\dagger}$  is to integrate the LHS above by parts (given that  $\mathcal{L}$  is a differential operator) until we arrive at the RHS. Starting with the LHS:

$$\int_{-\infty}^{\infty} dx \mathcal{L}f^*(x)g(x) = \int_{-\infty}^{\infty} dx \left(\partial_x \frac{T(x)}{\xi(x)} \rho_{st}(x) \partial_x \rho_{st}^{-1}(x) f(x)\right)^* g(x), \tag{6.54}$$

where this choice of integration limits removes unwanted terms after integrating by parts. Here, the derivatives act to the right only on the terms inside the parentheses. Note also that the Langevin terms and probability densities must be purely real. Begin integrating by parts to find

$$\int_{-\infty}^{\infty} dx \mathcal{L}f^*(x)g(x) = -\int_{-\infty}^{\infty} dx \left(\frac{T(x)}{\xi(x)}\rho_{st}(x)\partial_x\rho_{st}^{-1}(x)f^*(x)\right)\partial_x g(x)$$
(6.55)

$$= -\int_{-\infty}^{\infty} dx \left(\partial_x \rho_{st}^{-1}(x) f^*(x)\right) \rho_{st}(x) \frac{T(x)}{\xi(x)} \partial_x g(x)$$
(6.56)

$$= \int_{-\infty}^{\infty} dx \rho_{st}^{-1}(x) f^*(x) \partial_x \rho_{st}(x) \frac{T(x)}{\zeta(x)} \partial_x g(x)$$
(6.57)

$$= \int_{-\infty}^{\infty} dx f^*(x) \rho_{st}^{-1}(x) \partial_x \rho_{st}(x) \frac{T(x)}{\xi(x)} \partial_x g(x)$$
(6.58)

$$= \int_{-\infty}^{\infty} dx f^*(x) \mathcal{L}^{\dagger} g(x).$$
(6.59)

We have used the fact that  $\rho_{st}(\infty) = \rho_{st}(-\infty) = 0$ . Thus, the adjoint of  $\mathcal{L}$  is found to be

$$\mathcal{L}^{\dagger} = \rho_{st}^{-1}(x)\partial_x \rho_{st}(x)\frac{T(x)}{\xi(x)}\partial_x, \qquad (6.60)$$

and the differential equation for the mean first-passage time is

$$\rho_{st}^{-1}(x)\partial_x\rho_{st}(x)\frac{T(x)}{\xi(x)}\partial_x\tau(x) = -1,$$
(6.61)

with the boundary condition  $\tau(x_b) = 0$ . Finally, the mean first-passage time can be solved for via the following:

$$\partial_x \rho_{st}(x) \frac{T(x)}{\xi(x)} \partial_x \tau(x) = -\rho_{st}(x), \tag{6.62}$$

$$\rho_{st}(x')\frac{T(x')}{\xi(x')}\partial_{x'}\tau(x') = -\int_{-\infty}^{x'} dx \rho_{st}(x),$$
(6.63)

$$\partial_{x'}\tau(x') = -\frac{\xi(x')}{T(x')\rho_{st}(x')} \int_{-\infty}^{x'} dx \rho_{st}(x),$$
(6.64)

$$\tau(x_0) = \int_{x_0}^{x_b} dx' \frac{\xi(x')}{T(x')\rho_{st}(x')} \int_{-\infty}^{x'} dx \rho_{st}(x).$$
(6.65)

This is our final equation for the mean first-passage time through a barrier at  $x_b$ , given a starting position of  $x_0$ .

#### 6.2.2 Underdamped limit

#### 6.2.2.1 Energy-diffusion form of the Fokker-Planck equation

In the underdamped regime the classical oscillations are approximately harmonic and the energy is approximately conserved over time-scales associated with classical oscillations. It is then convenient for us to re-express the Fokker-Planck equation for the phase space probability density to be in terms of the probability density of the energy of the classical coordinate. The probability density for the energy can be found by

$$\rho(E,t) = \int dx dp \delta(H(x,p) - E)\rho(x,p,t).$$
(6.66)

The  $\delta$ -function chooses only the phase space coordinates which yield H(x, p) = E. It is clear that  $\rho(E, t)$  is normalised since

$$\int dE\rho(E,t) = \int dE \int dx dp \delta(H(x,p) - E)\rho(x,p,t)$$
(6.67)

$$= \int dx dp \rho(x, p, t) \int dE \delta(H(x, p) - E)$$
(6.68)

$$= \int dx dp \rho(x, p, t) = 1. \tag{6.69}$$

Let's now define the operator

$$\Omega(E) = \int dx dp \delta(H(x, p) - E).$$
(6.70)

By applying  $\Omega(E)$  to the left of each side of (6.2) we obtain

$$\Omega(E)\partial_t \rho(x, p, t) = \Omega(E) \left( \Lambda + \xi(x) \left[ \partial_p \frac{p}{m} + \partial_p^2 T(x) \right] \right) \rho(x, p, t).$$
(6.71)

We expect that the  $\Omega(E)\Lambda\rho(x, p, t)$  term should go to zero since it corresponds to the case of no interactions with the environment; thus the energy distribution should be constant in time. Indeed, we can show this rigorously via

$$\Omega(E)\partial_t \rho_0(x, p, t) = \Omega(E)\Lambda \rho_0(x, p, t),$$
(6.72)

$$\partial_t \rho_0(E,t) = \int dx dp \delta(H(x,p) - E) \Lambda \rho_0(x,p,t)$$
(6.73)

$$= \int dx dp \delta(H(x,p) - E) \left[ \frac{\partial H}{\partial x} \partial_p - \frac{\partial H}{\partial p} \partial_x \right] \rho_0(x,p,t)$$
(6.74)

$$= \int dx dp \delta(H(x,p) - E) \left[ U'(x)\partial_p - \frac{p}{m}\partial_x \right] \rho_0(x,p,t)$$
(6.75)

$$= \int dx dp \delta(H(x,p) - E) \left[ U'(x) \frac{p}{m} \partial_H - \frac{p}{m} U'(x) \partial_H \right] \rho_0(x,p,t)$$
(6.76)

$$= 0,$$
 (6.77)

where  $\rho_0$  is the probability density in the unperturbed case. As a result, we are left with

$$\Omega(E)\partial_t \rho(x, p, t) = \Omega(E)\xi(x) \left[\partial_p \frac{p}{m} + \partial_p^2 T(x)\right] \rho(x, p, t).$$
(6.78)

Let's consider each of the two bracketed terms individually. The first term is given by

$$A^{(1)} = \Omega(E)\xi(x)\partial_p \frac{p}{m}\rho(x, p, t)$$
(6.79)

$$= \int dx\xi(x) \int dp\delta(H(x,p)-E) \left[\frac{1}{m}\rho(x,p,t) + \frac{p}{m}\partial_p\rho(x,p,t)\right].$$
 (6.80)

We make the assumption that the phase-space probability density can be expressed as a function of the Hamiltonian *H*, such that

$$\rho(x, p, t) = \phi(H, t). \tag{6.81}$$

The function  $\phi$  is determined by enforcing that it leads to the correct energy distribution:

$$\rho(E,t) = \int dx dp \delta(H(x,p) - E)\rho(x,p,t) = \int dx dp \delta(H(x,p) - E)\phi(H,t)$$
(6.82)

$$=\phi(E,t)\int dxdp\delta(H(x,p)-E)$$
(6.83)

$$=\phi(E,t)\Omega(E). \tag{6.84}$$

Let's now take (6.80) and replace  $\rho(x, p, t)$  by  $\phi(H, t)$  while utilizing the fact that  $\partial_p = \frac{p}{m} \partial_H$ :

$$A^{(1)} = \int dx \xi(x) \int dp \delta(H(x,p) - E) \left[ \frac{1}{m} \phi(H,t) + \left(\frac{p}{m}\right)^2 \partial_H \phi(H,t) \right].$$
(6.85)

The  $\delta$ -function allows us to consider H = E under the integral. We will then make use of the following  $\delta$ -function identity:

$$\int dp f(p) \delta(p^2 - a^2) = \frac{f(a)}{2a}, \qquad a > 0.$$
(6.86)

In order to use the identity, we will introduce the arbitrary variable  $q = \frac{p}{\sqrt{2m}}$ ; we then need to change the integration variable to *q*. With some manipulation, we find

$$A^{(1)} = \frac{1}{m} \int dx \xi(x) \int dp \delta\left(\frac{p^2}{2m} - (E - U(x))\right) \left[\phi(E, t) + \frac{p^2}{m} \partial_E \phi(E, t)\right]$$
(6.87)

$$=\frac{1}{m}\int dx\xi(x)\int dp\delta\left(\left[\frac{p}{\sqrt{2m}}\right]^2 - \sqrt{E - U(x)}^2\right)\left[\phi(E,t) + \frac{p^2}{m}\partial_E\phi(E,t)\right]$$
(6.88)

$$=\frac{\sqrt{2m}}{m}\int dx\xi(x)\int dq\delta\left(q^2-\sqrt{E-U(x)}^2\right)\left[\phi(E,t)+2q^2\partial_E\phi(E,t)\right]$$
(6.89)

$$=\frac{\sqrt{2m}}{2m}\phi(E,t)\int dx\frac{\xi(x)}{\sqrt{E-U(x)}}+\frac{\sqrt{2m}}{m}\partial_E\phi(E,t)\int dx\frac{\xi(x)(E-U(x))}{\sqrt{E-U(x)}}$$
(6.90)

$$=\frac{1}{2}\sqrt{\frac{2}{m}}\phi(E,t)\int dx\frac{\xi(x)}{\sqrt{E-U(x)}}+\sqrt{\frac{2}{m}}\partial_E\phi(E,t)\int dx\xi(x)\sqrt{E-U(x)}$$
(6.91)

$$=\partial_E \left\{ \sqrt{\frac{2}{m}} \phi(E,t) \int dx \xi(x) \sqrt{E - U(x)} \right\}$$
(6.92)

$$= \partial_E \left\{ \mu(E)\phi(E,t) \right\}.$$
(6.93)

An equivalent method of simplification can be applied to the second term in (6.78). The main steps are as follows:

$$A^{(2)} = \Omega(E)\xi(x)\partial_p^2 T(x)\rho(x,p,t), \tag{6.94}$$

$$= \int dx dp \delta(H(x,p) - E)\xi(x)T(x)\partial_p^2 \phi(H,t)$$
(6.95)

$$= \int dx dp \delta(H(x,p) - E)\xi(x)T(x)\partial_p \frac{p}{m}\partial_E \phi(E,t)$$
(6.96)

$$= \int dx dp \delta(H(x,p) - E)\xi(x)T(x) \left[\frac{1}{m}\partial_E + \left(\frac{p}{m}\right)^2 \partial_E^2\right]\phi(E,t)$$
(6.97)

$$= \int dx \xi(x) T(x) \int dp \delta(H(x,p) - E) \left[\frac{1}{m}\partial_E + \left(\frac{p}{m}\right)^2 \partial_E^2\right] \phi(E,t)$$
(6.98)

$$= \frac{1}{m} \partial_E \phi(E,t) \int dx \xi(x) T(x) \int dp \delta(H(x,p) - E) + \frac{1}{m} \int dx \xi(x) T(x) \int dp \delta(H(x,p) - E) \frac{p^2}{m} \partial_E^2 \phi(E,t)$$
(6.99)

$$=\frac{\sqrt{2m}}{2m}\partial_E\phi(E,t)\int dx\frac{\xi(x)T(x)}{\sqrt{E-U(x)}}+\frac{\sqrt{2m}}{m}\partial_E^2\left\{\phi(E,t)\right\}\int dx\xi(x)T(x)\sqrt{E-U(x)} \quad (6.100)$$

$$=\partial_E \left\{ \sqrt{\frac{2}{m}} \int dx \xi(x) T(x) \sqrt{E - U(x)} \partial_E \phi(E, t) \right\}$$
(6.101)

$$= \partial_E \left\{ \nu(E) \partial_E \phi(E, t) \right\}.$$
(6.102)

Putting all the components back together, our Fokker-Planck equation in the energy-diffusion form is given by

$$\partial_t \rho(E,t) = \partial_E \left( \mu(E) + \nu(E) \partial_E \right) \phi(E,t)$$
(6.103)

$$= \partial_E \left( \mu(E) + \nu(E) \partial_E \right) \Omega^{-1}(E) \rho(E, t), \tag{6.104}$$

where we have defined

$$\mu(E) = \sqrt{\frac{2}{m}} \int dx \xi(x) \sqrt{E - U(x)}, \qquad \nu(E) = \sqrt{\frac{2}{m}} \int dx \xi(x) T(x) \sqrt{E - U(x)}.$$
(6.105)

We can additionally find a more useful form for  $\Omega(E)$ . To do so, we again utilise (6.86) to obtain

$$\Omega(E) = \int dx dp \delta(H(x, p) - E)$$
(6.106)

$$= \int dx dp \delta \left( \left[ \frac{p}{\sqrt{2m}} \right]^2 - \sqrt{E - U(x)}^2 \right)$$
(6.107)

$$=\sqrt{2m}\int dxdq\delta\left(q^2-\sqrt{E-U(x)}^2\right) \tag{6.108}$$

$$=\sqrt{\frac{m}{2}}\int dx \frac{1}{\sqrt{E-U(x)}}.$$
(6.109)

#### 6.2.2.2 Stationary solution to the energy-diffusion equation

The energy-diffusion equation given in (6.104) has a form very reminiscent of the overdamped diffusion equation in (6.6). As such, many of the same techniques used in the overdamped case are also applicable here and we will gloss over the intimate details where appropriate. Repeating the logic from Section 6.2.1.1, the probability current (now in terms of energy) must go to zero at  $E = \infty$  to retain the normalisation of the probability distribution. So,

$$S(E,t) = (\mu(E) + \nu(E)\partial_E) \,\Omega^{-1}(E)\rho(E,t), \tag{6.110}$$

$$S(\infty, t) = 0. \tag{6.111}$$

This implies that in the stationary case, S(E) = 0 for all *E*, and the equation for the stationary distribution satisfies

$$0 = \mu(E)\Omega^{-1}(E)\rho_{st}(E) + \nu(E)\partial_E\Omega^{-1}(E)\rho_{st}(E).$$
(6.112)

This is a separable first-order differential equation for  $\Omega^{-1}(E)\rho_{st}(E)$  which can be solved to give

$$\rho_{st}(E) = \Omega^{-1}(a)\rho_{st}(a)\Omega(E)e^{-\int_{a}^{E} dE'\frac{\mu(E')}{\nu(E')}},$$
(6.113)

where *a* is arbitrary. Enforcing  $\rho_{st}$  to be normalised then yields

$$\rho_{st}(a) = \frac{\Omega(a)}{\int_0^\infty dE \Omega(E) e^{-\int_a^E dE' \frac{\mu(E')}{\nu(E')}}}.$$
(6.114)

The resultant stationary solution then takes the form

$$\rho_{st}(E) = Z^{-1} \Omega(E) e^{-\int_a^E dE' \frac{\mu(E')}{\nu(E')}},$$
(6.115)

where the partition function, Z, is given by

$$Z = \int_0^\infty dE \Omega(E) e^{-\int_a^E dE' \frac{\mu(E')}{\nu(E')}}.$$
 (6.116)

#### 6.2.2.3 Alternate form of the Energy-Diffusion equation

Similar to the overdamped case, knowledge of the stationary distribution allows us to reexpress the energy-diffusion equation in a more tenable form via

$$\partial_t \rho(E,t) = \partial_E D(E) \rho_{st}(E) \partial_E \rho_{st}^{-1}(E) \rho(E,t), \qquad (6.117)$$

where we have introduced the energy diffusion according to  $D(E) = \frac{\nu(E)}{\Omega(E)}$ . This is verified by substituting (6.115) into (6.117) and re-deriving (6.104):

$$\partial_t \rho(E,t) = \partial_E \frac{\nu(E)}{\Omega(E)} Z^{-1} \Omega(E) e^{-\int_a^E dE' \frac{\mu(E')}{\nu(E')}} \left[ \partial_E \left\{ \rho_{st}^{-1} \right\} \rho(E,t) + \rho_{st}^{-1} \partial_E \rho(E,t) \right]$$
(6.118)

$$=\partial_{E}\nu(E)Z^{-1}e^{-\int_{a}^{E}dE'\frac{\mu(E')}{\nu(E')}}\left[\left(Z\partial_{E}\left\{\Omega^{-1}(E)\right\}e^{\int_{a}^{E}dE'\frac{\mu(E')}{\nu(E')}}+Z\Omega^{-1}(E)\frac{\mu(E)}{\nu(E)}e^{\int_{a}^{E}dE'\frac{\mu(E')}{\nu(E')}}\right)\rho(E,t)\right]$$

$$+ Z\Omega^{-1}(E)e^{\int_{0}^{E} dE' \frac{\mu(E')}{\nu(E')}} \partial_{E}\rho(E,t) \Big]$$
(6.119)

$$= \partial_E \nu(E) \left[ \left( \partial_E \left\{ \Omega^{-1}(E) \right\} + \Omega^{-1}(E) \frac{\mu(E)}{\nu(E)} \right) \rho(E, t) + \Omega^{-1}(E) \partial_E \rho(E, t) \right]$$
(6.120)  
=  $\partial_E \left( \Omega^{-1}(E) \nu(E) \rho(E, t) + \nu(E) \partial_E \left\{ \Omega^{-1}(E) \right\} \rho(E, t) + \nu(E) \Omega^{-1}(E) \partial_E \rho(E, t) \right)$ 

$$= \partial_E \left( \Omega^{-1}(E) \mu(E) \rho(E,t) + \nu(E) \partial_E \left\{ \Omega^{-1}(E) \right\} \rho(E,t) + \nu(E) \Omega^{-1}(E) \partial_E \rho(E,t) \right)$$
(6.121)

$$=\partial_E \left(\Omega^{-1}(E)\mu(E)\rho(E,t) + \nu(E)\partial_E \Omega^{-1}(E)\rho(E,t)\right)$$
(6.122)

$$= \partial_E \left(\mu(E) + \nu(E)\partial_E\right) \Omega^{-1}(E)\rho(E,t).$$
(6.123)

Thus, it is satisfied.

#### 6.2.2.4 Calculation of the mean first-passage times

Noting the equivalence between our governing equations in the overdamped case in (6.23) and the underdamped case in (6.117), the derivations for the mean first-passage time are also equivalent, requiring only a change in variables and some alternate boundary conditions. Rather than repeat the derivation of Section 6.2.1.3, we simply present the result in the underdamped regime:

$$\tau(E_0) = \int_{E_0}^{E_b} dE' \frac{1}{D(E')\rho_{st}(E')} \int_0^{E'} dE\rho_{st}(E).$$
(6.124)

We use  $E_0$  to denote the initial energy of the classical coordinate which we will generally take to be at the minimum of the reaction potential.  $E_b$  then denotes the energy of the barrier between reactants and products.

# 6.3 Results

#### 6.3.1 The blowtorch effect

In this section we investigate Landauer's proposed blowtorch effect [215], in which a nonequilibrium system allows for coordinate-dependent variations to the dissipative forces acting on a particle which then has an effect on the properties of the steady-state distribution. Landauer's blowtorch effect plays a critical role in chemical reactions in molecular electronic junctions, therefore we first discuss its general features which will be relevant for our subsequent discussion. For pedagogical purposes, we will treat the coordinate-dependent diffusion and viscosity coefficients as inputs in this section in the hopes to gain a better understanding of the blowtorch effect before proceeding to the following sections in which we calculate the Langevin coefficients using our usual methods. For consistency with Kramers' seminal paper [208] on chemical reaction rates, our analysis is formulated in terms of the mean first escape time from the left minimum of a bistable potential, which we model according to a quartic of the form

$$U(x) = -ax^2 + bx^4, (6.125)$$

where *x* is our reaction coordinate. The constants *a* and *b* are adjustable parameters which determine the width and depth of the minimum. In all tests in this section, we set a = 0.04 and b = 0.008, such that  $U_b = 0.05$ . In addition, the particle always begins its trajectory with zero velocity at the minimum of the reaction potential. To begin with, the viscosity  $\xi_0$  and diffusion coefficients  $D_0$  are set to a constant value over the range of *x*, yielding a constant temperature as determined by the fluctuation-dissipation theorem.



Figure 6.2: An adjustable temperature spike is introduced which heats a chosen part of our reaction coordinate potential.

In order to introduce an inhomogeneity into the temperature, a Gaussian spike is applied to the diffusion coefficient locally at position  $x_0$ ,

$$D(x) = D_0 + D_{peak}(x), (6.126)$$

where

$$D_{peak}(x) = D_m e^{-\frac{(x-x_0)^2}{\sigma^2}},$$
(6.127)

with adjustable width  $\sigma$  and magnitude  $D_m$  parameters. The effective temperature profile is given by (4.38), the effective temperature at the peak is then given by

$$T_{max} = T_0 (1 + \frac{D_m}{D_0}), \tag{6.128}$$

where

$$T_0 = \frac{D_0}{2\xi_0}.$$
 (6.129)

This represents Laundauer's so-called "blowtorch" which heats a small segment of the reaction coordinate, as shown diagramatically in Figure 6.2. Here, the intention is to study the effect of shifting the temperature spike along the reaction coordinate on the mean first-passage time  $\tau$ . We analyse the overdamped and underdamped regimes separately for the same parameters except for the mass *m* of the Brownian particle, which is chosen to satisfy the desired regime. In Figure 6.3, we observe the behaviour of the mean first-passage time as the position of the temperature peak is shifted along the reaction coordinate (shown in blue), while the reaction



Figure 6.3: The calculated mean first-passage time  $\tau$  as a function of the temperature peak's position along the reaction coordinate, for the (a) overdamped and (b) underdamped regime (m = 1000a.u). The black line denotes  $\tau$  in the absence of an applied blowtorch. Parameters:  $D_0 = 0.01$ ,  $\xi_0 = 1$ ,  $\sigma = 0.05$ .

potential is shown as a reference in orange. In the underdamped regime, we observe  $\tau$  to be minimized when the heating is applied to the bottom of the potential. This enables the molecule to heat up quickly at low energies, and repeatedly attain more energy as it passes through this region in a near-harmonic manner.

The overdamped regime differs, in that  $\tau$  is minimized when the heating is applied approximately halfway up the potential, around the point of steepest ascent. In the overdamped regime, the escaping particle will very quickly equilibrate to any given temperature fluctuation to which it is exposed. As such, the heated region causes a flattening of the probability distribution in that region, nullifying the dependence of the distribution on the reaction coordinate. This causes an effective reduction to the height of the energy barrier  $U_b$  as elucidated by Landauer [214, 215]; a phenomenon which is maximized when the heating is applied in the region of steepest ascent. We note the counter-intuitive observation that if the heating is applied to the bottom of the potential in the overdamped case, this causes only a small reduction to  $\tau$ . This is because the particle will quickly lose the obtained energy as it returns to the cooler regions when it attempts to escape.

It is insightful for us to also study the effect of the strength of interaction of a Brownian particle with the environment, while maintaining a homogeneous temperature. This entails that any changes in the diffusion coefficient as a function of x will be counteracted by a corresponding changes in the viscosity coefficient at the same x, enforcing a homogeneous temperature as per the fluctuation-dissipation theorem. Here, we perform a similar analysis as above, such that we have a moveable peak of increased interaction (simultaneously locally increased diffusion *and* viscosity) while the temperature is homogeneous. The results of this are displayed in Figure 6.4.



Figure 6.4: The calculated mean first-passage time as a function of the interaction peak's position along the reaction coordinate, for the (a) overdamped and (b) underdamped regime ( $m_e = 1000$ a.u). The black line denotes  $\tau$  in the absence of an applied blowtorch. Parameters:  $D_0 = 0.01$ ,  $\xi_0 = 1$ ,  $\sigma = 0.05$ .

In the underdamped regime, we observe that the largest reduction to  $\tau$  occurs when the interaction peak is placed at the minimum. The decrease in  $\tau$  agrees with the homogeneouscase solution, with the distinction that reaction coordinates at higher energies in the potential have diminishing contributions to the decreasing  $\tau$ . In the overdamped regime, it is seen that the interaction peak results in an increase to  $\tau$  as also predicted in the homogeneous case. However, we observe that this is dominated by the increased interaction strength near to the maximum of the potential, while changing the interaction strength in the rest of the potential has negligible effect. This demonstrates that  $\tau$  has little regard for the interaction strength in the overdamped regime, except in the region approaching the maximum.

This general analysis arms us with the required physical intution before proceeding to the next section, in which we first observe how a Landauer blowtorch emerges naturally from a simple molecular junction model, then demonstrate the effect on hypothetical chemical reaction rates.

#### 6.3.2 Application to a molecule with a single current-carrying molecular orbital

In this section, we analyze the calculated mean first-passage time  $\tau$  for our model of a molecular junction. Contrary to Section 6.3.1, the viscosity and diffusion coefficients will be computed using nonequilibrium Green's functions according to eqs. (3.146) and (3.209). We consider the case of a single electronic level coupled to the left and right leads under some applied bias voltage. The molecular Hamiltonian is given by

$$H_M = (h_0 + \lambda x)a^{\dagger}a, \qquad (6.130)$$

where subscript  $a^{\dagger}$  and  $a^{\dagger}$  denote the creation and annihilation operators for an electron on the molecular orbital. Here, the dependency of  $H_M$  on the reaction coordinate acts to shift the electronic level, as scaled by the tuneable parameter  $\lambda$ . The left and right lead are each at room temperature (0.001au) and are symmetrically coupled to the central electronic state such that our level-width function is given by  $\Gamma_L = \Gamma_R = 0.03$ .

In the interest of consistency, we again utilize the same quartic to describe our classical nuclear potential for the reaction coordinate, which is now acted on by an additional adiabatic force term computed using nonequilibrium Green's functions according to equation 3.145. This has the effect of shifting and shallowing/deepening the reaction potential depending on the parameters chosen. We also allow for the manual shift of the external potential along the reaction coordinate according to some parameter  $x_a$ :

$$U(x) = -a(x - x_a)^2 + b(x - x_a)^4.$$
(6.131)

This means that when  $x_a = 0$ , the potential minimum (ignoring the effects of the adiabatic force) occurs at x = 0, while a positive  $x_a$  shifts the input potential to the right. Any bias voltage is applied symmetrically, such that  $\mu_L = -\mu_R = V/2$ , where  $\mu_L$  and  $\mu_R$  are the chemical potentials of the left and right leads.

We study the effect of applying a gate voltage to the system, as modelled by a shift in the  $h_0$ value. This allows for a degree of controllability of the reaction rates for a given system. Figures 6.5a and 6.5b demonstrate the resultant viscosity coefficient and temperature respectively, as a function of the reaction coordinate. Application of a gate voltage acts to shift the curve along the reaction coordinate. This analysis is performed for a non-zero bias voltage such that the temperature is now inhomogeneous in addition to the viscosity. In the underdamped regime shown in Figure 6.5d,  $\tau$  is minimized when the viscosity and temperature peaks are shifted near to the minimum of the reaction potential (note however, that the minimum in audoes not occur exactly when the peaks are shifted to the minimum of the potential due to the slight asymmetry of the reaction potential). In contrast, the overdamped regime displays highly non-trivial behaviour, arising as a result of the interplay between the strength of the viscosity and the temperature. In our analysis of the overdamped regime in the previous section, we noted that the dependence of  $\tau$  on the temperature is dominated by the region of steepest ascent up towards the maximum. Here, we again observe this behaviour as the large peak in Figure 6.5c corresponds to when the dip in the temperature occurs in this region (when the temperature peak has been shifted to the right). A corresponding but smaller peak also occurs due to a shift to the left in the temperature such that the low temperature aligns with the steep region of the potential. The difference in peak sizes arises as a result of the inhomogeneous viscosity, which per the previous section, we know is important in the region



Figure 6.5: The effect of an applied gate voltage to (a) the viscosity coefficient and (b) the effective temperature. The mean first-passage time  $\tau$  in the (c) overdamped and (d) underdamped regime is plotted against the peak coordinate of the viscosity and temperature (as determined by the applied gate voltage) for different  $\lambda$ . The coordinates of the minimum and maximum of the reaction potential are denoted by the vertical black lines in (c) and (d).

near the maximum of the reaction potential. The large peak in  $\tau$  occurs when the temperature is low in the steep region, while the viscosity is high towards the maximum. The small peak has a low viscosity near the maximum, explaining its comparatively smaller magnitude.

#### 6.3.3 Model of a two-level molecule

In this section, we expand the model to consider a two-level system. In our model, the molecular energy levels are taken to correspond to the bonding and anti-bonding states of a free  $H_2^+$  molecule [169]. As such, the molecular Hamiltonian now reads

$$H_M(t) = \sum_{ij} h_{ij}(q(t)) a_i^{\dagger} a_j,$$
(6.132)

where  $a_i^{\dagger}$  and  $a_j$  are now in the molecular orbital basis. The electronic Hamiltonian elements are represented in the form of a 2 × 2 matrix according to

$$h = \begin{pmatrix} H_b(q) & 0\\ 0 & H_a(q) \end{pmatrix}, \tag{6.133}$$

where we use  $H_b(q)$  and  $H_a(q)$  to denote the bonding and anti-bonding molecular orbitals, respectively, while *q* is the bond-length. The values for  $H_b(q)$  and  $H_a(q)$  are calculated according to molecular orbital theory [169] and are given by

$$H_b(q) = \frac{H_{AA} + H_{AB}}{1 + S_{AB}},$$
(6.134)

and

$$H_a(q) = \frac{H_{AA} - H_{AB}}{1 - S_{AB}},$$
(6.135)

where  $H_{AA}$  and  $H_{AB}$  are the Hamiltonian elements in the atomic basis and  $S_{AB}$  is the overlap integral between atomic 1s Slater orbitals. The constituent components are then given by

$$H_{AA} = -\frac{1}{2} + e^{-2q} \left( 1 + \frac{1}{q} \right) - \frac{1}{q},$$
(6.136)

$$H_{AB} = -\frac{S_{AB}(q)}{2} - e^{-q}(1+q), \qquad (6.137)$$

and

$$S_{AB} = e^{-q} (1 + q + q^2/3).$$
(6.138)



Figure 6.6: The adiabatic potential as a function of the bond-length presented for (a) varying bias voltages and (b) varying the magnitude of leads coupling to  $H_a$ . Parameters: V = 0,  $\Gamma_{aa}/\Gamma_{bb} = 1$ , unless otherwise specified.  $\Gamma_{bb} = 0.03$  in all calculations.



Figure 6.7: The effect of varying the bias voltage is shown for the (a) viscosity coefficient and (b) the effective temperature, as a function of the bond length. Insets: Shows the same quantity at V = 0.02 for  $\Gamma_{aa}/\Gamma_{bb} = 0$  (dashed) and  $\Gamma_{aa}/\Gamma_{bb} = 0.5$  (solid). Parameters;  $\Gamma_{aa}/\Gamma_{bb} = 1$  in the main plots.  $\Gamma_{bb} = 0.03$  in all calculations.



Figure 6.8: The mean first-passage time  $\tau$  as a function of the bias voltage, varying the coupling to  $H_a$  in the (a) overdamped and (b) underdamped cases.

In the interest of simplicity, each of the molecular orbitals is symmetrically coupled to the left and right leads; as controlled by the parameter  $\Gamma$  which now takes the form of a matrix as per

$$\Gamma_{\alpha} = \begin{pmatrix} \Gamma_{\alpha,bb} & \Gamma_{\alpha,ba} \\ \Gamma_{\alpha,ab} & \Gamma_{\alpha,aa} \end{pmatrix}$$
(6.139)

for the  $\alpha$  lead, where the off-diagonal components can be defined according to,

$$\Gamma_{\alpha,ba} = \Gamma_{\alpha,ab} = \sqrt{\Gamma_{\alpha,aa}\Gamma_{\alpha,bb}}.$$
(6.140)

In each test, we have  $\mu_L = -0.7$  and  $\mu_R = \mu_L - V$ , while the lead temperatures are again set to room temperature.

The external potential now represents the classical nuclear repulsion, which in atomic units is given by

$$U(q) = \frac{1}{q}.$$
 (6.141)

Inclusion of the electronic forces allows us to generate modified electronic potentials for varied parameters in order to assess the molecular stability. Examples of these potentials are shown in Figure 6.6; where in (a) an applied bias voltage is shown to decrease the energy required for bond rupture, while (b) shows the effect of the additional electronic level which when occupied, acts to increase the bond stability.

Along with the shape of the effective potential, the bond stability is also determined by the electronic viscosity and effective temperature, which are demonstrated in Figure 6.7. In the viscosity coefficient, each curve shows a peak at small q, which approximately corresponds to when  $H_a$  crosses the fermi-level of the left lead. Likewise, the peaks at large q are a result of  $H_b$  crossing the fermi-level of the right, then left, leads (these split peaks merge together when

V = 0). The inset plot demonstrates the effect of allowing an additional transport channel through the excited state which not only introduces the peak at small q, but also increases the magnitude of the viscous forces overall. The effective temperature is equal to the leads temperature for V = 0, while non-zero voltages yield a complex array of localized heating and cooling effects, which arise as the energy levels shift in and out of the resonance region as the bond-length is increased.

These competing effects culminate in our calculation of the mean first-passage time, which is demonstrated in Figure 6.8 as a function of the bias voltage, for different coupling values to the excited electronic state. In both limiting regimes, an increase to the bias voltage acts to destabilize the bond and decrease  $\tau$ , both due to the increased effective temperatures and the weakening of the bond due to the current-induced forces. In the overdamped regime, allowing the leads to be coupled to an additional level in the central region has a stabilizing effect for all voltages tested, increasing the average amount of time for bond rupture. The underdamped case shows similar behavior for very low voltages; however, at higher voltages the availability of the additional transport channel through the excited state increases the current-induced forces such that the energy required for a bond-rupture is found more easily, decreasing  $\tau$ .

# 6.4 Summary

In this section, we have demonstrated that the rates of chemical reactions for molecules in electronic junctions depend on three crucial ingredients; the potential energy surface which defines the energy required for a configuration change or bond rupture, the rate of the energy removal from vibrational to electronic degrees of freedom given by the electronic viscosity coefficient, and lastly, the effective temperature dynamically established in the molecule. While the magnitude of these quantities is of high importance, the local distribution of the viscosity and effective temperature along the potential energy surface (Landauer's blowtorch effect) also proves to be critical.

The addition of localized heating and cooling effects as a result of inhomogeneity with respect to the molecular configuration has been shown to induce significant variations in the mean first-passage time, as calculated according to a Fokker-Planck description. This has been demonstrated for a single-level molecular junction model, as well as a two-level model inspired by  $H_2^+$  molecular orbitals with the bond length considered as the reaction coordinate. This interplay between the amount of energy required for bond rupture and the energy supplied due to tunneling electrons has been shown to be strongly dependent on the choice of experimentally tuneable parameters for the system. This enables the possibility of a high degree of controllability for molecular junction systems, with promises of controlled initiation of chemical reactions or conversely, enforcing the stability of specific configurations within the system.

# **Ehrenfest dynamics**

This chapter contains material that has been previously published in the following journal article:

*Emergence of negative viscosities and colored noise under current-driven Ehrenfest molecular dynamics,* R.J. Preston, T.D. Honeychurch, D.S. Kosov, arXiv preprint, arXiv:2204.08278

# 7.1 Motivation

In this chapter, we extend the quasi-classical formalism by utilising a numerically exact method to calculate the forces acting on our classical coordinates without resorting to the assumption of a time-scale separation within the system. This is commonly known as the Ehrenfest approach to classical dynamics and it has garnered significant interest in the modelling of nuclear motion in nanoscale systems [100, 132–140]. This approach treats the electron-nuclear interaction on a mean-field level; it therefore does not provide a full description of the inelastic scattering between electrons and nuclei and cannot fully capture the effects of joule heating within the system [133, 134, 154–156]. Efforts have been made to remedy these caveats via perturbative corrections to the electron-nuclear correlations with some success [155, 156]. However, in this study we seek only to utilise Ehrenfest dynamics as a basis for comparison for predictions made by the perturbative Langevin approach which we have applied thus far.

One such predicted phenomenon which we encountered in Section 4 is the notion of a negative dissipation; under a Langevin approach, this implies that the viscosity coefficient becomes negative [132, 140, 143, 146, 152, 165, 166]. In this regime, energy is applied to rather than dissipated from the classical coordinate until it reaches unsustainable temperatures for the device. Negative dissipations have also been predicted using purely quantum mechanical methods in which a population inversion in the quantized phonons leads to ever-increasing temperatures [89, 232–237]. The physicality of such theoretical results have often been called into question, thought to arise as an artifact of assumptions applied in the theory rather than a demonstration of real behaviour [83]. The application of Ehrenfest dynamics allows us to avoid assuming a time-scale separation in the system. In doing so, we once again observe the emergence of negative dissipations and validate the results of the perturbative Langevin approximation, depending on the parameter range applied. We note, however, that implicit in the assumption of classical vibrations is an assumption of time-scale separation between the massive, slow-moving classical particle and the surrounding quantum environment. However, one can conceive of regimes in which a classical description for vibrations is valid even in the absence of a time-scale separation; for example, in the case of very high vibrational temperatures. The approach introduced in this chapter allows us to probe these regimes.

The Ehrenfest approach additionally allows for the exploration of the autocorrelations in the stochastic force. In general, the stochastic force is correlated at different times dependent on the electronic structure of the system considered; this corresponds to coloured noise [120, 162, 238]. The correlations are additionally dependent on the non-adiabatic motion of the classical coordinate. However, it is often computationally infeasible to account for coloured noise and it becomes necessary to employ a white-noise approximation. Under this approximation, the coloured-noise diffusion is replaced by a Markovian, white-noise equivalent which attempts to produce the same dynamical behaviour [142–144, 149, 152, 172]. We apply our method to investigate the effects of a time-scale separation on the diffusion coefficient along with assessing the validity of the white-noise approximation to the diffusion under a variety of regimes.

In Section 7.2 we introduce the theory which describes the classical dynamics. This involves the introduction of the Ehrenfest force along with its corresponding perturbative Langevin approximation, both expressed in terms of non-equilibrium Green's functions. We also discuss our iterative method for evaluating the Ehrenfest force through time. In Section 7.3.1, we demonstrate the accuracy of the perturbative approximation for a simple system consisting of a single classical degree of freedom, while in Section 7.3.2 we then apply Ehrenfest dynamics to a system with two classical degrees of freedom. Finally, in Section 7.3.3 we utilise our method to evaluate the diffusion coefficient and the suitability of the white-noise approximation for the stochastic force over a range of parameters.

# 7.2 Theory

#### 7.2.1 The Ehrenfest force

Under the influence of a quantum environment, a system of vibrational degrees of freedom in the classical limit is calculated in its most general form according to

$$\mathbf{f}(t) = -\nabla U(\mathbf{x}) - \langle \nabla H(\mathbf{x}) \rangle + \delta \mathbf{f}(t).$$
(7.1)

The main object of this chapter is the Ehrenfest force, defined as

$$\mathbf{F}^{\text{ehr}}(t) = -\langle \nabla H(\mathbf{x}) \rangle. \tag{7.2}$$

For our Hamiltonian where we neglect any motion on the leads interface, the Ehrenfest force can be represented in terms of the lesser component of exact non-equilibrium Green's functions as

$$F_{\nu}^{\rm ehr}(t) = i {\rm Tr} \Big\{ \partial_{\nu} h(t) G^{<}(t,t) \Big\}, \tag{7.3}$$

where *h* contains the elements of the molecular Hamiltonian. A Langevin description is found by applying a time-scale separation to the Ehrenfest force, where following the steps detailed in Section 3.3, we find for an arbitrary classical degree of freedom  $\nu$ ,

$$F_{\nu}^{\rm ehr}(t) = i {\rm Tr} \left\{ \int \frac{d\omega}{2\pi} \partial_{\nu} h(t) \left( \widetilde{G}_{(0)}^{<}(t,\omega) + \widetilde{G}_{(1)}^{<}(t,\omega) + \ldots \right) \right\}$$
(7.4)

$$= \underbrace{F_{\nu,(0)} + F_{\nu,(1)}}_{\text{retained in Langevin approach}} + F_{\nu,(2)} + \dots$$
(7.5)

Retaining only the zeroth and first order contributions to the Ehrenfest force yields the deterministic forces present in the Langevin description, namely the adiabatic force and frictional force.

Ehrenfest dynamics is the process of evolving the vibrational degrees of freedom according to only the Ehrenfest force while neglecting the contribution due to the stochastic force  $\delta f(t)$  in (7.1). As discussed, the Ehrenfest force alone is ill-equipped to capture the entirety of the dynamics of the system. However, Ehrenfest dynamics simulations allow for a direct insight into the importance of the higher order forces present in (7.5) which are ordinarily neglected in the Langevin approach.

### 7.2.2 Time-stepping approach to the evolution of the Green's function

Clearly, if we are able to calculate  $G^{<}(t,t)$  at each time, then (7.3) allows us to readily calculate the Ehrenfest force without need to resort to a perturbative approach involving time-scale separation. In this section, we introduce our algorithm for iteratively evolving  $G^{<}(t,t)$  forwards in time. In approaching these calculations, we borrow the main defined quantities from reference [195]. The lesser and greater Green's function in the time domain are given by the Keldysh equation,

$$G^{}(t,t') = \int dt_1 \int dt_2 G^R(t,t_1) \Sigma^{}(t_1,t_2) G^A(t_2,t').$$
(7.6)

For the sake of clarity, in this section we will use (...) to denote a functional dependence, whereas [...] will denote a term in the equation. Now we will take (7.6) and express the  $\Sigma^{</>}$  term according to the inverse Wigner transform of (3.58). In the lesser case, we find

$$G^{<}(t,t') = i\sum_{\alpha} \int dt_1 \int dt_2 G^R(t,t_1) \int \frac{d\omega}{2\pi} e^{-i\omega[t_1-t_2]} f_{\alpha}(\omega) \Gamma_{\alpha} G^A(t_2,t')$$
(7.7)

$$= i \sum_{\alpha} \int dt_1 \int dt_2 G^R(t, t_1) \int \frac{d\omega}{2\pi} e^{-i\omega[t_1 - t_2]} f_{\alpha}(\omega) \Gamma_{\alpha} G^A(t_2, t) e^{i\omega[t - t]} e^{i\omega[t' - t']}$$
(7.8)

$$=i\sum_{\alpha}\int \frac{d\omega}{2\pi}f_{\alpha}(\omega)e^{i\omega[t'-t]}\int dt_{1}e^{i\omega[t-t_{1}]}G^{R}(t,t_{1})\Gamma_{\alpha}\int dt_{2}e^{-i\omega[t'-t_{2}]}G^{A}(t_{2},t')$$
(7.9)

$$=i\sum_{\alpha}\int \frac{d\omega}{2\pi}e^{-i\omega\tau}f_{\alpha}(\omega)A(\omega,t)\Gamma_{\alpha}A^{\dagger}(\omega,t').$$
(7.10)

An equivalent derivation can be applied in the greater case to find

$$G^{>}(t,t') = -i\sum_{\alpha} \int \frac{d\omega}{2\pi} e^{-i\omega\tau} [1 - f_{\alpha}(\omega)] A(\omega,t) \Gamma_{\alpha} A^{\dagger}(\omega,t').$$
(7.11)

Here we have defined the quantity,

$$A(\omega, t) = \int dt_1 e^{i\omega[t-t_1]} G^R(t, t_1).$$
(7.12)

The evolution of  $G^R$  is found via the Kadanoff-Baym equation in the time domain:

$$\left(i\frac{\partial}{\partial t} - h(t)\right)G^{R}(t,t') = \delta(t-t') + \int dt_{1}\Sigma^{R}(t,t_{1})G^{R}(t_{1},t').$$
(7.13)

By utilising the fact that

$$\Sigma^{R}(t,t') = -\frac{i}{2}\Gamma\delta(t-t'), \qquad (7.14)$$

we can solve for the general solution of (7.13) as

$$G^{R}(t,t') = -i\Theta(t-t')\hat{T}\exp\Big\{-i\int_{t'}^{t} dt_{1}h(t_{1}) - \frac{1}{2}\Gamma[t-t']\Big\}.$$
(7.15)

Here,  $\hat{T}$  is the time-ordering operator and  $\Theta$  is the Heaviside step function. By substituting (7.15) into (7.12), we arrive at

$$A(\omega,t) = -i \int_{-\infty}^{t} dt_1 \hat{T} \exp\left\{i\omega[t-t_1] - i \int_{t_1}^{t} dt_2 h(t_2) - \frac{1}{2}\Gamma[t-t_1]\right\}.$$
(7.16)

This is the quantity which we will iteratively evolve forwards in time, from which we can then extract  $G^{<}$  via (7.10). We begin by applying a step  $\Delta t$  forwards in time to (7.16)),

$$A(\omega, t + \Delta t) = -i \int_{-\infty}^{t + \Delta t} dt_1 \hat{T} \exp\left\{i\omega[t + \Delta t - t_1] - i \int_{t_1}^{t + \Delta t} dt_2 h(t_2) - \frac{1}{2}\Gamma[t + \Delta t - t_1]\right\}$$
(7.17)

$$= -i \int_{-\infty}^{t} dt_1 \hat{T} \exp\left\{i\omega[t + \Delta t - t_1] - i \int_{t_1}^{t + \Delta t} dt_2 h(t_2) - \frac{1}{2}\Gamma[t + \Delta t - t_1]\right\}$$
(7.18)

$$-i\int_{t}^{t+\Delta t} dt_{1}\hat{T}\exp\left\{i\omega[t+\Delta t-t_{1}]-i\int_{t_{1}}^{t+\Delta t} dt_{2}h(t_{2})-\frac{1}{2}\Gamma[t+\Delta t-t_{1}]\right\}$$
(7.19)

$$= A^{A}(\omega, t + \Delta t) + A^{B}(\omega, t + \Delta t).$$
(7.20)

Here we have split *A* into  $A^A$  which reflects how the history before *t* informs the system at  $t + \Delta t$ , and  $A^B$  which contains the effects of the system from *t* to  $t + \Delta t$ .  $A^A$  can be further simplified by partitioning the inner integral as follows:

$$A^{A}(\omega, t + \Delta t) = -i \int_{-\infty}^{t} dt_{1} \hat{T} \exp\left\{i\omega\Delta t - i \int_{t}^{t+\Delta t} dt_{2}h(t_{2}) - \frac{1}{2}\Gamma\Delta t\right\}$$
(7.21)

$$\times \hat{T} \exp\left\{i\omega[t-t_1] - i\int_{t_1}^t dt_3 h(t_3) - \frac{1}{2}\Gamma[t-t_1]\right\}$$
(7.22)

$$= \hat{T}\exp\left\{i\omega\Delta t - i\int_{t}^{t+\Delta t} dt_{2}h(t_{2}) - \frac{1}{2}\Gamma\Delta t\right\}A(\omega, t).$$
(7.23)

We will make the assumption that for a sufficiently small  $\Delta t$ , h(t) can be approximated as being piecewise constant. Thus, at some time-step  $t_n$ , we assume that for  $t_n < t < t_{n+1}$ , we have  $h(t) = h(t_n)$ . This entails that our time step size should be sufficiently small in the computational implementation when calculating classical trajectories. This enables us to directly calculate the integrals over h(t) appearing in (7.23) and (7.19) along with removing the time-ordering operators. We thus re-express  $A^A(\omega, t + \Delta t)$  and  $A^B(\omega, t + \Delta t)$  according to

$$A^{A}(\omega, t + \Delta t) = \exp\left\{i\Delta t\left(\omega - h(t) + \frac{i}{2}\Gamma\right)\right\}A(\omega, t),$$
(7.24)

and

$$A^{B}(\omega, t + \Delta t) = -i \int_{0}^{\Delta t} dt_{2} \exp\left\{it_{2}\left(\omega - h(t) + \frac{i}{2}\Gamma\right)\right\},$$
(7.25)

$$= -i\left(e^{\Lambda\Delta t} - I\right)\Lambda^{-1},\tag{7.26}$$

where *I* is the identity matrix and for cleanliness, we have used  $\Lambda = i \left( \omega - h(t) + \frac{i}{2} \Gamma \right)$ . Here we have used the matrix exponential identity:

$$\int_{0}^{T} dt e^{Xt} = \left(e^{XT} - I\right) X^{-1}.$$
(7.27)

Now we have everything we need to be able to perform an Ehrenfest simulation of the classical dynamics. The algorithm functions as follows. First, we assume an adiabatic initial condition such that (7.12) at the initial time is given by

$$A(\omega,t) = \tilde{G}^R_{(0)}(T,\omega), \qquad (7.28)$$

for which we already have an explicit expression for. The initial force can then be computed according to (7.10) and (7.3) given the chosen initial conditions for the classical coordinate. The calculated Ehrenfest force feeds into an external algorithm which updates the nuclear dynamics to the next time step, at which point we use (7.24) and (7.26) to non-adiabatically compute *A* at the next time step. From here the process repeats, yielding a wholly non-adiabatic, classical trajectory in time.

# 7.3 Results

#### 7.3.1 Single classical degree of freedom

With our time-stepping algorithm at our disposal, we can simulate classical vibrations using Ehrenfest dynamics. For the purposes of our simulations, we entirely disregard the stochastic force and instead focus solely on the deterministic forces. When we refer to the *perturbative* method of simulation, this means we are evolving the classical coordinate according to the deterministic forces present in the Langevin equation; namely, the adiabatic and frictional forces along with any external potentials.

It must be emphasized that the demonstrated dynamics are not physical since we do not include the stochastic force and so we cannot hope to have a full description of heating effects. However, it is not intended to be; the goal of this study is to identify the applicable regimes of the Langevin method via comparison with Ehrenfest dynamics.

First, we present results for a two-level system with a single classical degree of freedom. The matrix elements of the molecular Hamiltonian take the form

$$H_M = \begin{pmatrix} -\lambda x & \eta \\ \eta & \lambda x \end{pmatrix}, \tag{7.29}$$



Figure 7.1: The viscosity coefficient as a function of the classical coordinate.

where the classical coordinate *x* has the effect of linearly shifting the two atomic orbitals and  $\eta$  dictates the overlap. We choose the left lead to be coupled to the first state and the right lead to be coupled to the second state which gives our  $\Gamma$  matrices the following form:

$$\Gamma_L = \begin{pmatrix} \gamma & 0 \\ 0 & 0 \end{pmatrix}, \quad \Gamma_R = \begin{pmatrix} 0 & 0 \\ 0 & \gamma \end{pmatrix}.$$
 (7.30)

We choose to model the classical potential for any degree of freedom according to a harmonic potential as given by

$$U(\mathbf{x}) = \sum_{\nu} \frac{1}{2} k_{\nu} (\nu - \nu_0)^2, \qquad (7.31)$$

where  $k_{\nu}$  is the spring constant for the  $\nu$  degree of freedom, and  $\nu_0$  is a parameter which shifts the potential along the  $\nu$  coordinate. In this section, the common parameters are  $\lambda = \eta = 0.1$ ,  $\gamma = 0.05$ , k = 1,  $x_0 = -0.22$  and  $\mu_L = -\mu_R = 0.12$ , where  $\mu_{\alpha}$  is the chemical potential of the  $\alpha$ lead. In contrast to the single-level case, this model allows us to observe negative viscosities. An example of this is shown in Figure 7.1 where the coordinate dependent viscosity coefficient (now a scalar function in the case of a single classical degree of freedom) becomes negative in a small region around  $x \approx -0.2$ .

By utilising our time-stepping algorithm to evolve  $G^{<}$  in time as presented in the previous section, we can calculate the Ehrenfest force as a function of time from which we can then computationally simulate the dynamics of the classical coordinate. In Figure 7.2, we calculate a classical Ehrenfest trajectory and record  $F^{ehr}$  at each time step. We also record the corresponding forces which the classical coordinate would experience under the perturbative truncation of  $F^{ehr}$  after the first order. We note that the methods clearly differ in the transient



Figure 7.2: Trajectory in time of  $F^{\text{ehr}}(t)$  (Ehrenfest) and  $F_{(0)}(t) + F_{(1)}(t)$  (perturbative).  $\Omega/\Gamma \approx 0.32$ .



Figure 7.3: Comparison of the first order force against the sum of all higher order forces. (a)  $\Omega/\Gamma \approx 0.14$ , (b)  $\Omega/\Gamma \approx 3.2$ .

regime depending on the chosen initial conditions, before each settles into periodicity as the coordinate oscillates in time. The cause of the differences between the calculated Ehrenfest and perturbative forces are made clearer in Figure 7.3, where a direct comparison has been made of the magnitude of the first order force relative to the sum of all higher order forces  $(F_{(2)} + F_{(3)} + ...)$  for different values of  $\Omega/\Gamma$ . This is achieved by varying the effective mass of the classical coordinate while keeping all other parameters constant. We can then estimate  $\Omega$  by assuming that the oscillations are approximately harmonic. We observe that when  $\Omega/\Gamma$  is small in (a), the higher order forces have only a small relative contribution. In (b) however,  $\Omega/\Gamma$  is no longer small and thus our perturbative assumption is no longer satisfied, meaning the higher order forces have become increasingly relevant.

Calculation of the time-dependent forces allows us to then simulate the phase-space trajectory of the classical coordinate as a function of time. Figure 7.4 shows time dependent trajectories of the classical coordinate *x* for three different values of the small parameter  $\Omega/\Gamma$ . We also calculate the instantaneous power of the classical coordinate at each time step according to  $(F^{\text{ehr}} - F_{(0)}) \cdot \frac{p}{m}$ , which includes only the effects of the excitational and dissipative forces. The classical coordinate is intentionally confined to the region of negative viscosity shown in Figure 7.1 via our choice of U(x) such that under the perturbative assumption, the instantaneous power will be positive at all time-steps. We observe that when  $\Omega/\Gamma \ll 1$  as in (a); rendering

the perturbative approximation as valid, the instantaneous power is overwhelmingly positive in agreeance with the perturbative approximation. This entails that the oscillations will increase until reaching regions of positive viscosity, whereby they will form a limit cycle. This is further illustrated in Figure 7.6 via long trajectories for the same parameters, where the amplitude of oscillations increases in both the Ehrenfest and perturbative approaches. This result demonstrates that even in the absence of time-scale separation, negative viscosities emerge and dictate the behaviour of the system. However, we observe the resultant trajectories from the two methods to diverge from each other over longer time-scales, demonstrating the importance of the higher order forces even for these parameters where we expect they can be reasonably neglected. We note that Ehrenfest dynamics has been used to observe the effects of negative viscosities in different regimes in the literature [132, 136, 140, 237]. In Figure 7.4 (b) and (c) where  $\Omega/\Gamma > 1$  and our perturbative assumption is no longer adequate, we observe that the instantaneous power is more often negative wherein the electronic environment is taking energy away from the classical coordinate. This means that the higher order terms (2nd order and above) in our perturbative expansion for  $F^{ehr}$  have become more relevant and the dissipative nature of these forces are overwhelming the negative viscosity produced by  $F_{(1)}$ . These results are summarised in Figure 7.5 in which the average power input to the classical coordinate over a period of oscillation is calculated and classified as negative (blue) or positive (red). We observe that the average power input to the classical coordinate is positive far beyond when the perturbative assumption is valid. We anticipate that this cut-off between positive and negative average power input is highly dependent on the model and parameters at hand. However, this demonstrates that while negative viscosities will still emerge under a numerically exact approach, it can be dominated by dissipative higher order forces for large values of  $\Omega/\Gamma$ . These results suggest that the inclusion of the higher order forces which emerge through Ehrenfest dynamics acts to further subdue classical vibrations within the system.

#### 7.3.2 Two classical degrees of freedom

The algorithm for calculating  $F^{\text{ehr}}$  can be readily extended to account for many classical degrees of freedom. In this section, we consider another 2-level model consisting now of two classical degrees of freedom; a stretching component and an angular component. The stretching coordinate *q* modulates the hopping amplitude between electronic sites in the central region, while the angular coordinate  $\theta$  accounts for the shift in electric levels due to the electric field produced by the applied voltage bias. Thus, the molecular Hamiltonian now takes the form

$$H_M = \begin{pmatrix} h_L(\theta) & \eta(q) \\ \eta(q) & h_R(\theta) \end{pmatrix}.$$
 (7.32)


Figure 7.4: Samples of Ehrenfest trajectories of the classical coordinate against time for (a)  $\Omega/\Gamma \approx 0.14$ , (b)  $\Omega/\Gamma \approx 2.2$ , (c)  $\Omega/\Gamma \approx 3.2$ . Colour shows the instantaneous power of the classical coordinate.



Figure 7.5: Regimes of negative (blue) or positive (red) average power input to the classical coordinate over a period of oscillation. The green points refer to the corresponding plots in Figure 7.4.



Figure 7.6: Comparison of long trajectories of the classical coordinate in time using the Ehrenfest approach and the truncated perturbative approach. The viscosity coefficient is negative between the red dashed lines and positive outside.  $\Omega/\Gamma \approx 0.14$ .

The hopping amplitude is given by

$$\eta(q) = \eta e^{-q} \left( 1 + q + q^2/3 \right). \tag{7.33}$$

This is a generic 1*s*-orbital overlap scaled by some constant  $\eta$  [169]. Meanwhile, the atomic levels are given by

$$h_{L/R}(\theta) = \pm Eq_0 \cos(\theta), \tag{7.34}$$

where  $q_0$  is the constant bond-length parameter which appears in our classical potential for q, while E is the linear approximation to the electric field across the junction as determined by

$$E = \frac{\mu_L - \mu_R}{L},\tag{7.35}$$

and *L* is the junction length. For all results in this section, we set  $\eta = 0.1$ ,  $q_0 = 2$ ,  $\theta_0 = 0$ , L = 4,  $k_q = 0.1$ ,  $k_{\theta} = 0.05$ , and  $\mu_L = -\mu_R = 0.1$ . All other components of the full Hamiltonian take the same form as in section 7.3.1.

In Figure 7.7, we calculate an Ehrenfest trajectory and record the Ehrenfest and perturbative forces on each degree of freedom separately. Given that we have more than one classical degree of freedom, this also includes the so-called non-equilibrium anti-symmetric forces in which the motion of  $\theta$  induces a force on q and vice versa; the net anti-symmetric force being perpendicular to the motion of the classical coordinate. Figure 7.8 performs a direct comparison between the time dependent trajectories calculated via the Ehrenfest force and the perturbative approximation. To do so, we first calculate a classical Ehrenfest trajectory of our two coordinates. From this trajectory at some point in time after the unusual transient behaviour in  $F^{ehr}$  has subsided, we extract the initial conditions for a comparative trajectory



Figure 7.7: The force trajectories in time for the Ehrenfest force (blue) and perturbative force (black) acting on (a) q and (b)  $\theta$ .  $\Omega_q/\Gamma \approx 0.32$ ,  $\Omega_\theta/\Gamma \approx 0.22$ .

where the forces are calculated according to the perturbative approximation. In Figure 7.8 (a), the trajectories are compared for large effective masses for each coordinate such that the perturbative assumption should be satisfied. We observe only small differences between the trajectories resulting from the different methods in this case. Contrarily, Figure 7.8 (b) demonstrates for small effective masses that the trajectories deviate away from each other almost instantly and undergo largely different oscillatory behaviour. This is because the perturbative assumption is no longer valid since  $\Omega/\Gamma$  is not sufficiently small.

## 7.3.3 Evaluating the diffusion coefficient

The stochastic force term which we have thus far avoided in the calculation of dynamics in this chapter is a stochastic Gaussian process entirely defined by the following [162]:

$$\langle \delta f(t) \rangle = 0, \qquad \langle \delta f(t) \delta f(t') \rangle = D(t, t'),$$
(7.36)

where D(t, t') is the exact diffusion coefficient. We will consider a system consisting of a single electronic level coupled to a single classical degree of freedom. Our molecular Hamiltonian is given by



Figure 7.8: Short classical trajectories in the coordinate-space comparing the Ehrenfest method and perturbative method. Green(red) points denote the start(end) of the trajectory. The vector field shows  $\nabla U(\mathbf{x}) + F_{(0)}$ . (a)  $\Omega_q / \Gamma \approx 0.32$ ,  $\Omega_\theta / \Gamma \approx 0.22$ , and a trajectory length of 600, and (b)  $\Omega_q / \Gamma = 1$ ,  $\Omega_\theta / \Gamma \approx 0.7$ , and a trajectory length of 200.

where *x* represents any generic classical degree of freedom. We will let  $h_0 = 0$  and our  $\Gamma_{\alpha}$  become scalar inputs in the single level case. As illustrated in Section 3.3, the exact diffusion coefficient in (7.36) for our model (in the absence of motion on the leads interface) can then be expressed in terms of nonequilibrium Green's functions according to

$$D(t,t') = \lambda^2 G^{>}(t,t') G^{<}(t',t).$$
(7.38)

Since D(t, t') represents the correlations in a *classical* force, we require it to be a purely real quantity. This further implies that we should have D(t, t') = D(t', t). This, however, is not strictly the case since the derivations leading to (7.38) treat  $\delta f$  as a quantum object. To remedy this, upon mapping the quantum force,  $\delta \hat{f}$ , onto the classical stochastic force,  $\delta f$ , which appears in our Langevin equation, we must symmetrize (7.38) in time by considering only the real component:

$$\operatorname{Re}\left\{D(t,t')\right\} = \frac{1}{2}\left(D(t,t') + D^*(t,t')\right),\tag{7.39}$$

$$= \frac{1}{2} \left( D(t, t') + D(t', t) \right). \tag{7.40}$$

Thus, we treat this real component as our classical diffusion coefficient. In doing so, our expression for D(t, t') is now in correspondence with reference [162] as per

$$D(t,t') = \operatorname{Re}\left\{\lambda^2 G^{>}(t,t') G^{<}(t',t)\right\}.$$
(7.41)

Note that we have previously not had to consider this symmetrization procedure since we employed the white-noise approximation which immediately enforces that D(t, t') = D(t', t) = 0 when  $t \neq t'$ .

D(t, t') accounts for the effects of the random fluctuations about the mean-field of the electronic environment on the classical degrees of freedom along with accounting for the feedback of the classical coordinate on the electronic environment due to its motion. However, generally a time-scale separation within the system is utilised in order to produce a perturbative solution to D(t, t') in which the feedback due to the motion of the classical coordinate is not included; in other words, the classical coordinate evolves adiabatically. In order to easily identify the different time-scales within the system, we first transform (7.41) into the Wigner domain as follows. We have

$$D(t,t') = \lambda^2 \left( G^{>}(t,t') G^{<}(t',t) + G^{<}(t,t') G^{>}(t',t) \right).$$
(7.42)

Direct application of the Wigner transform then yields

$$\tilde{D}(\omega,T) = \lambda^2 \int d\tau e^{i\omega\tau} \left( G^{>}(t,t') G^{<}(t',t) + G^{<}(t,t') G^{>}(t',t) \right).$$
(7.43)

We will apply an equivalent process to each of the two terms; for brevity, we only show the first explicitly. We replace  $G^{<}$  in the time domain by the corresponding inverse Wigner transform of  $\tilde{G}^{<}$  and simplify to find

$$\lambda^2 \int d\tau e^{i\omega\tau} G^>(t,t') G^<(t',t) = \frac{\lambda^2}{2\pi} \int d\tau e^{i\omega\tau} G^>(t,t') \int d\omega' e^{-i\omega'(-\tau)} \tilde{G}^<(\omega',T)$$
(7.44)

$$=\frac{\lambda^2}{2\pi}\int d\omega'\int d\tau e^{i(\omega+\omega')\tau}G^>(t,t')\tilde{G}^<(\omega',T)$$
(7.45)

$$=\frac{\lambda^2}{2\pi}\int d\omega' \tilde{G}^>(\omega+\omega',T)\tilde{G}^<(\omega',T),$$
(7.46)

where we have used the definition of the Wigner transform. Applying the same process for the second term then yields the diffusion coefficient in the Wigner domain as

$$\tilde{D}(\omega,T) = \frac{\lambda^2}{2\pi} \int d\omega' \left( \tilde{G}^>(\omega+\omega',T) \tilde{G}^<(\omega',T) + \tilde{G}^<(\omega+\omega',T) \tilde{G}^>(\omega',T) \right).$$
(7.47)

Now, the adiabatic diffusion is found by taking  $\tilde{G}^{</>}$  to be our adiabatic Green's functions. The subsequent application of the inverse Wigner transform then yields the adiabatic diffusion in the time domain as

$$D_{(0)}(\tau,T) = \lambda^2 \int \frac{d\omega}{2\pi} e^{-i\omega\tau} \int \frac{d\omega'}{2\pi} \left( \tilde{G}_{(0)}^{>}(\omega+\omega',T) \tilde{G}_{(0)}^{<}(\omega',T) + \tilde{G}_{(0)}^{<}(\omega+\omega',T) \tilde{G}_{(0)}^{>}(\omega',T) \right).$$
(7.48)

The adiabatic diffusion will serve as a base of comparison with the exact diffusion in order to analyse the effects of a time-scale separation within the system. We additionally analyse the validity of the white-noise approximation for different parameters. The white-noise approximation is a method of coarse-graining the diffusion coefficient which allows for a simpler mathematical and computational treatment. This is done by assuming that the non-Markovian exact diffusion coefficient can instead be replaced by a Markovian equivalent according to

$$D(t,t') \equiv D^{w}(T)\delta(t-t'), \qquad (7.49)$$

where we have introduced the white-noise diffusion coefficient  $D^w$ . Thus, the aim is to accurately reproduce the effects of the stochastic force under the assumption that it is entirely uncorrelated in time. In order to replicate the correct dynamics using this approximation, we observed in Section 3.3.6.1 that  $D^w$  must then take the form

$$D^{w}(t_{f}) = \int_{-t_{f}}^{t_{f}} d\tau D(t_{f}, \tau),$$
(7.50)

where to avoid ambiguity,  $t_f$  denotes a specific point along the trajectory. (7.50) is just the Wigner transform of D(t, t') when  $\omega = 0$  such that  $D^{\omega}$  is independent of  $\omega$ ; hence the name "white-noise" diffusion. Thus, the white-noise diffusion coefficient contains information about the correlations in the stochastic force but applies that information in a Markovian manner. A time-scale separation can be applied to the white-noise diffusion in a similar way as previously, where the adiabatic white-noise diffusion is given by

$$D_{(0)}^{w}(t_f) = \int_{-t_f}^{t_f} d\tau D_{(0)}(t_f, \tau).$$
(7.51)

The adiabatic white-noise diffusion is the most commonly used approximation to the diffusion coefficient [142, 143, 152]. The white-noise approximation is valid when correlations in the exact diffusion coefficient decay over time-scales in which the effects of other forces present in the system (in our case, the Ehrenfest and the classical forces) are negligible. In order to quantify its validity, we introduce the correlation time defined according to

$$t_{\rm corr}(t_f) = \frac{\int_{-t_f}^{t_f} d\tau D(t_f, \tau)}{D(t_f, \tau = 0)}.$$
(7.52)

This is a measure of the persistence of correlations in the stochastic force, independent of their strength. The numerator of (7.52) is our expression for the white-noise diffusion while the denominator is the variance in the stochastic force at time  $t_f$ . With all quantities now defined, we can begin to discuss the results.

We once again apply the time-stepping algorithm presented in Section 7.2.2 to find classical Ehrenfest trajectories in time for our classical coordinate. In doing so, we store  $A(\omega, t)$  at each time-step. The two-time lesser and greater Green's functions can then be computed according to (7.10) and (7.11) by inputting  $A(\omega, t)$  at different points in the stored trajectory and numerically integrating over  $\omega$  for each possible value of  $\tau$ . We then calculate the exact diffusion coefficient as a function of  $\tau$  according to (7.38), where  $D(\tau = 0)$  corresponds to the variance in the stochastic force at the end point of the trajectory and  $D(\tau > 0)$  is the



Figure 7.9: Exact diffusion coefficient as a function of  $\tau$  for where time *t* occurs at: (a)/(b) x = 0, (c)/(d) a turning point. Left: V = 0, Right: V = 0.2. Dashed line is the corresponding  $D_{(0)}(t, t')$  for the same parameters.

correlation in the stochastic force between the times t and  $t - \tau$ . To clarify the method, the stochastic force is not included in the simulation. We instead calculate the trajectory using Ehrenfest dynamics as a means to assess the behaviour of the exact diffusion coefficient. The common parameters in this section are  $\lambda = 0.1$ , k = 1 and  $x_0 = 0$ .

In Figure 7.9 (a)-(d) we observe the exact diffusion as in (7.38) for different values of our small parameter (solid line) plotted against the corresponding adiabatic diffusion as per (7.48) (dashed line). Here, time t corresponds to the end point of the trajectory where in (a)/(b) the trajectory is ended at a point when x = 0, while in (c)/(d) the trajectory is ended at a turning point. The left plots are calculated in equilibrium while the right plots are calculated at a non-zero voltage. The differences between the solid and dashed lines give an indication of the effects of the feedback on the electronic environment due to the motion of the classical coordinate. As expected, this feedback becomes especially important when the small parameter becomes larger, such that the perturbative truncation of (7.38) is no longer satisfied. However, we observe that an increase to the voltage nullifies the effects of the feedback. This is justified by the knowledge that the electronic tunnelling time-scale is faster at higher voltages [239], meaning that the electronic environment can more readily equilibrate to any changes in the classical geometry. Thus, the time-scale separation becomes increasingly justifiable further from equilibrium, even despite  $\Omega/\Gamma$  being large. We also find that the correlations in the stochastic force are dissipated over shorter time-scales when  $\Omega/\Gamma$  is smaller such that  $D(\tau)$ approaches a shape more reminiscent of a delta function. Finally, we note that the time-scale separation appears less satisfactory at the turning points of the trajectory. The acceleration of the classical coordinate is largest around the turning points and we posit that acceleration dependent terms become important here, which are otherwise unaccounted for under the assumption of adiabatic motion.

The effectiveness of the time-scale separation for different ending positions along the trajectory is quantified in Figure 7.10, in which we have calculated  $D^w/D_{(0)}^w$  for different end positions along a period of the trajectory when  $\Omega/\Gamma = 1$ . For these parameters, the time-scale separation is ineffective as  $D^w$  is over twice as large as  $D_{(0)}^w$  at a minimum. We observe the adiabatic assumption to be at its weakest in the vicinity of the turning points.

In Figure 7.11(a), we use  $t_{corr}/T$  as a measure of the suitability of the white-noise approximation, where *T* is the period of oscillations in the classical coordinate. Here,  $t_{corr}$  contains any information about the electronic forces acting on the coordinate, while *T* contains information on the classical force. We observe that an increase to  $\Omega/\Gamma$  results in a corresponding increase to  $t_{corr}/T$ , implying that the white-noise approximation is more valid at smaller  $\Omega/\Gamma$  where the time-scale separation is more well-defined. However, we note that the validity decreases upon increasing the voltage which would ordinarily serve to further increase the time-scale separation. For this system, a larger voltage results in more persistent correlations in the



Figure 7.10: An example trajectory of the classical coordinate. Colour scale shows the calculated  $D^w/D_{(0)}^w$  at that point in the trajectory. Parameters:  $\Omega/\Gamma = 1$ , V = 0.



Figure 7.11: The ratio of the correlation time to the period of classical oscillation, (a) as a function of  $\Omega/\Gamma$  for equilibrium and non-equilibrium cases, trajectory length = 300, (b) for shifted values of  $h_0$ . The dashed blue lines show the edges of the voltage window. Parameters:  $\Omega/\Gamma = 1$ .

stochastic force which emerges in the numerator of (7.52), while the change in the denominator is comparatively irrelevant.

This counter-intuitive result also indirectly emerges in Figure 7.11(b) where we observe the white-noise approximation to become more applicable outside of the voltage window and away from the chemical potentials of the leads. In this region, electrons tunnel more slowly through the central region. We do not yet have a convincing explanation for this.

## 7.4 Summary

In this chapter, we have introduced a novel time-stepping algorithm for evaluating the exact lesser Green's function at equal times, which allows us to simulate the trajectory of multiple classical coordinates simultaneously via an Ehrenfest approach. We use this to benchmark the commonly used Langevin approach which necessitates the use of a time-scale separation between classical and electronic coordinates within the system. We observe that despite our avoidance of a time-scale separation within our system, we observe negative dissipations (positive power input to the classical coordinate) as predicted by the Langevin approach. We also note that these negative dissipations can be overwhelmed by positive dissipations due to higher order forces unaccounted for in the Langevin approach. We also apply our method to the calculation of the diffusion coefficient in which we observe the effect of the feedback of the classical coordinate onto the electronic environment and its behaviour under a time-scale separation. Additionally, we assess the validity of the white-noise approximation for the diffusion coefficient for a range of parameters and find that it is most applicable under a clear time-scale separation within the system and is better applied outside of the voltage window.

## Conclusion

This thesis was a theoretical exploration into the current-induced forces experienced by nuclei in molecular electronic junctions. In Chapters 2 and 3, using the framework of non-equilibrium Green's functions we were able to cast the equations of motion for a set of classically-described vibrational degrees of freedom in terms of a Langevin equation, from which we self-consistently derived the forces acting on the classical degrees of freedom. The main ingredients of our Langevin description are the adiabatic force, which quantifies the renormalisation of the vibrational potential due to the coupling to the leads and occupation of electronic states in the central region, along with the viscosity coefficient and diffusion coefficient which together describe heating effects. Each was derived for the case of many classical degrees of freedom, allowing for motion in both the central region and on the leads interface.

Motion on the leads interface was the focus of Chapter 4. We found that for the case of a single electronic level on the molecular bridge with only a central region dependence on the classical coordinate, the viscosity coefficient must be purely positive. Allowing for motion on the leads interface then enables the viscosity coefficient to become negative at high voltages which may quickly lead to device breakdown. Additionally, we observed the formation of bistable potentials as dependent on the strength of the electronic coupling between the central region and leads, as well as the stiffness of the classical potential. We used the mechanical current noise, an experimental observable, as a means of quantifying the classical dynamics under an applied voltage, summarised in terms of a Fano factor. We found strongly super-Poissonian noise ( $F \approx 400$ ) in the bistable regime.

Chapter 5 saw us expand the theory to allow for a slow, sinusoidal, time-dependent driving in the leads energy levels. This involved the calculation of additional corrections to the Langevin coefficients due to the motion of the leads energy levels. We found the AC case to produce considerable heating or cooling over the DC case, dependent on the parameter regime considered. Increasing the cooling involves increasing the viscosity coefficient, which is maximised when the central electronic level is in resonance with the fermi-energy of the lead. Whether the AC case produces additional heating or cooling depends on the energy of the electronic

level on the molecular bridge relative to the fermi-energy. We observed the application of an AC driving to produce in excess of 50 percent cooling relative to the DC case while producing the same average current, which would result in a monumental increase to device lifetimes.

Device lifetimes were analysed in detail in Chapter 6, in terms of reaction rates. Here, we utilised a Fokker-Planck description for the phase space probability density of our classical vibration. We considered two limiting cases; the overdamped case, in which the probability density was described by the Smoluchowski equation, and the underdamped case where we instead utilised an energy-diffusion equation. This allowed us to derive analytical expressions for the mean first passage time in both regimes. We found that the ingredients governing the reaction rate were the size of the energy barrier as determined by the adiabatic force, as well as the inhomogeneous effective temperature over the reaction potential which is calculated via the viscosity and diffusion coefficients. The natural emergence of localised heating in the junction leads to an effect reminiscent of Landauer's blowtorch effect in which there is an effective lowering of the energy barrier due to localised heating. We considered a  $H_2^+$  molecule in the central region where the chemical bond length acted as the vibrational degree of freedom and subsequently calculated the device lifetimes in both limiting regimes.

The Langevin approach to dynamics relies upon assuming a clear separation of time-scales in the system, along with assuming that the stochastic force can be reasonably estimated as being delta-correlated. We benchmarked these assumptions in detail in Chapter 7, where we introduced a novel algorithm for calculating the lesser Green's function exactly, avoiding the need for a time-scale separation. This allowed us to rephrase the classical dynamics in terms of an Ehrenfest force. We found that negative viscosities are robust, emerging even when using Ehrenfest dynamics. This validates the result in contradiction with claims that negative viscosities are an unphysical artifact of applying a time-scale separation. We calculated the coloured noise over trajectories and observed the effects of the feedback of the non-adiabatic motion of the classical vibrations onto the electronic environment. We found that the whitenoise approximation is in general, a valid approximation to make when there is a clear timescale separation within the system. We did, however, find that its validity is decreased when the electronic level of the molecular bridge is in the resonance region.

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