

Time-Dependent Quantum Transport and Fluctuations in Molecular Junctions

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for the degree of Doctor of Philosophy

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DECLARATION OF ORIGINALITY

I, Michael Ridley, sincerely affirm that the work contained in this thesis is my own. Where the work of others has been used in the process of obtaining my results, I have thoroughly referenced the original source material.

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Foreword

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Abstract

This thesis contains a theoretical treatment of the time-dependent quantum transport of electrons through molecular junctions. In particular, the nonequilibrium Green's function (NEGF) method is used to obtain the time-dependent current and current fluctuations in response to an arbitrarily time-dependent spatially homogeneous bias in the leads and molecular region. All subsystems in the nanojunction are assumed to be noninteracting throughout, and in addition the wide-band limit approximation (WBLA) is made in order to simplify the treatment of the lead-molecule coupling.

The theoretical work involves a complete analytical solution in the two-time plane of the Kadanoff-Baym equations for all components of the molecular region Green's function defined on the imaginary time Konstantinov-Perel' contour. This enables the derivation of expressions for time-dependent quantities such as the particle number in the molecular region and a generalized time-dependent Landauer-Büttiker (LB) formula for the current through an arbitrarily large conducting molecule. The partition-free approach is assumed for the switch-on of a bias in the leads, which enables us to study the effects on the transient transport of the initial coupling between the subsystems of the nanojunction.

The analytical expression for the full two-time Green's function is then used to study the quantum correlations between currents in the different leads. Using many-body methods, the two-time current correlation function is expressed in terms of a matrix product of Green's functions which are all known exactly. Therefore, in similar fashion to the generalized LB current, the current correlations generalize the LB theory of shot and thermal noise so that it is (i) partition-free and (ii) valid for an arbitrary time-dependent bias. To check its generality, this formula is shown to reproduce results for the zero- and finite-frequency current noise that are known from the literature on this topic.

The formulas for the current and current fluctuations are originally obtained in terms of integrals over the frequency and time planes. To render these formulas useful for calculations on large molecules they are then re-expressed with all frequency integrals replaced with special functions, which may be computed via the Padé expansion of the Fermi function. This results in a formalism which is ideally multiscale in time, i.e. which does not get more expensive with increasing number of time steps, and which can therefore be used to study the short-time transient and steady-state transport quantities with identical computational expense. Some numerical calculations of the current and noise response to the switch-on of a time-dependent bias are then performed.

The first kind of time-dependent driving considered in this thesis is periodic. Some preliminary calculations are performed on periodically-driven quantum dots, and the effect on the current of varying the driving frequency, temperature, lead-molecule coupling and driving amplitude is studied. Next, the problem of quantum pumping is considered, and sufficient conditions are found for a periodically driven system with zero time-average bias to generate a net time-averaged current through the system. The effects of finite size on the current response to static and periodic biases are investigated, again using the molecular wire as an illustrative model. Next, calculations of the quantum pump current are presented for a particular biharmonic bias model, and in particular the effect on this current of breaking the sinusoidal shape of the driving field. Finally, the discussion turns to calculations of the cross-lead current correlations in extended systems in response to static and periodic biases. By investigating molecular wires of different lengths and internal hopping parameters, a signature of the traversal time for electrons crossing the sample is found in both the transient and steady-state cross-lead current correlations.

As there are no restrictions on the nature of the time-dependent bias driving the system out of equilibrium, one can use this formalism to study the electronic response to a classically fluctuating bias in the leads. The second kind of time-dependent driving studied in this thesis is therefore non-deterministic, and exact formulas for the bias-averaged current response to a stochastic bias are derived for the first time. This problem is formally analogous to the use of the Langevin equation approach to obtain a relation between the conductance in a classical circuit and

the strength of fluctuations in an external driving bias: the so-called Nyquist theorem. An exact quantum version of the Nyquist theorem is derived for a driving bias with colour noise which relates the strength of fluctuations, the correlation time of fluctuations, the temperature and conductance in a molecular junction. Due to the nonlinear relation between current and driving bias in these junctions, it is not always true that the conductance will decrease with increasing fluctuation strength. Instead, there can be particular intermediate values of the fluctuation strength at which peaks in the conductance are observed, in a stochastic resonance effect.

List of Publications

The author has carried out the majority of the analytical work and has produced all the numerical results in the following publications whilst working on this PhD thesis:

- [1] M. Ridley, A. MacKinnon and L. Kantorovich, “Current through a multilead nanojunction in response to an arbitrary time-dependent bias”, *Phys. Rev. B* **91** (12), 125433 (2015)
- [2] M. Ridley, A. MacKinnon and L. Kantorovich, “Calculation of the current response in a nanojunction for an arbitrary time-dependent bias: application to the molecular wire”, *J. Phys.: Conf. Ser.* **696** (1), 012017 (2016)
- [3] M. Ridley, A. MacKinnon and L. Kantorovich, “Fluctuating bias-controlled electron transport in molecular junctions”, *Phys. Rev. B* **93** (20), 205408 (2016)
- [4] M. Ridley, A. MacKinnon and L. Kantorovich, “Partition-free theory of time-dependent current correlations in nanojunctions for an arbitrary time-dependent bias”, *Phys. Rev. B* **95**(16), 165440 (2017)

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Chapter 1

Introduction to Experiment and Theory

1.1 Why Molecular Electronics?

Much of the remarkable explosion in information technology since the 1960s has followed a rule of thumb known as *Moore's Law*. Taking the number of transistors in a microprocessor as a measure of computational power, G. E. Moore predicted in 1965 that this number would roughly double every year [5], and in 1975 he revised this prediction to a two-year doubling time [6]. In 1971, Intel, which was co-founded by Moore, released its first ever microprocessor, the 4004 chip. These chips contained transistors with a half-pitch (half the spacing between transistors on a dynamical random access memory (DRAM) chip) of $10\mu m$. Since then, Moore's prediction of exponential growth has proven to be a self-fulfilling prophecy as the semiconductor industry devised a coordinated roadmap geared towards the exponential down-scaling of silicon-based microprocessor elements. Sub- μm integrated circuits became commercially available in the late 1980s, and in the 1990s the strategy of 'More Moore' became codified by the International Technology Roadmap for Semiconductors (ITRS). To keep up with Moore's Law in the 2000s, Intel has operated a two-year "tick-tock" manufacturing strategy, that alternates a downscaling of the half-pitch (the "tick"), with improvements in the architecture of the chip at the new scale (the "tock").

Echoing Feynman's assertion that there was 'plenty of room at the bottom' [7], Moore made the following assertion in his 1975 paper [6]:

"With respect to dimensions, in these complex devices we are still far from the minimum device sizes limited by such fundamental considerations as the charge on the electron or the atomic structure of matter."

In 2017, this is no longer true. The state of affairs in 2017 is one in which over 50 years of unabated Moore's Law has reduced the 'room at the bottom' to the point where the quantum structure of nature poses a very real problem to the semiconductor industry. In the early 2000s, the first signs emerged that Moore's Law was collapsing, as silicon features began to shrink below $90nm$. At this scale, heating caused by electron leakage through the transistor channels in a complementary metal-oxide semiconductor (CMOS) device becomes a fundamental problem. The solution taken at the time was to set a limit on microprocessor speed whilst continuing to downscale transistor size [8]. 2012 saw the introduction of Intel's new "FinFET" design which was introduced specifically to reduce electron leakage and the heating that results from it, but these structures are fast approaching the atomic limit in dimensions. The current generation of microprocessors possesses a half-pitch of $14nm$, initiated by the Broadwell chip (the "tick") in 2014, and followed up by the Skylake chip (the "tock") with a new microarchitecture. The Skylake contains transistors made up of around 100 atoms. Initially, Intel had intended to release the Cannonlake

microprocessor, a $10nm$ successor to the Skylake, in 2016, but was forced to delay this model into 2017, instead releasing another “tock”, the $14nm$ Kaby Lake, in 2016 [9]. This was mainly due to electron tunneling between the source and drain electrodes [10]. By the early 2020s, silicon-based microprocessors will contain device features at a scale of less than $10nm$, at which point quantum effects will dominate the electron transport, and already the cadence for microprocessor generation renewal has slowed from Moore’s prediction of a two-year cycle, so that it is now closer to three years.

Hence, in 2017 the microelectronics industry finds itself at a unique crossroads, where the traditional strategy of cramming more FETs onto microchips to improve processor speed is beginning to break down. Lithographic techniques for constructing complementary metal FETs has reached a scaling limit where the reliable fabrication of sub- $20nm$ device features has ceased to make economic sense [11, 12, 13]. The world is used to a rate of improvement in electronic devices and information technology that is largely due to the miniaturization of active circuit components, and there are three broad directions that scientists can take to attempt to keep up with this demand for ever more powerful devices:

1. Proceed with silicon-based devices and try to keep up with Moore’s Law without relying solely on the miniaturization of transistors. Ways to do this include new architectural techniques such as 3D microchip design [14], or devices that harness quantum effects, such as the tunnelling transistor introduced by Banerjee et al. [15], which operates at a much lower voltage than the currently manufactured silicon-based devices, and therefore reduces heat dissipation.
2. Move to a different basic physical representation of information in integrated circuits. This could come from spintronics, which represents logical 0s and 1s in terms of spin-up and spin-down states. Alternatively, quantum computing offers an entirely new model of computation itself, and is provably faster than classical computation for certain tasks such as the factorization of integers into prime numbers [16].
3. Move to non-silicon based materials that reduce heating and therefore enable improved microprocessor speed, and which may enable scaling down to the level of single molecules. This represents the final frontier of miniaturization, but also provides a massive incentive to investigate how far single- or few-molecule structures can be used as active device components.

The third-listed possibility for the future direction of microelectronics is the primary reason why today molecular electronics represents one of the largest subfields of nanoscience, and motivates the investigation into time-dependent molecular electronics that is the topic of this thesis.

1.2 Experimental Developments

1.2.1 MMM Junctions

Molecular electronics is based upon the idea that chemical fabrication techniques will enable the mass production of custom-designed molecules that are fit for use as active components in electronic circuits. In 1974, Aviram and Ratner gave the first theoretical description of a single molecular diode, based upon an organic molecule coupled to metallic leads with energy levels of the molecule all located within the bias window [17]. An energetic schematic of their proposal is shown in Fig. (1.2.1) (a), which depicts the left metal electrode L , the right metal electrode R , and the molecular region C sandwiched between them to create a metal-molecule-metal (MMM) structure. In Ref. [17], the C region consists of an acceptor molecule A , whose lowest unoccupied molecular orbital (LUMO) energy lies below the Fermi energy μ_L of the left electrode. A donor molecule D is coupled to the right electrode, whose highest occupied molecular orbital (HOMO) energy lies above the Fermi μ_R energy of the right electrode, so that

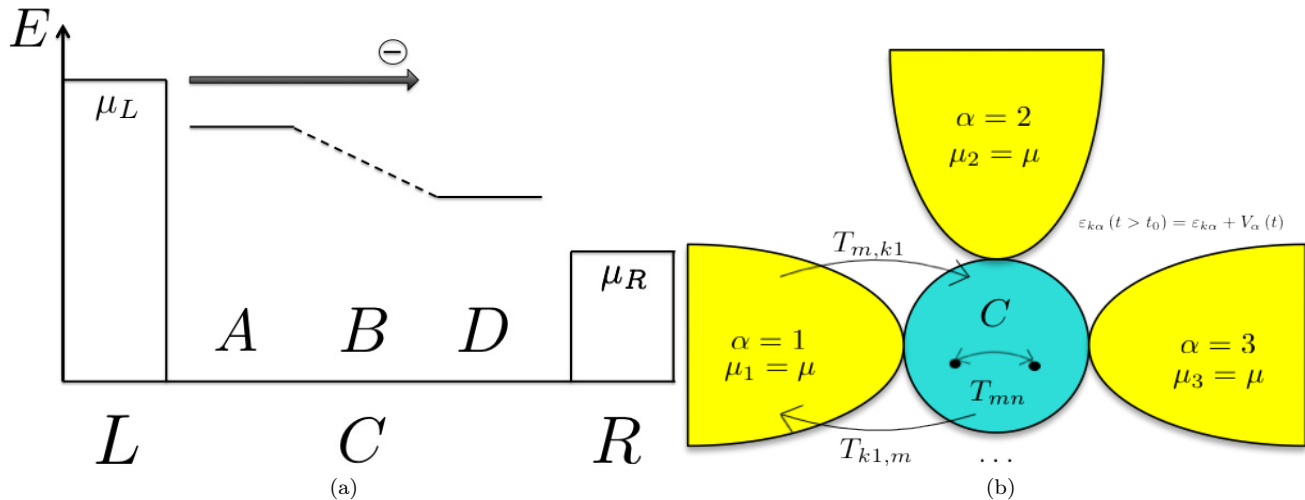


Figure 1.2.1: (a) Energy diagram of Aviram and Ratner's proposal for a molecular diode, with asymmetric left and right lead Fermi levels $\mu_L > \mu_R$ and a molecular region C made up of an acceptor (A), a bridge (B) and a donor (D). (b) Schematic for a molecular junction consisting of leads labelled by α , with chemical potentials μ , coupled to a molecular region C .

the HOMO and LUMO levels both lie within the bias window $[\mu_L, \mu_R]$. The diode is completed with a bridging molecule B , which enables electrons to hop between the LUMO and HOMO levels via intramolecular processes, thereby travelling from L to R as indicated by the thick arrow in Fig. 1.2.1 (a). It was then observed that, due to asymmetry of the molecular energy levels and an imbalance between the source and drain Fermi levels, a diode-like current-voltage ($I - V$) characteristic could be obtained for the current passing through the molecule, assuming that reversal of the direction of the voltage gradient does not cause the LUMO and/or HOMO energies to shift too much. This nonlinear $I - V$ behaviour arises from the asymmetry of the molecule, but nonlinearities in the current characteristic can also occur in a single-level device, as will be discussed in Section 1.4.1.2. With this proposal of Aviram and Ratner, the field of molecular electronics began to take off. Experimental progress in molecular electronics accelerated on the basis of early observations of quantum tunneling through fatty acid salt monolayers, where the expected exponential decay of conductance was seen for the first time [18]. The invention of scanning probe microscopy (SPM) methods such as scanning tunneling microscopy (STM) [19] and atomic force microscopy (AFM) [20] followed in the 1980s; these enabled the manipulation and imaging of individual nanoscale objects on a substrate.

In modern molecular transport experiments, a single molecule or molecular structure is contacted to macroscopic leads, and the quantum nature of the electrons involved in the transport influences the first and second moments of the current passing between the leads. This thesis is primarily concerned with electron transport through a nanojunction, consisting of a molecular central region C , contacted with a set of conducting (usually metallic) leads labelled by α , themselves in contact with an external circuit and battery. A schematic for a typical molecular junction is illustrated in Fig. 1.2.1 (b).

The actual construction of MMM junctions has become possible due to the development of metallic contacts with atomic dimensions, and by chemical techniques which enable the preparation of interfaces between metal and molecules that enable a stable contact to form [21]. It is only in the past ~ 25 years that serious experimental attempts have been made to actually connect molecules to electrodes. When a molecule is coupled to an electrode, novel behaviour and even loss of functionality can occur compared with the properties of the isolated molecule. This is because the coupling of the leads to the molecule, also known as the *hybridization*, can cause energy levels to shift, and it also causes the distribution of states on the molecule to broaden in energy space [22]. Generally speaking,

physisorption of molecules on the lead surface through a van der Waals interaction leads to weak hybridization, whereas a strong coupling is established via *chemisorption*, in which the molecule-lead bonding is covalent [23]. The hybridization of a molecule tends to slow down the fabrication of real devices, as further optimization stages may be necessary to regain functionality. In general, no two MMM junctions are exactly identical, as the geometry of the junction is determined by the precise configuration of the molecule between the leads. In particular, the strength of the coupling between the molecule and the electrodes can fluctuate between experiments [24] and there is also an intrinsic misalignment between the energy levels of the molecule and the Fermi energies of the leads, so that resonant transport can only be achieved by applying a voltage across the junction [10]. For this reason it has become common practice to extract information on the electron transport from conductance histograms constructed out of many different measurements performed on different MMM junctions fabricated in the same way [25, 26, 27, 28, 13].

One way of creating metallic contacts at the nanoscale is provided by STM needles, which are held close to a molecule or self-assembled monolayer deposited on a substrate, thereby creating a potential gradient across the molecular region and enabling electrons to tunnel through the molecule. This technique provided the first reliable conductance data on single molecular structures in 1996, when the conductivity of self-assembled monolayers on Au substrates was measured [29]. However, since the STM technique depends on the current signal to control its position above the substrate, it is difficult to know in some cases which part of the conductance comes from the molecule and which part comes from the vacuum. This difficulty can be circumvented by other SPM techniques, such as conducting-probe atomic force microscopy (CP-AFM), which uses an additional variable, i.e. the normal force, to determine its position [30, 31, 24]. SPM-based techniques have lead to the characterization of multiple features of molecular transport, including the exponential decay of the conductance through molecules with increasing length of the molecular backbones [27] and the dependence of conductance upon the anchoring groups of the molecule [32]. Recently, an STM-based lithographic method was used to fabricate the first single-atom transistor out of a phosphorus impurity in bulk silicon [33].

Mechanically controllable break junctions (MCBJs) provide another commonly-used means of fabricating metal contacts. These are formed by breaking a thin ductile wire, typically made of Au or Ag, via mechanical bending [25, 34, 35, 36, 37, 38, 27, 39]. Recent work on a FET-like device formed by an MCBJ with external gate electrode demonstrated sub-nanometre precision in the size of the gap between electrodes [40]. A similar concept to the MCBJ underlies electromigrated break junctions (EBJs), which are formed by running a very high current through a thin wire causing the metal atoms to migrate and the wire to snap. In these junctions the inserted molecule is usually chosen to have thiol or amino anchor groups in order to achieve a robust contact [37]. Many variants of this basic setup have been realised, including hybrid junctions that connect benzene to large Pt contacts via an atomic Pt wire [28]. SPM-break junctions (SPM-BJ) represent a further development in this area, involving break junctions whose conductance properties are measured by repeatedly crashing a scanning probe tip into a substrate surface supporting the target molecule [32, 41]. Recently an STM-BJ method was used to show that a molecular rectifier, similar to the one proposed by Aviram and Ratner, could be constructed using DNA as the active component [42]. A key problem for both EBJ and MCBJ structures is the identification of exactly which molecule has been contacted in the electrode gap. Identification of the contacted molecule can be achieved using surface-enhanced Raman spectroscopy [43] and also inelastic tunneling spectroscopy (IETS), whereby the molecule is identified via determination of its vibrational spectra [13].

Various recent studies indicate that molecular self-assembly could provide a bottom-up alternative to the top-down fabrication methods discussed so far [10, 13]. These include self-assembly of Au-molecule-Au dimers [44], Au nanorods [45], and carbon nanotubes (CNTs) [46] which are then inserted between lithographically etched electrodes to create an active molecular component in the gap. This approach facilitates the mass production of molecular components with small variability, and avoids the need for fabricating nanosized gaps by means of a mechanical breaking process.

In all methods discussed so far, there are significant problems with stochastic variability across different experiments. This is due to the diffusion of atoms across metal electrode surfaces, causing large fluctuations in the potential energy surface there, and the resultant fluctuations in measured conductance spectra can be very large. Attempts to address this problem include the use of anchoring molecules that provide a bridge between the metal and molecule, such as fullerene, which is known to strongly hybridize with noble metals and therefore the uncertainty in the electrode landscape is transferred to the more stable C_{60} molecule [47]. This idea may be extended to carbon-terminated electrodes made up of carbon nanotubes (CNTs) or 2D graphene nanoribbons (GNRs), which reduce the dimensionality of the electrodes and therefore reduce the possibility for atomic migration at the molecular contact point [48, 49, 10, 50]. Graphene point contacts may then be covalently bonded to the ends of a molecule situated in a sub-10nm gap [51]. Recent studies have demonstrated rectification in a graphite substrate-molecule-Au structure due to the asymmetric densities of states at the molecular contacts, thus introducing the possibility of tuning the electrodes in order to achieve nonlinear current characteristics [41]. In addition to their use as layers shielding a molecule or SAM from invasive metal electrodes, thin graphene layers may be used as the conducting molecular channel itself. In recent work, GNRs deposited on a dielectric substrate have been contacted to metal terminals using electron beam lithography and evaporation techniques. These are early candidates for graphene field effect transistors (GFETs), which provide an exciting alternative to silicon due to the low resistivity and high Fermi velocity (about $10^6 ms^{-1}$) of charge carriers in graphene [52]. A sub-10nm CNT transistor was recently shown to sustain much higher current densities than Si-based transistors operating at that scale [53]. Due to its lack of a bandgap, it can be difficult to turn off the current signal in graphene, but 2D graphene-based materials can be engineered to circumvent this problem. Due to its planar structure, graphene suffers from no scalability problems - it enables device engineers to target the single molecule limit of Moore's law. Other uses of carbon-based nanoscale components include CNT interconnects, which may eventually provide an alternative to Cu as the conducting material of choice in microelectronic processors [54].

1.2.2 Functional Nanodevices and Time-Dependence

A plethora of electronic circuit components with nanoscale dimensions can now be fabricated and tuned to form various active circuit components. In addition to the massive speed-up in processing power that arises from nanometre size, molecular junctions also enable a massive speedup in device operation due to THz intramolecular transport processes and fast electron transit time [55]. Subsequent to the initial proposal of molecular rectification by Aviram and Ratner, chemical fabrication techniques have lead to the realization of many interesting devices, including single-electron transistors [56, 57], molecular wires [58, 59], frequency doublers and detectors [60, 61] and switches for fast memory storage [62, 63]. A recent paper used the nonlinear $I - V$ characteristic of organic molecules sandwiched between two carbon electrodes to create an unusual distortion of the audio signal in a guitar amplifier [64].

Molecular wires are molecular structures that are confined to atomic dimensions in at least two directions, but which have some extended structure in the direction of electron flow. They might consist of chains of metal atoms [65, 66, 67], organic molecules [68], CNTs, conducting polymers [60], or combinations thereof, such as the MCBJ-formed Pt atomic chains with benzene impurities that were fabricated by the authors of Ref. [28]. A related system is that of a 1D crystal, which is composed of a linear sequence of 0D quantum dots, formed for instance by the 2D electron gas of a semiconductor heterostructure [69].

Molecular switches provide one of the most promising possibilities for a functional molecular device [62]. As well as operating at the limits of miniaturization, bistable molecules can be switched between their stable configurations with a sub-nanosecond switching time [62], offering a massive potential speed-up from GHz to THz in the clock-rates of microprocessors based on these molecules [55]. In conformational switches, a stimulated reaction takes place that

alters the 3D structure of the molecule between different isomers [70]. In charging switches, the molecule moves between different charge states, caused by intramolecular electron transitions. These transitions occur at a much faster rate than conformational changes in the molecule and it has been suggested that control of the picosecond dynamics involved can be achieved using an external laser pulse [55, 71]. Various different external stimuli can be used to switch molecules; these include current-induced switching [72], electrochemical gating-based tuning of the molecule and Fermi levels [73, 74], applied external electric fields [75], or light-induced photoisomerization [76, 49, 77]. In Ref. [78], photochromic molecular switches were built out of conjugated molecular units connected to gold electrodes via thiol groups in an MCBJ. The molecule was then switched between two different bonding states with distinct conductance properties when illuminated by light in the visible spectrum.

The development of molecular switches and molecular frequency multipliers and detectors has caused recent experimental work to increasingly focus on dynamical properties of nanojunctions. The basic question of this field is to determine the AC current response to an external periodic electromagnetic field causing electronic excitations in the GHz-THz frequency range [79, 80, 81, 82, 83]. A phenomenon known as photon-assisted tunneling (PAT), in which irradiated tunnel junctions acquire additional peaks in their conductance spectra has been experimentally demonstrated as an additional transport channel in a variety of structures, beginning with tunneling between oxide films in superconductors in 1962 [84]. Photon-assisted transport through quantum dots formed by small conducting subsystems in semiconductor heterostructures has also been observed [85], in frequency regimes again typically lying somewhere in the microwave [86, 87] to infrared [88] region. Such systems may find use as frequency-sensitive detectors in the specified range, as the additional peaks in their conductance spectra are highly sensitive to changes in the amplitude and frequency of the external irradiating field [88, 86].

Usually an electronic current flowing through a conductor requires a net bias to be applied across the device via some external battery. However, when the current response to the applied bias is nonlinear, it is possible for an external field which is periodic, but zero on average over a full time period, to induce a direct current in the conductor. The mechanism behind this phenomenon is similar to one known in the engineering literature as AC-DC conversion, or *rectification*. In the quantum transport literature, nanoscale structures are known as quantum pumps if they possess periodically-varying parameters that result in a net directed current, and the phenomenon of AC-DC conversion itself is known as charge pumping [89, 90, 91]. Quantum pumps can be created by the dynamical breaking of dynamical symmetries in the driving bias [92, 93, 94], in addition to adiabatically varying the physical parameters of the nanojunction [91]. In the adiabatic regime, the driving frequency is much smaller than the inverse of the time taken for an electron to cross the sample (typically of the order of tens of GHz), and adiabatic pumping has been realized in systems driven by two out-of-phase external driving fields in carbon nanotube quantum dots [95]. Experimental demonstrations of two-parameter charge pumping have been carried out [96, 97, 98]. Recent theoretical work has demonstrated the possibility of single-parameter charge pumping, in which a single periodic source may be used to generate a pump current [99, 100, 101, 102, 103]. This was demonstrated experimentally for the low-GHz frequency range in nanowires etched into semiconductor heterostructures [104, 105, 106, 107]. It was initially thought that to get large pump current signals from single-parameter pumping, one would have to move beyond the adiabatic regime, but experimental [108] and theoretical [109] work on carbon nanotubes indicates that single-parameter pumping can be greatly enhanced via matching of the external driving frequency to low frequency mechanical modes.

1.2.3 Noise in Nanojunctions

The ultimate goal of studying molecular electronics is to produce tunable time-dependent devices that can be used to control and steer currents in coherent conductors. However, the current which flows through a molecular junction does not have a deterministic value at any point in time - rather, it fluctuates about an average value, which in

the ideal steady state is time-independent. These fluctuations around the mean value create a noisy signal, and they are usually more sensitive to the configuration, excitation and interference within the molecular junction than the current itself. The frequency-dependent current noise characteristic is referred to as the *power spectrum* of the current. In 1918, W. Schottky formulated the theory of shot noise in conductors as a source of noise due to the granularity of charge [110]. In 1928, Johnson and Nyquist reported and theoretically interpreted a second source of noise - a thermal noise due to the fluctuations in the number densities of electrons, present even when there is no net flow of current [111, 112]. Both sources of noise are remarkable in that they have no dependence upon the material of the conductor or on any impurities present in the metal [113].

In contrast to classical electronics, the time-dependent current in molecular structures may undergo fluctuations that have a comparable magnitude to the current signal itself. Moreover, time-dependent current-current correlations and their associated frequency-dependent noise spectra contain information which is not present in the first moment of the current [114], a fact which was highlighted in a 1998 paper by Landauer entitled ‘The noise is the signal’ [115]. Additional information included in the noise spectra includes deviation from classical behaviour in the Fano factor due to Pauli repulsion [116, 117], detection of fractional charges for quantum Hall quasiparticles [118] and the determination of transmission probabilities [119]. When the external field driving the current is time-dependent, the transient current correlations provide information on intramolecular ‘circular’ currents that cannot be studied using the current alone [71]. Recent measurements of shot noise in graphene irradiated by THz fields showed an enhancement of the shot noise due to the excitation of electron-hole pairs in the sample [120].

Nanoelectronic devices possess noise spectra which can be complicated nonlinear functions of the frequency of the measuring device [121]. When in equilibrium, there are two regimes, namely the low ω regime, in which Johnson-Nyquist thermal noise makes the strongest contribution, and the high ω scenario in which zero-point photon fluctuations dominate [122]. When a bias is applied to the system, one observes in addition the shot noise, which results from the discreteness of electronic charge and the Pauli exclusion principle [114]. At high frequencies, it was shown that the correct noise spectra is an asymmetric function of the frequency due to the dominance of zero-point fluctuations there [122, 123]. Distinct negative and positive frequency components of the current noise due to quasiparticle tunneling across a Josephson junction have been measured experimentally [124], and may be physically interpreted in terms of the transfer of energy quanta during the corresponding absorption and emission processes of electrons, holes, and electron-hole quasiparticles [125, 126].

1.3 Molecular Junctions are Many-Electron Systems

1.3.1 Statistical Nature of the Problem

A molecular junction is a thermal system of atomic and subatomic particles, consisting of a molecular subsystem electronically coupled to two or more electrodes, which serve as particle and heat reservoirs. It is impossible to have complete knowledge of this kind of system, so our description of it is unavoidably statistical. The probabilistic nature of electron transport through a molecular junction arises from two distinct sources:

1. Electrons cannot be described classically. Instead they are described by quantum mechanics, in which the basic physical state of a system is described by a probability amplitude. As a result, it is impossible to predict with certainty which state the system will be in at any given time.
2. Thermal systems are subject to environmental buffeting, which causes rapid transitions between microstates on the timescale of measurement [127]. Thus, thermal fluctuations make it impossible to experimentally determine the microstate of these systems at any given time.

We note that, whereas the first kind of uncertainty is a fundamental limitation on what we can know in principle, the second limits what can be known in practice. In the next sections we will introduce the key formal concepts required by the statistical nature of the quantum transport problem.

1.3.2 First and Second Quantization

1.3.2.1 Single Particle Quantum Mechanics

The first postulate of quantum mechanics states that all physical systems may be represented with a *state vector* $|\Psi\rangle$, which contains all the obtainable physical information of that system. The state vector is expressible as a linear superposition of the states the system can be found in after a measurement has occurred, each labelled by a quantum number n and weighted by a complex number c_n :

$$|\Psi\rangle = \sum_n c_n |\varphi_n\rangle \quad (1.3.1)$$

The Born Rule tells us that the probability of finding the system in the state $|\varphi_m\rangle$ is given by the square modulus of the projection of $|\Psi\rangle$ along the direction labelled by this vector:

$$Prob(|\varphi_m\rangle) = |\langle\varphi_m|\Psi\rangle|^2 = c_m c_m^* \quad (1.3.2)$$

In general, quantum states $|\Psi\rangle = |\Psi(t)\rangle$ will be time-dependent, and will satisfy the time-dependent Schrodinger equation (TDSE):

$$\hat{H}(t) |\Psi(t)\rangle = i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} \quad (1.3.3)$$

In this expression, $\hat{H}(t)$ is an Hermitian operator known as the *Hamiltonian* of the system, and $\hbar = 1.054 \times 10^{-34} Js$ is the modified Planck's constant. Eigenvalues of $\hat{H}(t)$ are real and correspond to the permitted energies of the system. For the remainder of this thesis, we set $\hbar = 1$ and work in arbitrary units. Electrons can be measured in position or momentum states, which are indexed by a continuous quantum number. We consider the continuous function Ψ of x which returns probability amplitudes of measuring electrons in the state labelled by x :

$$\Psi = \{\langle x, y \rangle : y = \Psi(x)\} \quad (1.3.4)$$

This is just a set of ordered pairs, no two of which have the same first member. Labelling the different degrees of freedom in Ψ by continuously indexed basis vectors $\{|x\rangle\}$, we collect every value of this function into a vector, expressed as an integral sum over all 'directions' in $\{|x\rangle\}$:

$$|\Psi\rangle = \int_{-\infty}^{\infty} dx \Psi(x) |x\rangle \quad (1.3.5)$$

This defines the *wavefunction*, $\Psi(x) = \langle x | \Psi \rangle$ in quantum mechanics. The Born Rule dictates the following interpretation of this object:

$$|\Psi(x)|^2 dx = \text{probability of finding a particle in the element } [x, x + dx] \text{ surrounding the point } x \quad (1.3.6)$$

The wavefunction is the set of complex numbers obtained by projecting $|\Psi\rangle$ along each member of the basis set $\{|x\rangle\}$. It should not be confused with the wavevector, which is $|\Psi\rangle$ itself. The *physical Hilbert space* for a single particle,

denoted $\mathcal{H}_{SP}$, is a linear vector space in which the values of wavefunctions are stored in linear superpositions such as the one given in Eq. (1.3.5). A *complete basis* for $\mathcal{H}_{SP}$ is a set of vectors $\{|\varphi_n\rangle\}$, which can be used to express any wavevector in the Hilbert space in the form of Eq. (1.3.1). This defines the set of basis functions in the x -representation, $\{\varphi_n(x)\}$, via $\langle x | \Psi \rangle \equiv \sum_n c_n \varphi_n(x)$. In practice, one chooses a finite basis set that can be used to incorporate as much information as possible on the specific system being studied.

1.3.2.2 The N-Body Hilbert Space

The Hilbert space for a system of N identical particles is the space $\mathcal{H}_N$ of vectors containing the values of all complex, square-integrable functions, defined on the configuration space of the N particles. Consider a system containing N identical particles. One extends the single-particle theory by defining the N -particle state function:

$$\langle \mathbf{x}_1 \dots \mathbf{x}_N | \Psi(t) \rangle = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) \quad (1.3.7)$$

Here, $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ is a space-spin variable. In accordance with the Born Rule, we interpret this object as follows:

$$|\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N = \text{probability of finding } N \text{ particles in the volume element } \prod_{i=1}^N d\mathbf{x}_i \quad (1.3.8)$$

surrounding the point $(\mathbf{x}_1, \dots, \mathbf{x}_N)$

Formally, $\mathcal{H}_N$ is the tensor product of N single particle Hilbert spaces, where we introduce the notation $\mathcal{H}^{(i)}$ for the Hilbert space of the i -th particle:

$$\mathcal{H}_N = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} \otimes \dots \otimes \mathcal{H}^{(N)} \quad (1.3.9)$$

The vast majority of members of $\mathcal{H}^{(N)}$ will not be possible to express as tensor products of single particle states, and such states are said to be *correlated* or *entangled*, and the propagation of correlated states in time is the central problem of many body quantum theory [128].

In classical mechanics, one could in principle mark every particle in an N -body system and follow its trajectory in $6N$ -dimensional phase space. Unfortunately this property of classical states does not carry over to systems governed by quantum mechanics. Identical particles in quantum mechanics are *indistinguishable in principle* - no conceivable experiment can distinguish between the intrinsic physical properties of two electrons - they have the same mass, charge, and total spin. This peculiarly quantum type of indistinguishability means that, given the N -particle wavefunction $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$, the physical state is unchanged under the action of the pairwise permutation operator $\hat{P}_{ij}$, which exchanges the space-spin coordinates of the i -th and j -th particles. This operation scales the wavefunction by some parameter λ , which is real. Applying $\hat{P}_{ij}$ twice to the N -body wavefunction gives $\hat{P}_{ij}^2 \Psi = \lambda^2 \Psi = \Psi$, from which it follows that $\lambda = \pm 1$, and so the discrete permutation symmetries of N -body wavefunctions fall into two categories:

1.

$$\Psi(\mathbf{x}_1 \dots \mathbf{x}_i \dots \mathbf{x}_j \dots \mathbf{x}_N) = \Psi(\mathbf{x}_1 \dots \mathbf{x}_j \dots \mathbf{x}_i \dots \mathbf{x}_N) \quad (\text{bosonic}) \quad (1.3.10)$$

2.

$$\Psi(\mathbf{x}_1 \dots \mathbf{x}_i \dots \mathbf{x}_j \dots \mathbf{x}_N) = -\Psi(\mathbf{x}_1 \dots \mathbf{x}_j \dots \mathbf{x}_i \dots \mathbf{x}_N) \quad (\text{fermionic}) \quad (1.3.11)$$

Since the N -body wavefunctions of interest in this thesis will be electronic, and electrons are fermions, we will only be considering wavefunctions with the fermionic permutation symmetry (1.3.11). If one now considers any

orthonormal, complete single-particle basis $\{\varphi_n(\mathbf{x})\}$, then it is possible to show that the normalized members of the basis set for the expansion of an arbitrary N -electron wavefunction have the form:

$$\begin{aligned}\Phi_\kappa(\mathbf{x}_1 \dots \mathbf{x}_N) &= \frac{1}{\sqrt{N!}} \sum_P (-1)^{\xi_P} \varphi_{n_{P(1)}}(\mathbf{x}_1) \dots \varphi_{n_{P(N)}}(\mathbf{x}_N) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{n_1}(\mathbf{x}_1) & \varphi_{n_2}(\mathbf{x}_1) & \dots & \varphi_{n_N}(\mathbf{x}_1) \\ \varphi_{n_1}(\mathbf{x}_2) & \varphi_{n_2}(\mathbf{x}_2) & \dots & \varphi_{n_N}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{n_1}(\mathbf{x}_N) & \varphi_{n_2}(\mathbf{x}_N) & \dots & \varphi_{n_N}(\mathbf{x}_N) \end{vmatrix}\end{aligned}\quad (1.3.12)$$

¹This object is called a *Slater Determinant*. The set $\{\Phi_\kappa\}_\kappa$ of Slater Determinants spans the N -particle Hilbert space, and so tells us *which* linear combinations of product states are *physically* appropriate for the representation of fermions satisfying the antisymmetry property (1.3.11). Note that if $n_i = n_j$ for any pair of rows i, j then the Slater determinant vanishes according to a well-known theorem of determinants.

One can work directly with Slater Determinants to evaluate inner products and eigenvalues in quantum mechanics using the so-called Slater Rules [129, 130]. However, this can become very cumbersome, especially in the context of time-dependent problems, and it is possible to massively simplify the algebra through the method of *second quantization*. The central idea of second quantization is to revert to a representation of N -body systems in terms of the number of particles occupying each single-particle state, rather than the states themselves [131]. It is motivated by convenience - it is an algebra that encodes the antisymmetry property of electrons into the operators of the theory, which map between elements in a fermionic N -particle Hilbert space $\mathcal{F}_N$. It also enables us to easily study systems which have variable numbers of particles, i.e. statistical mechanical systems coupled to a reservoir at finite temperature [132].

Consider the following wave vector:

$$|n_{n_1}, n_{n_2}, \dots, n_{n_N}\rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\xi_P} |\varphi_{P n_1}\rangle \otimes \dots \otimes |\varphi_{P n_N}\rangle \quad (1.3.13)$$

Each number in this ket denotes the number of particles existing in each single particle state of a Slater determinant. By the Pauli Exclusion Principle, $n_{n_i} = 1$ or 0 , such that we replace the above notation with $|n_1, n_2, \dots, n_N\rangle$, where the presence of n_i just means that the single particle state ψ_{n_i} is occupied. The *fermionic creation operator* $\hat{d}^\dagger$ is defined so that one can map from N to $N + 1$ electron states:

$$\hat{d}_k^\dagger |n_1, \dots, n_N\rangle = (-1)^{N-k} (1 - n_{n_k}) |n_1, \dots, n_{k-1}, n_k, n_{k+1}, \dots, n_N\rangle \quad (1.3.14)$$

Here, the prefactor of $(1 - n_{n_k})$ is equal to 1 when the n_k state is unoccupied, and 0 when it is occupied, so that no fermions can be added to an already occupied state. The prefactor of $(-1)^{N-k}$ arises as the n_k state is added to the right hand column of the occupation number-represented state vector, before being moved to the k -th slot by pairwise exchanges. Note that the Particle creation operators do not operate within $\mathcal{F}_N$, but instead map from $\mathcal{F}_N$ to $\mathcal{F}_{N+1}$. They operate within an enlarged Hilbert space, known as the *Fock space* $\mathcal{F}_{FS}$, which contains all possible linear combinations of all possible N -body wave vectors for all possible N . The *fermionic annihilation operator* $\hat{a}$ removes a particle from the N -particle state:

¹ κ denotes an *equivalence class* of states which are identical up to a global multiplicative phase factor, and $\sum_P$ denotes a sum over permutations.

$$\hat{d}_k |n_1, \dots, n_k, \dots, n_N\rangle = (-1)^{N-k} n_{n_k} |n_1, \dots, n_{k-1}, n_{k+1}, \dots, n_N\rangle \quad (1.3.15)$$

The factor of $(-1)^{N-k}$ in front of the vector on the right hand side of this expression indicates that the n_k index was shifted to the final column of the product, where the annihilation operator removed it. It follows from the definition (1.3.15) that

$$\hat{d}_i \hat{d}_j + \hat{d}_j \hat{d}_i \equiv \left\{ \hat{d}_i, \hat{d}_j \right\} = 0 \quad (1.3.16)$$

Here, the bracketed term denotes the *anti-commutator* of the two operators. The creation and annihilation operators are Hermitian conjugates of each other². Thus, we can take the Hermitian conjugate of the previous anticommutator to give:

$$\left\{ \hat{d}_i^\dagger, \hat{d}_j^\dagger \right\} = 0 \quad (1.3.17)$$

Finally, if one operates upon the N -particle state (1.3.13) with $\hat{d}_i \hat{d}_j^\dagger$ and employs the definitions (1.3.10), (1.3.11), one can show after some tedious algebra that it is equal to $-\hat{d}_j^\dagger \hat{d}_i + \delta_{ij}$:

$$\left\{ \hat{d}_i, \hat{d}_j^\dagger \right\} = \delta_{ij} \quad (1.3.18)$$

The three key field operator identities (1.3.16), (1.3.17) and (1.3.18) allow us to greatly simplify manipulations involving Slater Determinants due to the bijection which exists between that representation and the occupation number representation.

It is possible to depart from the basis-dependent creation (annihilation) operators $\hat{d}_i^\dagger$ ($\hat{d}_i$), and define operator valued functions of any continuous parameter ξ which map N -body wavefunctions in the ξ representation onto $N - 1$ and $N + 1$ -body wavefunctions. Let $\{\varphi_i(\xi)\}$ be a complete, orthonormal basis for 1-particle Hilbert space, then define the creation and annihilation operators of the field:

$$\hat{\psi}(\xi) = \sum_{i=1}^{\infty} \hat{d}_i \varphi_i(\xi) \quad (1.3.19)$$

$$\hat{\psi}^\dagger(\xi) = \sum_{i=1}^{\infty} \hat{d}_i^\dagger \varphi_i^*(\xi) \quad (1.3.20)$$

The fundamental anticommutation relations obeyed by $\hat{\psi}$ and $\hat{\psi}^\dagger$ are easily shown to be the following:

$$\left\{ \hat{\psi}(\xi), \hat{\psi}(\xi') \right\} = 0 \quad (1.3.21)$$

$$\left\{ \hat{\psi}^\dagger(\xi), \hat{\psi}^\dagger(\xi') \right\} = 0 \quad (1.3.22)$$

$$\left\{ \hat{\psi}^\dagger(\xi), \hat{\psi}(\xi') \right\} = \delta(\xi - \xi') \quad (1.3.23)$$

²To see this, let $n_k \in \langle n_1 \dots n_N \rangle$ and $n_k \notin \langle m_1 \dots m_M \rangle$, with $N = M + 1$ and $\langle n_1, \dots, n_{N-1} \rangle = \hat{P} \langle m_1, \dots, m_M \rangle$. Then:

$$\langle n_1 \dots n_N | \hat{d}_k^\dagger | m_1 \dots m_M \rangle = \langle n_1 \dots n_N | m_1 \dots m_M, n_k \rangle = (-1)^{2\xi_P} \langle n_1 \dots n_N | \hat{d}_k | m_1 \dots m_M \rangle^\dagger$$

A single-particle operator defined on $\mathcal{F}_N$ maps between elements of this Hilbert space. $\hat{T} = \sum_{i=1}^N \hat{T}_i$ is a one-body operator acting on $|n_1 \dots n_N\rangle$ if it can be written in terms of the following tensor product of operators acting on every single-particle Hilbert space $\mathcal{H}^{(i)}$ making up $\mathcal{F}_N$:

$$\hat{T}_i = \hat{I}^{(1)} \otimes \dots \otimes \hat{T}^{(i)} \otimes \dots \otimes \hat{I}^{(N)} \quad (1.3.24)$$

Here, $\hat{A}^{(1)} \otimes \hat{B}^{(2)} |\varphi_{n_1}\rangle |\varphi_{n_2}\rangle = |\hat{A}\varphi_{n_1}\rangle |\hat{B}\varphi_{n_2}\rangle$, i.e. operators with the superscript (i) are defined on the i -th single particle Hilbert space. In the $\{|\mathbf{x}\rangle\}$ basis, a one-body operator has elements $\langle \mathbf{x}_i | \hat{T}^{(i)} | \mathbf{x}'_i \rangle \equiv \hat{T}(\mathbf{x}_i) \delta(\mathbf{x}_i - \mathbf{x}'_i)$, such that:

$$\left(\langle \mathbf{x}_1 | \otimes \dots \otimes \langle \mathbf{x}_N | \right) \hat{T} \left(| \varphi_{n_1} \rangle \otimes \dots \otimes | \varphi_{n_N} \rangle \right) = \left[\sum_i \hat{T}(\mathbf{x}_i) \right] \varphi_{n_1}(\mathbf{x}_1) \dots \varphi_{n_N}(\mathbf{x}_N) \quad (1.3.25)$$

In terms of the field operators introduced above, we can then derive the following representations of the single particle operator, assuming it is diagonal in $\mathbf{x}$ -space:

$$\hat{T} = \sum_i \hat{T}(\mathbf{x}_i) = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{T}(\mathbf{x}) \hat{\psi}(\mathbf{x}) = \sum_{i,j} T_{ij} \hat{d}_i^\dagger \hat{d}_j \quad (1.3.26)$$

Two-body operators are encountered in many-body theory in the form of the Coulomb interaction. In general, $\hat{V}$ is a two-body operator if it can be written in the form

$$\hat{V} |\varphi_{n_1}\rangle \otimes \dots \otimes |\varphi_{n_N}\rangle = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \hat{V}_{ij} \left(|\varphi_{n_1}\rangle \otimes \dots \otimes |\varphi_{n_N}\rangle \right) \quad (1.3.27)$$

where, $\hat{V}_{12} = \hat{V}^{(1)} \otimes \hat{V}^{(2)} \otimes \hat{I}^{(3)} \otimes \dots \otimes \hat{I}^{(N)}$, i.e. $\hat{V}_{ij}$ acts non-trivially in the two-particle subspace $\mathcal{H}^{(i)} \otimes \mathcal{H}^{(j)}$, in that it cannot in general be decomposed into a tensor product of operators on each of $\mathcal{H}^{(i)}$ and $\mathcal{H}^{(j)}$. We impose that each such operator is diagonal in the $|\mathbf{x}_i\rangle |\mathbf{x}_j\rangle$ basis, such that any two-body operator $\hat{V} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \hat{V}_{ij}$ has an action which can be written:

$$\langle \mathbf{x}_1, \dots, \mathbf{x}_N | \hat{V} | \Psi \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{y}) \hat{v}(\mathbf{x}, \mathbf{y}) \hat{\psi}(\mathbf{y}) \hat{\psi}(\mathbf{x}) \Psi(\mathbf{x}_1 \dots \mathbf{x}_N) \quad (1.3.28)$$

where the two-particle interaction $\hat{v}(\mathbf{x}, \mathbf{y})$ is defined by the identity:

$$\langle \mathbf{x}_i | \langle \mathbf{x}_j | \hat{V}_{ij} | \mathbf{x}'_i \rangle | \mathbf{x}'_j \rangle \equiv v(\mathbf{x}_i, \mathbf{x}_j) \delta(\mathbf{x}_i - \mathbf{x}'_i) \delta(\mathbf{x}_j - \mathbf{x}'_j) \quad (1.3.29)$$

A Hamiltonian $\hat{H} = \hat{T} + \hat{V}$ consisting of a one-body kinetic part added to a two-body interacting part can then be represented as

$$\hat{H} = \sum_{i,j} T_{ij} \hat{d}_i^\dagger \hat{d}_j + \sum_{i,j,k,l} V_{ijkl} \hat{d}_i^\dagger \hat{d}_j^\dagger \hat{d}_k \hat{d}_l \quad (1.3.30)$$

where we make the definition:

$$T_{ij} = \int d\mathbf{x} \varphi_i^*(\mathbf{x}) \hat{T}(\mathbf{x}) \varphi_j(\mathbf{x}) \quad (1.3.31)$$

$$V_{ijkl} = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{y}) \hat{v}(\mathbf{x}, \mathbf{y}) \varphi_j(\mathbf{y}) \varphi_i(\mathbf{x}) \quad (1.3.32)$$

This can be seen immediately by substituting the defining relations (1.3.19) and (1.3.20) into the second-quantized form of $\hat{H}$. This allows us to represent a few useful operators.

(i) In Hartree units, the kinetic energy operator is written:

$$\hat{T} = -\frac{1}{2} \sum_i \nabla_i^2 = -\frac{1}{2} \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \nabla^2 \hat{\psi}(\mathbf{x}) \quad (1.3.33)$$

(ii) The Coulombic interaction between electrons is given by:

$$\hat{V} = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} \frac{\hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{y}) \hat{\psi}(\mathbf{y}) \hat{\psi}(\mathbf{x})}{|\mathbf{x} - \mathbf{y}|} \quad (1.3.34)$$

(iii) An external time-dependent scalar potential is written:

$$\hat{v}(t) = \sum_i v(\mathbf{x}_i, t) = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) v(\mathbf{x}, t) \hat{\psi}(\mathbf{x}) \quad (1.3.35)$$

(iv) The central physical quantity in Hartree-Fock theory and Density Functional Theory (DFT) is the electron density $n(\mathbf{x})$. The electron density at any point is an eigenvalue of the electron-density operator. This operator-valued function is expressible purely in terms of the field operators:

$$\hat{n}(\mathbf{x}) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i) = \int d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}') \delta(\mathbf{x} - \mathbf{x}') \hat{\psi}(\mathbf{x}') = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \quad (1.3.36)$$

From the definition of the field operators, we can also write this as:

$$\hat{n}(\mathbf{x}) = \sum_{i,j} \varphi_i^*(\mathbf{x}) \varphi_j(\mathbf{x}) \hat{d}_i^\dagger \hat{d}_j \quad (1.3.37)$$

It follows that the total number operator can be written:

$$\hat{N} = \int d\mathbf{x} \hat{n}(\mathbf{x}) = \sum_i \hat{d}_i^\dagger \hat{d}_i \quad (1.3.38)$$

We infer from this expression that the number of particles in the i -th single particle state is given by the eigenvalue of the operator $\hat{n}_i \equiv \hat{d}_i^\dagger \hat{d}_i$.

1.3.3 Time-Dependent Quantum Statistical Mechanics

The second source of uncertainty in the problem of quantum transport through molecular junctions follows from the fact that nanojunctions consist of a nanosized subsystem coupled to a set of macro- or mesoscopic particle and heat reservoirs. The effect of the reservoirs is to buffet the molecule, and cause it to continually fluctuate between

the allowed quantum states $\{|\psi_i\rangle\}$ with energies $\{E_i\}$. It also causes the number of electrons in the molecule to vary, though it should be noted that the total number of electrons in the molecule plus that of the leads remains a constant. The system visits each possible quantum state with probability p_i , and $p_i = p_i(t)$ may depend on time if the lead parameters are time-dependent. When the lead parameters are static, the effect of the nanosystem-reservoir coupling is to cause the system to visit each of its allowed energy states as often as possible, and with a fixed relative frequency on the time scale over which the experiment takes place, consistently with the constraints of a fixed total particle number

$$N = \sum_i p_i n_i \quad (1.3.39)$$

and fixed total internal energy:

$$U = \sum_i p_i E_i \quad (1.3.40)$$

In this case, the system is said to be in a state of *equilibrium*, and the molecular region of the nanojunction is said to have *equilibrated* with the leads. When the system is in equilibrium, we have no reason to expect the system to be in one state rather than any other. The information that we receive from a measurement of the system in the i -th state may be thought of in terms of our ‘surprise’ at measuring that state. We are more ‘surprised’ to observe a state that has a very low probability of occurring, and so our measure of ‘surprise’, S_i , at obtaining the i -th outcome must be a monotonically decreasing function of p_i , in addition to satisfying the desideratum that $S_{i+j} = S_i + S_j$ when the i -th and j -th states are statistically independent of each other. Under these criteria, it was proven by Shannon that $S_i = -k \ln p_i$, where k is an arbitrary multiplicative constant [133]. Our expected ‘surprise’ at obtaining a given outcome of an experiment is then given by the Gibbs (or Shannon, up to a multiplicative constant $k_B = 8.3 \times 10^{-5} \text{ eV K}^{-1}$) entropy:

$$S[\{p_i\}] = -k_B \sum_{p_i} p_i \ln p_i \quad (1.3.41)$$

In addition we define the chemical potential $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$, which quantifies the amount of energy required to add a particle to the system, and the temperature $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$, which measures how difficult it is, energetically speaking, to increase the complexity of a system.

The fact that, in equilibrium, the system is moving between between allowed states of the ensemble as rapidly as possible is described mathematically by maximizing the expected ‘surprise’ subject to the macroscopic constraints in equations (1.3.39) and (1.3.40). In other words, the state of the system has been randomized as much as possible, so we should be maximally surprised to obtain any given result when any other could have resulted from the randomization. Mathematically, this dynamical situation is described by a maximization of the following information functional:

$$I[\{p_i\}] = k_B \sum_i p_i \ln p_i + \lambda_0 \left(\sum_i p_i - 1 \right) + \lambda_1 \left(\sum_i p_i E_i - U \right) + \lambda_2 \left(\sum_i p_i N_i - N \right) \quad (1.3.42)$$

Here, $\lambda_0, \lambda_1, \lambda_2$ are parameters which can be determined by finding the p_i extremizing this functional and substituting back into the constraint equations. The result is the grand-canonical distribution for systems in equilibrium:

$$p_i = Z^{-1} \exp \left[-\frac{(E_i - \mu n_i)}{k_B T} \right] \quad (1.3.43)$$

Here,

$$Z \equiv \sum_i \exp \left[-\frac{E_i - \mu n_i}{k_B T} \right] \quad (1.3.44)$$

is the *grand partition function*. To incorporate both the quantum and thermal sources of probability into our calculation of static physical quantities accessible to the experimentalist, we equate them with equilibrium averages over quantum expectation values, or ensemble averages. The ensemble average of the arbitrary operator $\hat{O}$ is given by:

$$\langle \hat{O} \rangle \equiv \sum_i p_i \langle \Psi_i | \hat{O} | \Psi_i \rangle = \text{Tr} [\hat{\rho}_0 \hat{O}] \quad (1.3.45)$$

Here, we have introduced the trace and the density matrix

$$\hat{\rho}_0 = \sum_i p_i |\Psi_i\rangle \langle \Psi_i| = \frac{e^{-\beta \hat{H}^M}}{\text{Tr} [e^{-\beta \hat{H}^M}]} \quad (1.3.46)$$

where $\hat{H}^M = \hat{H} - \mu \hat{N}$ is the Matsubara Hamiltonian and $\beta \equiv 1/k_B T$ is the inverse temperature.

If one wishes to propagate states in a statistical ensemble between some initial time t_0 and t , one inserts unitary time evolution propagators into the ensemble averages, defined by the relation:

$$|\Psi(t)\rangle = \hat{U}(t, t_0) |\Psi(t_0)\rangle \quad (1.3.47)$$

For a generic time-dependent Hamiltonian $\hat{H}(t)$, one can then derive the associated propagator:

$$\hat{U}(t, t_0) = \hat{T} \left[\exp \left(-i \int_{t_0}^t d\tau \hat{H}(\tau) \right) \right] \quad (1.3.48)$$

Here, the time-ordering operator $\hat{T}$ orders exponentials of later times to the left, i.e. the above describes propagation in time over infinitesimal increments of time, and each such propagation may be determined by a Hamiltonian that does not commute with the Hamiltonian at other times.³ When we propagate each member of the ensemble in time, for example by applying an external electromagnetic field to the system, one replaces the expectation value of operator $\hat{O}(t)$ with the *dynamical ensemble average* $\langle \hat{O}(t) \rangle$, which is just a classical average over the quantum dynamical averages for each propagated (via Eq. (1.3.47)) member of the statistical ensemble:

$$\langle \hat{O}(t) \rangle \equiv \sum_i p_i \langle \Psi_i(t) | \hat{O}(t) | \Psi_i(t) \rangle = \text{Tr} [\hat{\rho}_0 \hat{O}_H(t)] \quad (1.3.50)$$

Here, we introduce the *Heisenberg representation* of an operator:

$$\hat{O}_H(t) \equiv U^\dagger(t, t_0) \hat{O} U(t, t_0) \quad (1.3.51)$$

Thus, for a closed quantum system, the macroscopic, dynamical value of the observable O is fixed by the initial condition $\hat{\rho}_0$ (which depends upon the history of how the system was prepared), and the propagator $U(t, t_0)$ (which depends on the system Hamiltonian at times $t > t_0$).

³This fact prevents us from writing the above without $\hat{T}$, as the following operator inequality is valid in general:

$$\exp [\hat{A}] \exp [\hat{B}] \neq \exp [\hat{A} + \hat{B}] \quad (1.3.49)$$

The equation (1.3.49) becomes an equality only in the case that $[\hat{A}, \hat{B}] = 0$, i.e. when the exponentiated operators all commute.

1.4 Theoretical Developments

1.4.1 Landauer-Büttiker Theory

1.4.1.1 Physical Meaning of the Current

There have been two main research directions in the theoretical treatment of molecular transport. The first mainly focuses on the detailed electronic structure of specific chemical systems, through the use of DFT-based calculations of system parameters [134, 135, 136, 137, 138, 139]. In these approaches, the system is prepared in an equilibrium state whose electronic structure is obtained from *ab initio* calculations of orbitals relevant for the motion of free electrons through the system, before the external field is applied. In the vast majority of work done on molecular transport to date, the conducting molecule is assumed to possess a static conformation, and the accessible energies on the molecule are contained within a time-independent Hamiltonian.

The second main school of thought focuses on model calculations coupled with some phenomenology to get qualitative information on transport properties. A great deal of physics is readily accessible with a simple tight-binding model and a simplified treatment of the coupling. Indeed, in Refs. [140, 141, 142, 143], parameterizations of tight-binding models enabled qualitatively accurate results for real systems to be obtained.

For noninteracting systems the Landauer-Büttiker (LB) formalism has enjoyed great success as a tool for the description of transport processes in the steady-state regime, when a long time has passed after the switch-on of a constant bias [144, 145, 146, 147, 148]. This success may be attributed to its formal and conceptual simplicity, and a set of equations for the steady-state current and power spectrum that can be combined with DFT calculations to access the electron transport properties of a system [134, 136, 138, 139]. It is useful for the description of transport processes in the ballistic regime, where the time separating electron-electron interaction events exceeds the time taken for an electron to cross the molecular region. The LB formalism is convenient for the description of several features of transport processes accessible to experimentalists: temperature-dependence [149], quantization of the conductance [150], exponential decay of conductance as a function of junction length [31, 151], and the shot and thermal noise associated with the current [146, 147, 114]. It also enables the theorist to define and understand physical properties such as the traversal time for particles crossing the nanojunction in an intuitive way [152, 153]. The generic set-up of a nanojunction studied with this formalism contains at least three parts, illustrated schematically in Fig. 1.4.1. The central region C represents the scattering molecule, and is connected to the left and right electron reservoirs, L , R which continue along the x -direction (parallel to the direction of current flow) to $\mp\infty$, respectively.

We take an arbitrary cross-sectional surface S cutting the nanojunction at the point we wish to define the current flow, and define $\hat{n}$, the unit vector to S , in the $L \rightarrow R$ direction. The rate of transfer of charge across the surface dS in time dt is given by $\frac{dQ}{dt} = \mathbf{J} \cdot \hat{n} dS$, where the current density $\mathbf{J}$ is defined in terms of the rate of change of number density, $\mathbf{J} \equiv qn(\mathbf{x}, t) \mathbf{v}(\mathbf{x}, t)$, with $\mathbf{v}(\mathbf{x}, t)$ the *drift velocity* (this refers to the average velocity, and is due to the bias only, i.e. it is independent of thermal agitation. and the charge q of electrons traversing S). The total average current across a large region of surface S is then the sum of these contributions, $I(t) = \int_S \mathbf{J}(\mathbf{x}, t) \cdot d\mathbf{S}$, where $d\mathbf{S} = d\mathbf{r}_\perp \hat{i} = dydz \hat{i}$ is an infinitesimal element of surface area with normal along the x -direction. In the absence of a magnetic field, we can define an operator $\hat{J}(\mathbf{x}, t)$ giving the flux of current out of an infinitesimal sphere surrounding the point $\mathbf{x}$:

$$\hat{J}(\mathbf{x}, t) \equiv q \frac{d\hat{n}_H(\mathbf{x}, t)}{dt} = -\nabla \cdot \hat{j} \quad (1.4.1)$$

Here, we have introduced the *paramagnetic current density operator* $\hat{j}$, defined by

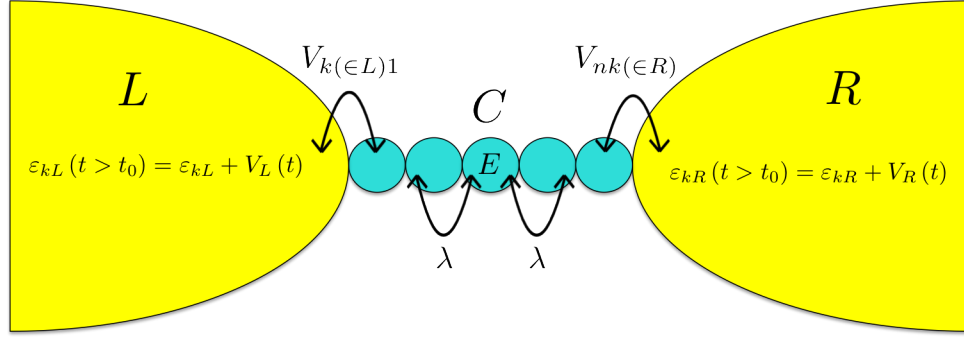


Figure 1.4.1: Schematic of a typical two-lead molecular junction consisting of the left (L) and right (R) leads bridged by a molecular system (C). In this schematic, C is a molecular wire composed of $N_s = 5$ atomic sites with nearest neighbour hopping.

$$\hat{j}(\mathbf{x}, t) \equiv \frac{iq}{2} \left[\hat{\psi}_H^\dagger(\mathbf{x}, t) \left[\nabla \hat{\psi}_H(\mathbf{x}, t) \right] - \left[\nabla \hat{\psi}_H^\dagger(\mathbf{x}, t) \right] \hat{\psi}_H(\mathbf{x}, t) \right] \quad (1.4.2)$$

Taking the field operators to refer to the creation/annihilation of states in the lead α , and using the divergence theorem, $\hat{J}(\mathbf{x}, t)$ can be integrated to obtain the operator returning the total current across the surface S in this lead:

$$\hat{I}_\alpha(t) = -\frac{iq}{2} \int_S dydz \left[\frac{\partial \hat{\psi}_{\alpha,H}^\dagger(\mathbf{x}, t)}{\partial x} \hat{\psi}_{\alpha,H}(\mathbf{x}, t) - \hat{\psi}_{\alpha,H}^\dagger(\mathbf{x}, t) \frac{\partial \hat{\psi}_{\alpha,H}(\mathbf{x}, t)}{\partial x} \right] \quad (1.4.3)$$

The standard picture corresponding to the process of switching on a voltage in an MMM junction or other nanostructure is as follows. Initially, each lead α is kept at temperature T and chemical potential μ_α . Electronic states of energy $\varepsilon_{k\alpha}$ in the lead are represented by lead creation (annihilation) operators $\hat{d}_{k\alpha}^\dagger$ ($\hat{d}_{k\alpha}$), and distributed in the lead energy space according to the Fermi function:

$$\langle \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha} \rangle = f(\varepsilon_{k\alpha} - \mu_\alpha) = \frac{1}{e^{\beta(\varepsilon_{k\alpha} - \mu_\alpha)} + 1} \quad (1.4.4)$$

Usually for simplicity in a typical $L-C-R$ junction it is assumed that each subsystem making up the nanojunction is completely decoupled from the others, i.e. the initial density matrix $\hat{\rho}_0$ of the nanojunction has the tensor product structure:

$$\hat{\rho}_0 = \hat{\rho}_L \otimes \hat{\rho}_C \otimes \hat{\rho}_R \quad (1.4.5)$$

Then, at the switch-on time t_0 , the leads are connected to the molecule, and the imbalance in chemical potentials of the leads causes a current to flow through the device region. This separation of the initial state into a product of its subsystems is known as the *partitioned* approach to the switch-on problem. In addition, a bias V_α may be added to the energies of lead α at this time to drive the system into a particular nonequilibrium state. The LB formalism assumes that the switch-on time $t_0 \rightarrow -\infty$ is relegated to the distant past, and that the bias established across the system at that time is static, so that one is only interested in the ensemble average of the steady state current:

$$I_\alpha^{(LB)} = \lim_{t_0 \rightarrow -\infty} \langle \hat{I}_\alpha(t) \rangle \quad (1.4.6)$$

This means that the specifics of the system preparation are ignored within this formalism, raising issues to be discussed further in Section 1.4.2.1.

Electrons obey fermionic statistics, so charge transfer across a sample in the $L \rightarrow R$ direction occurs when a state in L is filled but the corresponding state in R is empty. A constant bias applied to each lead (which may include the difference in Fermi levels) then opens an energy gap between the electronic states of each lead, known as the *bias window*, $[V_R, V_L]$, and electrons will flow from lead L to lead R if $V_L > V_R$. A further assumption of the LB formalism is to treat electrons in the leads as independent plane waves. The leads are populated with these waves according to the Fermi distribution function, and propagated onto the molecule, where they scatter. The molecular region is usually taken to be smaller than the distance travelled by electrons between electron-electron scattering processes, so that the electrons can be assumed noninteracting. Transport of this kind is described as *ballistic*, and the LB formalism can therefore only be used to treat interacting systems at the mean-field level. In the general case of a multilead system with initial Fermi levels all equal to $\mu_\alpha = \mu$, the current in lead α is given in terms of an energy-dependent transmission probability $T_{\gamma\alpha}(\omega)$ between leads γ and α multiplying the difference in Fermi functions of the leads ⁴:

$$I_\alpha^{(LB)} = \frac{1}{\pi} \sum_\gamma \int d\omega [f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)] T_{\gamma\alpha}(\omega) \quad (1.4.7)$$

The expression (1.4.7) suggests the interpretation of $T_{\gamma\alpha}$ as the probability for an electron in lead γ to be scattered into lead α . This formula is valid at long times after the switch on of a constant bias, when the system has relaxed into an ideal steady state [128]. The problem of static transport therefore reduces to calculation of the $T_{\gamma\alpha}$, which can be done e.g. by substituting scattering state solutions of the time independent Schrodinger equation into Eq. (1.4.3) [113]. For future reference, any description of a formula as being of the *LB type* in this thesis means that it has the same mathematical structure as Eq. (1.4.7).

1.4.1.2 Toy Model and WBLA

A common toy model of a two-terminal quantum dot molecular junction is the Fano model of a single energy interacting with a continuum of states in the leads. This model assumes that the molecular region is dominated by a single energy, ε_0 , and that this energy is coupled to the left and right leads, which are assumed to be noninteracting and populated by a discretized continuum of states, of energy $\varepsilon_{k\alpha}$, with α one of L and R [128]. The Hamiltonian of this system is thus given by:

$$\hat{H} = \sum_{k\alpha} \varepsilon_{k\alpha} \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha} + \varepsilon_0 \hat{d}_0^\dagger \hat{d}_0 + \sum_{k\alpha} [T_{0,k\alpha} \hat{d}_0^\dagger \hat{d}_{k\alpha} + T_{k\alpha,0} \hat{d}_{k\alpha}^\dagger \hat{d}_0] \quad (1.4.8)$$

In this Hamiltonian, the first term describes the energy states on the leads, the second term describes the single level and the third term describes the lead-molecule coupling with overlap integrals $T_{0,k\alpha}$ describing the energetics of hopping between the lead and dot states. The presence of the leads causes the dot energy to become effectively modified by the so-called embedding self-energy

$$\Sigma_{em}(\omega) = \sum_{\alpha \in L, R} \Lambda_\alpha(\omega) - \frac{i}{2} \sum_{\alpha \in L, R} \Gamma_\alpha(\omega) \quad (1.4.9)$$

where

$$\Lambda_\alpha(\omega) = \mathcal{P} \sum_k \frac{|T_{k\alpha,0}|^2}{\omega - \varepsilon_{k\alpha}} \quad (1.4.10)$$

$$\Gamma_\alpha(\omega) = 2\pi \sum_k |T_{k\alpha,0}|^2 \delta(\omega - \varepsilon_{k\alpha}) \quad (1.4.11)$$

⁴This form of the LB current includes a factor of 2 due to spin degeneracy.

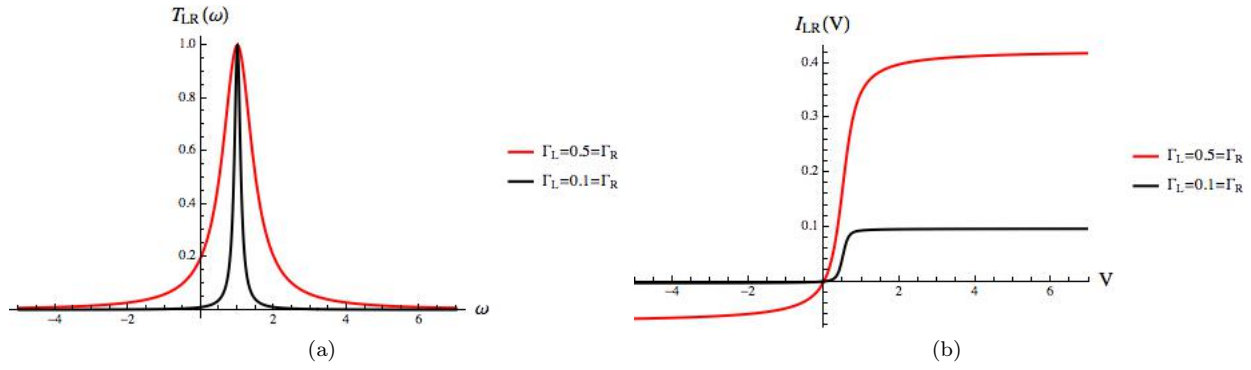


Figure 1.4.2: (a) Transmission probability for the quantum dot WBLA model at different values of the level width. (b) Current-voltage characteristics corresponding to the transmissions in (a), with $k_B T = 0.1$, $\mu = 0$, $V = V_L$ and $V_R = 0$.

In Eq. (1.4.10), $\mathcal{P}$ denotes the Cauchy principal part, and these two functions are related via the Hilbert transform:

$$\Lambda_\alpha(\omega) = \mathcal{P} \int \frac{dx}{2\pi} \frac{\Gamma_\alpha(x)}{\omega - x} \quad (1.4.12)$$

Within this model, it is well-known [154] that the transmission probability takes the *Breit-Wigner* form:

$$T_{RL}(\omega) = \frac{\Gamma_L(\omega) \Gamma_R(\omega)}{(\omega - \varepsilon_0 - \Lambda(\omega))^2 + \left(\frac{\Gamma(\omega)}{2}\right)^2} \quad (1.4.13)$$

These formulas will be derived in a much more rigorous way in Chapter 2; for now we simply state them in order to convey some key physical concepts. The first is the role played by the *level-width* $\Gamma_\alpha(\omega)$, which is responsible for the hybridization effects discussed in Section 1.2.1. In general, the level-width will depend on ω , but it is common practice in transport calculations to assume the band-width of the lead energies to run from $\omega = -\infty$ to $\omega = \infty$, in which case we approximate the level-width by its value at the Fermi energy of the leads, $\Gamma_\alpha(\omega) \simeq \Gamma_\alpha(\varepsilon_\alpha^F)$. In this case, Eq. (1.4.12) leads to a vanishing *level-shift*, $\Lambda_\alpha(\omega) = 0$. This assumption is known as the wide-band limit approximation (WBLA), and its drawbacks will be discussed in detail in Section 2.4. In Fig. 1.4.2 (a), we plot the transmission function for the quantum dot in the WBLA at different values of the level width. We see that this quantity is aptly named - when the level width is decreased, the width of the Lorentzian transmission function (given by $\Gamma/2$) is decreased, and so the energy window at which resonantly-enhanced transport can occur through the dot is decreased. In Fig. 1.4.2 (b), we set $k_B T = 0.1$, $\mu = 0$, define $V = V_L$ as a constant shift in the left lead Fermi level and $V_R = 0$, and plot the symmetrized current

$$I_{LR} \equiv \frac{I_L^{(LB)} - I_R^{(LB)}}{2} \quad (1.4.14)$$

as a function of V . A characteristic step-like structure is seen in the current with a voltage dependence that is linear in the vicinity of $\mu + V - \varepsilon_0 \sim \Gamma/2$, before saturating at values of $|\mu + V - \varepsilon_0| > \Gamma/2$, which corresponds physically to a regime where the energy required to hop between the lead and the dot is greater than the energy spread of the dot state. Nonlinear $I - V$ curves are ubiquitous in the quantum transport literature, and occur for a variety of different molecular structures with a multitude of transmission probability functions [155, 66, 156, 35].

Here we have briefly discussed the simplest kind of Fano resonance in the transmission function and its relation to the hybridization of the leads. More complex resonances in the transmission functions, with asymmetric line shapes that deviate from the Breit-Wigner form, can be seen in self-consistent calculations of the transmission through

complex molecules. In particular, the position of the molecular resonances can depend on the bias and the strength of the lead-molecule coupling in ways that cannot be captured within the simple model discussed here [137, 157]. For a thorough review on the effects of molecule-electrode interfaces in quantum transport, the reader is referred to Ref. [23].

1.4.1.3 The Quantum Noise

The Landauer-Büttiker (LB) theory of shot and thermal noise represents a significant milestone in the development of the theory of current fluctuations in nanoscale systems [146, 147, 158, 159, 114]. To compute the fluctuations of lead currents, one defines the current fluctuation operator as the current operator renormalized by its thermal average:

$$\Delta \hat{I}_\alpha(t) \equiv \hat{I}_\alpha(t) - \langle \hat{I}_\alpha(t) \rangle \quad (1.4.15)$$

Given two leads, α, β , where α may equal β , the original LB theory of quantum noise focused on the symmetrized current correlator:

$$P_{\alpha\beta}(t_1, t_2) \equiv \frac{1}{2} \langle \Delta \hat{I}_\alpha(t_1) \Delta \hat{I}_\beta(t_2) + \Delta \hat{I}_\beta(t_2) \Delta \hat{I}_\alpha(t_1) \rangle \quad (1.4.16)$$

This satisfies the identity

$$P_{\alpha\beta}^*(t_1, t_2) = P_{\alpha\beta}(t_1, t_2) \quad (1.4.17)$$

i.e. it is real and therefore measurable in principle. The assumptions of the standard LB theory for a constant bias switch-on imply that the current, considered as a stochastic variable, loses its dependence on time and instead tends to a constant value given by an equation of the form (1.4.7). It is well known from the theory of stochastic processes [160] that the two-time correlation function must then be a function of the time difference $\tau = t_1 - t_2$ only:

$$\lim_{t_0 \rightarrow -\infty} P_{\alpha\beta}(t_1, t_2) = P_{\alpha\beta}(\tau) \quad (1.4.18)$$

The *power spectrum* is then defined as the Fourier transform of this time difference:

$$P_{\alpha\beta}(\Omega) = \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} P_{\alpha\beta}(\tau) \quad (1.4.19)$$

Experiments have demonstrated a good agreement between experiment and the power spectra obtained from the scattering theory for both the low-frequency noise [161, 162] and for power spectra that depend upon the frequency of the measurement device [163, 122, 164]. We will see a derivation of the finite frequency power spectrum of a noninteracting model in Chapter 3. For now it is sufficient to state the expression for the zero-frequency power spectrum most often quoted in theoretical and experimental work:

$$\lim_{\Omega \rightarrow 0} P_{LL}(\Omega) = 4q^2 \int \frac{d\omega}{2\pi} [(1 - f(\omega - V_L - \mu)) f(\omega - V_L - \mu) + (1 - f(\omega - V_R - \mu)) f(\omega - V_R - \mu) T_{RL}(\omega) \quad (1.4.20)$$

$$+ (f(\omega - V_L - \mu) - f(\omega - V_R - \mu))^2 T_{RL}(\omega) (1 - T_{RL}(\omega))]]$$

The $T_{RL}(\omega)$ give the probability for electrons to pass from lead R to lead L and are sometimes written as the

sum $T_{RL}(\omega) = \sum_i T_i(\omega)$ over a set of discrete scattering channels. Then in systems where two scattering channels dominate experimentalists can fit their data on the first and second moments of the current to Eqs. (1.4.7) and (1.4.20) to determine the T_i empirically [165, 166]. The term in the first line of Eq. (1.4.20) describes the transmission of electron-hole pairs across the nanojunction, and contains electron-hole distribution functions $(1 - f(\omega - V_i - \mu)) f(\omega - V_j - \mu)$, for $i, j = L, R$. It can be attributed to fluctuations of the particle number due to thermal excitations of the junction [114], as it vanishes when the temperature $1/\beta = 0$. The term on the second line of Eq. (1.4.20) describes the so-called partition noise [114], and is also zero when the molecule is completely transparent ($T_{RL}(\omega) = 1$) or completely opaque ($T_{RL} = 0$) to the propagating electrons, i.e. it is non-zero as a consequence of the partitioning of the propagating electronic states into transmitted and reflected wavepackets. When $V_L = V_R$, the partition noise term vanishes, as in this case there is no net drift of electrons across the junction.

1.4.2 Time-Dependent Extensions of the Landauer-Büttiker Theory

1.4.2.1 Partitioned vs Partition-free Approaches

Transport processes are fundamentally problems in nonequilibrium statistical mechanics, because they typically involve a sudden ‘switch-on’ of a coupling between subsystems or a bias across subsystems which breaks the physical symmetry between the system at $t = -\infty$ and $t = +\infty$. This means that if the system was prepared in an equilibrium state in the distant past, it will not relax back to its initial state in the far future. Historically, there have been two main approaches to this kind of switch-on problem. In *partitioned* approaches [167, 168, 169, 154, 113] the system consists initially of decoupled leads with different chemical potentials μ_α , as discussed in Section 1.4.1 and illustrated in Fig. 1.4.3 (a) for a central region C coupled to an arbitrary number of leads. At the initial time t_0 , an idealized coupling between C and the leads is added to the Hamiltonian. Working within a partitioned approach, Jauho et al. obtained a closed (ω, t) -space integral expression for the TD current response to an arbitrary time varying bias [169, 154]. This formula was later successfully applied to the problem of photon-assisted transport in a double quantum dot device [170].

Partition-free approaches [171, 128, 172] represent an attempt to provide a more accurate treatment of the way most systems are prepared in practice. In partition-free approaches, the lead-molecule coupling is present in the Hamiltonian at equilibrium, prior to the switch-on of a bias, illustrated schematically in Fig. 1.4.3 (b). This is closer than the partitioned approach to the situation in most real experiments [173], where the junction - coupling and all - is fabricated by experimentalists before the switch-on occurs, so that the coupling will be fully present at equilibrium, and all regions of the junction equilibrate with a single inverse temperature β and single chemical potential μ .

The problem of computing the nonlinear current response to a bias dropped across a nanoscale structure can be treated within the framework of the Nonequilibrium Green’s Function (NEGF) formalism [174, 175, 176, 177, 178, 179, 180, 181, 128]. The equivalence of NEGF to the LB theory in the noninteracting case is well known [182, 113], but it can also be extended to self-consistent calculations of the current [183, 184, 185, 186] and perturbative calculations of the current noise [187, 188] in systems with a Coulombic interaction. The NEGF method provides the conceptual foundation for the original work presented in this thesis and therefore the whole of Section 1.5 will be devoted to its description.

Working within the NEGF approach, important progress was made in the direction of a fully time-dependent partition-free approach by Stefanucci and Almladh, who obtained an integral formula for the linear current response to a TD bias within the WBLA and proved theorems of asymptotic equivalence between the partitioned and partition-free approaches [189]. Specifically, they proved that the long-time limit of the current does not differ

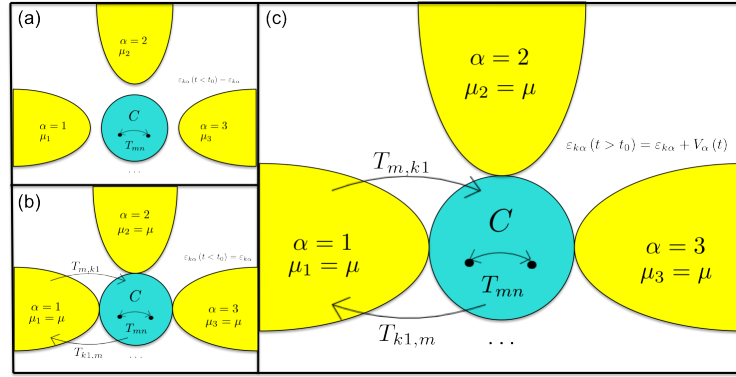


Figure 1.4.3: Schematic of the multi-terminal nanojunction in the time regimes before and after t_0 : (a) $t < t_0$ in the partitioned approach; (b) $t < t_0$ in the partition-free approach; (c) $t \geq t_0$ in either approach.

depending on whether the partitioned or partition-free approaches are taken (the Theorem of Equivalence), and that it is a unique function of the bias if the bias tends to a fixed value in the long-time limit (the Memory-loss Theorem). Recently, Tuovinen *et al.* obtained a closed frequency integral for the exact time-dependent current response to the switch-on of a static bias within a partition-free approach, making it increasingly possible to theoretically investigate short-time effects in nanoscale systems [190, 128]. Their formula clearly exhibits decaying modes in addition to a steady-state part, and has been applied to the study of transport through ring-shaped molecular junctions [190], graphene nanoribbons [172, 191] and superconducting junctions [192]. A related time-dependent formalism for phononic transport was derived that used a partitioned approach, and that goes beyond the WBLA [193, 194]. In another work that goes beyond the WBLA, Yang *et al.* used a master equation approach to compare the partitioned and partition-free switch on processes [195]. They found that, when the lead-molecule coupling is very strong, then not only the transient current but also the steady state current can differ due to the formation of localized states on the molecule.

This work was then extended in Refs. [1, 2, 3] to a closed integral formula for the nonlinear current response to an arbitrary time-dependent bias switched on in the leads, as detailed in Chapter 2 of this thesis. Unlike the previous approaches, which solved equations for the one-particle density matrix (lesser Green's function at equal times), this work included the derivation of an exact formula for the two-time lesser Green's function within the WBLA. This enabled the study of transient current fluctuations in both the partitioned and partition-free approaches in Ref. [4]. The analytical work published there is reproduced in Chapter 3 of this thesis, and the numerical work is included in Chapters 3 and 5.

1.4.2.2 Beyond DC Transport

Various approaches for going beyond the steady-state LB formalism exist. Neglecting interactions, these tend to involve extensions of the LB formalism to time-dependent systems (TD-LB). Early progress on this front was made by the Tien-Gordon theory of driven transport, which enabled qualitatively accurate calculations of the DC component of photon-assisted current through superconductor junctions [196, 197]. In this theory, the energies of one of the leads in a two-terminal biased system are all assumed to be shifted in a spatially homogenous manner by a periodic external field of driving frequency Ω_D , $V_{ac}(t) = V_{ac} \left(t + \frac{2\pi}{\Omega_D} \right)$, which is assumed to shift all energies in the leads homogeneously. Taking into account the constant bias shift, the TDSE for a state k in lead α is then given by:

$$i \frac{\partial |k, \alpha\rangle}{\partial t} = (\varepsilon_{k\alpha} + V_\alpha + V_{ac}(t)) |k, \alpha\rangle \quad (1.4.21)$$

The states then acquire a phase factor of

$$e^{-i(\varepsilon_{k\alpha} + V_\alpha)(t-t_0) - i \int_{t_0}^t d\tau V_{ac}(\tau)} \quad (1.4.22)$$

where t_0 is the initial time in the propagation. This is the same as in the constant bias case but with the additional phase factor $e^{-i \int_{t_0}^t d\tau V_{ac}(\tau)}$, which at $t_0 \rightarrow -\infty$ is periodic and can therefore be expanded into a Fourier series:

$$e^{-i \int_{-\infty}^t d\tau V_{ac}(\tau)} = \sum_n c_n e^{-in\Omega_D t} \quad (1.4.23)$$

where we introduce the Fourier coefficient:

$$c_m = \frac{\Omega_D}{2\pi} \int_0^{\frac{2\pi}{\Omega_D}} dt e^{-i \int_{-\infty}^t d\tau V_{ac}(\tau)} e^{im\Omega_D t} \quad (1.4.24)$$

Thus, the state $|k, \alpha\rangle$ is replaced by a weighted sum of states, with amplitude weighting provided by c_n and with energies split into sidebands of energy $\varepsilon_{k\alpha} + V_\alpha + n\Omega_D$, where $n \in \mathbb{Z}$. A common choice of time-dependent driving field is the harmonic one, $V_{ac}(t) = A \cos(\Omega_D t)$, in which case the phase factor is

$$e^{-i \int_{-\infty}^t d\tau V_{ac}(\tau)} = e^{-i \frac{A}{\Omega_D} \sin(\Omega_D t)} \quad (1.4.25)$$

Experimental work on tunneling between superconductors and in semiconductor heterostructures highlights the appearance of these sidebands in conductance spectra [84, 198]. In the initial Tien-Gordon theory of PAT, the time-averaged current for a constant bias V switched on in one of the leads was expressed as a summation over LB-type terms [196]:

$$I_L^{DC}(V) = \sum_{n=-\infty}^{\infty} |c_n|^2 I_L^{(LB)}(V + n\Omega_D) \quad (1.4.26)$$

Working within the time-dependent NEGF approach to mesoscopic transport developed in Ref. [154], it is also possible to express the current averaged over a driving period as a LB-type formula [85, 199]:

$$\lim_{t_0 \rightarrow -\infty} \frac{\Omega_D}{2\pi} \int_0^{\frac{2\pi}{\Omega_D}} d\tau I_\alpha(\tau) = \frac{1}{\pi} \sum_\gamma \int d\omega [f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)] \sum_{n=-\infty}^{\infty} |c_n|^2 T_{\gamma\alpha}(\omega + n\Omega_D) \quad (1.4.27)$$

Here, the transmission probability in Eq. (1.4.7) is replaced by an effective AC transmission consisting of a weighted sum of DC transmission functions with central peaks shifted by integer multiples of the driving frequency. In the simplest case of the single sinusoidal harmonic, we can substitute Eq. (1.4.25) into Eq. (1.4.24), and then make use of a well-known expression for the generating function for the n -th order Bessel functions of the first kind $J_n(x)$ ⁵:

⁵This identity can be used to get the analogous expression for the cosine, as

$$e^{\pm ix \sin(z + \frac{\pi}{2})} = e^{\pm ix \cos z} = \sum_{n=-\infty}^{\infty} J_n(x) e^{\pm in(z + \frac{\pi}{2})} = \sum_{n=-\infty}^{\infty} J_n(x) (\pm i)^n e^{\pm inz} = \sum_{n=-\infty}^{\infty} J_n(x) (\pm i)^n e^{\mp inz} \quad (1.4.28)$$

$$e^{\pm ix \sin(z+\phi)} = \sum_{r=-\infty}^{\infty} J_r(x) e^{\pm ir(z+\phi)} \quad (1.4.29)$$

This gives the following form for the effective transmission function:

$$T_{\gamma\alpha}(\omega, \Omega_D) = \sum_{n=-\infty}^{\infty} J_n^2\left(\frac{A}{\Omega_D}\right) T_{\gamma\alpha}(\omega + n\Omega_D) \quad (1.4.30)$$

Working within the system of a quantum dot coupled to two leads L, R in the WBLA, with the dot energy $\varepsilon_0 = 1$, driving frequency $\Omega_D = 1$ and $\Gamma_L = 0.5 = \Gamma_R$, we plot Eq. (1.4.30) for different values of the driving amplitude A in Fig. 1.4.4 (a). We observe that, as the driving amplitude is increased, the central resonance observed in the DC case (in Fig. 1.4.2 (a)) splits and spreads into several smaller sub-peaks. This is because the increased strength of the external field increases the access of electronic states to the energy side bands far from the central ($n = 0$) band, enabling absorption of single or multiple photons by electrons in the system. The peaks in the transmission function correspond to additional transport channels through the molecular junction: electrons may tunnel between ε_0 and the states in lead α excited by $V_\alpha + n\Omega_D$. Or equivalently, if the central region is illuminated by the external field, then electrons tunnel between lead states shifted by V_α and dot states of energy $\varepsilon_0 - n\Omega_D$. In Fig. 1.4.4 (b), we plot the dependence of the symmetrized current on the bias V , where the lead energies are shifted asymmetrically, i.e. $V_L = V = -V_R$, for the same parameters as in (a) and with the temperature $k_B T = 0.1$. As the amplitude is increased, the current characteristic goes from the steplike structure seen in Fig. 1.4.2 to a bumpy step as the additional transport channels are activated. We then decrease the level width to $\Gamma_L = 0.1 = \Gamma_R$, and plot the new transmission and current in Figs. 1.4.4 (c) and (d), respectively. We see that although there are no new transmission peaks, they are much more sharply defined as in this case the hybridization does not smear out the photon-assisted dot resonances in energy space. The current transitions to a more sharply defined ‘staircase’ structure. To understand where these steps come from, we may take the zero temperature limit of (the symmetrized version of) Eq. (1.4.27) in this model, which gives:

$$I_{LR} = \frac{2}{\pi} \frac{\Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)} \sum_{n=-\infty}^{\infty} J_n^2\left(\frac{A}{\Omega_D}\right) \left[\arctan\left(\frac{\mu + V_L + n\Omega_D - \varepsilon_0}{(\Gamma_L + \Gamma_R)/2}\right) - \arctan\left(\frac{\mu + V_R + n\Omega_D - \varepsilon_0}{(\Gamma_L + \Gamma_R)/2}\right) \right] \quad (1.4.31)$$

This is a weighted sum of steplike arctans, and the n -th term in the sum increases linearly when $|\mu + V_{L/R} + n\Omega_D - \varepsilon_0| \sim \Gamma/2$. Thus an increase in the amplitude A causes a transition to the aforementioned ‘staircase’ structure, as it activates more transmission channels which appear as arctan ‘steps’ in the summation of Eq. (1.4.31). When the level width is decreased, more steps appear without overlapping with each other (as in Fig. (1.4.4) (d)), as the additional transmission channels at large A are activated for a smaller bias window $|\mu + V + n\Omega_D - \varepsilon_0| \sim \Gamma/2$.

The recent experimental focus on low temperature transport in the GHz-THz range has motivated a range of more sophisticated numerical methods for the study of AC transport. Recent progress has been made by the construction of explicit scattering state solutions for electrons incident on time-periodic non-stationary scatterers, which may be applied to calculation of both the current and the current noise in such systems [100, 200, 92, 201, 202]. In these approaches, the energy-dependent scattering probability amplitudes are multiplied with the weights of additional sidebands resulting from the absorption/emission of photons. The interaction of MMM junctions with external light pulses has been studied using NEGF in Ref. [203], where it was shown that for a two-state (HOMO-LUMO) molecule in the WBLA an electric current can be stimulated with light. This study also modelled the inverse process, i.e. the radiation emitted when a bias causes charges to move between the HOMO and LUMO levels on

where the last equality holds because the cosine is an even function.

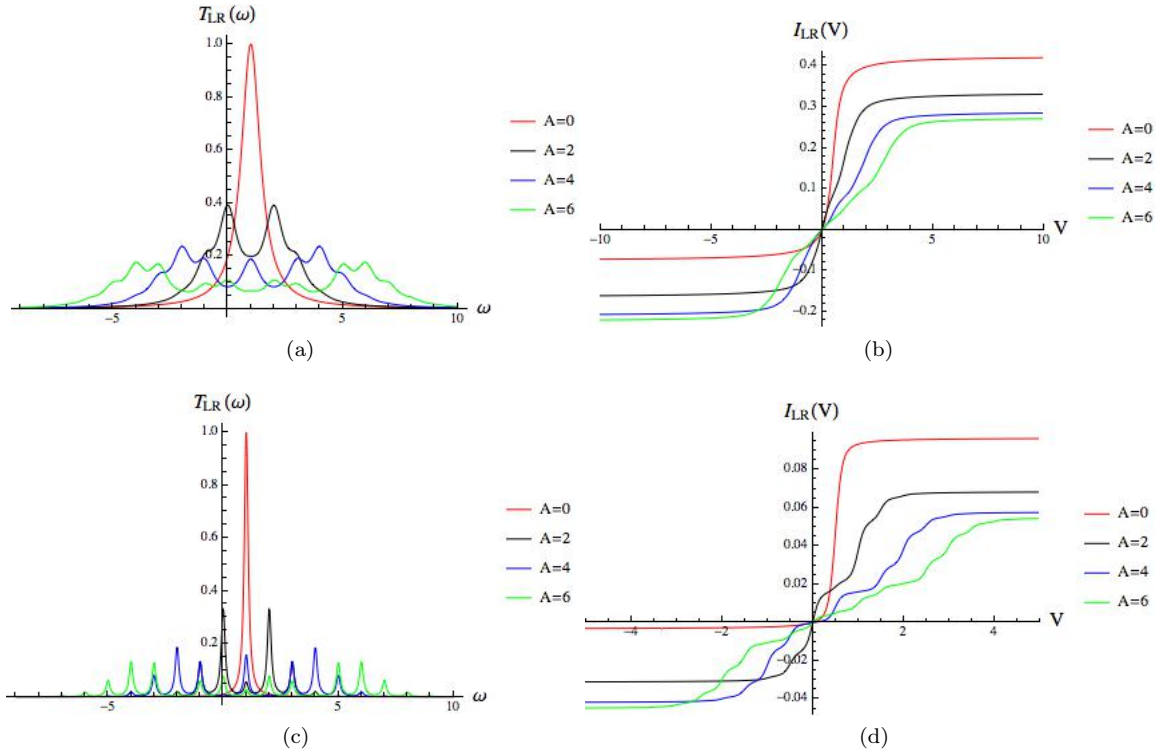


Figure 1.4.4: (a) The effective transmission $T(\omega, \Omega_D)$ at different values of the amplitude A , with $\Gamma_L = 0.5 = \Gamma_R$, and (b) the corresponding $I - V$ curve. (c) The effective transmission $T(\omega, \Omega_D)$ at different values of the amplitude A , with $\Gamma_L = 0.1 = \Gamma_R$, and (d) the corresponding $I - V$ curve.

the molecule, which is a single-molecule version of the light-emitting diode [204]. A non-Markovian density-matrix method going beyond the WBLA was used to investigate the femtosecond dynamical response of a molecular wire to a short laser pulse in Ref. [205]. In related work, a reduced density matrix approach has recently been developed for the study of quantum transport in nanojunctions with a time-dependent lead-molecule coupling [206].

Within noninteracting models, several numerical time-propagation schemes have been developed to go beyond the WBLA. In Ref. [207], Green's functions were propagated using a time-domain decomposition method that scaled with the number of time steps N_t as N_t^3 or N_t^4 , depending on the kind of pulse used to drive the system out of equilibrium. The first analytical solution for the Green's functions and current in a non-WBLA molecular junction was then derived in Ref. [208] for the case of a sudden voltage step and square voltage pulse, and this formalism was extended to equal-time current fluctuations in Ref. [209]. These works all focused on the case of a single molecular level due to the computational cost of scaling up to larger system sizes. Ref. [210] formulated the EoM of the molecular density matrix in terms of an energy integration over a product of single-time matrices which can be propagated in time by a time-stepping procedure. This work recognized the importance of an efficient scheme for removing these energy integrals, which was supplied by an expansion of the Fermi function into a sum of simple poles - the so-called Padé approximation [211]. In this thesis, extensive use will be made of this kind of expansion - see in particular Chapter 4 and Appendix A.3. An extension to this formalism was recently published [212] which, like other recent studies [213, 214, 215], achieved a massive speed-up by fitting the level-width matrix (Eq. (1.4.11) generalized to arbitrary molecules) to a sum of Lorentzians. This approach enabled the authors to propagate N_s -dimensional auxiliary-mode wave vectors instead of $N_s \times N_s$ matrices (where N_s is the system size), and therefore reduces the computational complexity.

In a rather general review on numerical simulation techniques in quantum transport, Gaury *et al.* compared Green's function-based approaches with numerical methods based upon the direct propagation of wavefunctions

in time [216]. They found the fastest method to be a wavefunction-based method which involved the inclusion of the lead interfaces into a generalized ‘central region’ and the treatment of lead sites beyond the interfacial region within the WBLA. This method scaled quadratically with the number of time steps N_t , and linearly with the system size N_s . A related algorithm has recently been presented in Ref. [217] which constructs scattering states by solving a generalized Schrödinger equation that includes effective ‘source’ (due to the external time-dependent perturbation) and ‘sink’ (due to the electrodes) terms. This algorithm scales linearly in both N_s and N_t , and was applied to the study of the Josephson effect (conversion of a DC signal into an AC current - see, for example Ref. [192]) in superconducting junctions. The WBLA partition-free formalism discussed in Section 1.4.2.1 was originally developed for constant bias switch-on processes, and a numerical comparison in Ref. [194] showed it to offer at least an order-of-magnitude speed-up when compared with time-propagation of the Kadanoff-Baym equations. Whereas this formalism scales as N_s^2 , it does not scale at all with increasing time, as all transport quantities are expressed as exact ‘single-shot’ functions of the time. This enables a trivial parallelization of the calculation of the time-dependent current, as the different ‘single-shot’ calculations can be distributed over the machine cores with no need to share information between cores. It would be desirable to achieve a similar scaling for systems driven by a time-dependent bias, and also for the calculation of quantities not addressed in Refs. [210, 216], such as the two-time Green’s function and the quantum noise. The potential speed-up on offer with this method motivates the analytic work carried out in this thesis.

1.4.2.3 Transport in a Stochastic Field

Whereas the two kinds of uncertainty discussed in Section 1.3.1 are basic to the theory of quantum statistical mechanics and must be encountered in all nanoelectronic systems, further sources of uncertainty are often encountered. For example, the lead-molecule-lead nanojunction itself could be considered as an open quantum system, in which case the Hamiltonian of the junction may be one of an ensemble of Hamiltonians and not uniquely specified [113]. In addition, quantum master equation approaches involve the tracing out of phononic degrees of freedom and the time-evolution of the system is then governed by a stochastic Liouville equation [218]. We consider yet another source of uncertainty in Chapter 6, where the external field driving the electron transport contains a stochastic term known only through its first and second statistical moments. This reflects a lack of control over the driving field by the experimentalist.

In classical conductors, the effects of a fluctuating voltage on the current characteristics have been well understood since 1928. In this landmark year for classical electronics, a linear relationship was found to hold between the fluctuation strength of the potential difference and both the electrical resistance of a conductor and its temperature. This relationship was demonstrated first in experimental work carried out by J. B. Johnson [111], and then explained in a theoretical model proposed by H. Nyquist [112]. The so-called Nyquist theorem has found wide applications in classical thermoelectric systems, but has an additional historical significance as one of the first statements of the *fluctuation-dissipation theorem* [160]. The (classical) fluctuation-dissipation theorem states that, in all linear dissipative systems driven by a fluctuating generalized force, the friction (or admittance) of the system is proportional to the magnitude of the fluctuations in the force and to the temperature [219, 220, 218]. Another example is provided by the Brownian particle, whose friction coefficient is directly proportional to the correlation function of the random force and to the temperature [220].

The possibility of fluctuation-driven transport of Brownian particles through spatially asymmetric systems has stimulated a great deal of research during the past two decades [221, 222, 223, 224, 225, 226], and has been shown to enhance the signal at certain resonant values of the parameters characterizing the noise, in a phenomenon known as *stochastic resonance* [227, 228, 229, 230, 231]. These studies involve the solution of a Langevin equation for the particle mobility and include periodically driven systems with various types of added stochasticity [232, 233, 234,

235, 236, 237]. The exciting possibility of stochastically enhanced quantum transport has been demonstrated in recent theoretical studies which use a master equation approach to treat exciton transport in photosynthetic systems [238, 239]. These studies have shown that a noisy environment can simultaneously destroy quantum coherence whilst enhancing the system transmission. This effect occurs when environmental perturbations open up new channels for excitation transfer, and was verified experimentally in related work on optical cavity networks [240].

Whereas the classical electronic response to a fluctuating bias is well characterized, the analogous physics in nanoscale electronic devices has only recently begun to be explored [241, 242, 211, 243, 244]. The assumption, made by the LB formalism, that the molecular energies and external bias are fixed in time will not be true in real systems, where the energies on the molecule are caused to fluctuate rapidly, e.g. for molecules immersed in a solution [245, 246, 243]. One of the first papers to acknowledge this fact was that of German et al., in which effective transmission probability functions were derived for electron tunneling through a fluctuating single level [241]. In this paper, a negative exponential two-time correlation function was used for the random part of the site energy, so that the interplay between the strength of fluctuations, environment-dot coupling strength, and correlation time could be analysed. An approach based on transition state theory was later used to study hopping transport through a 1D molecular chain whose sites fluctuate in time due to electron-electron interactions [247]. One may also consider another source of fluctuations in molecular junctions: random fluctuations of the bias applied to the leads, which is the quantum analogue of the Nyquist problem. This kind of stochasticity has been studied experimentally in carbon nanotube field effect transistors [248, 249] and in bistable nanoscale switches [250, 251], where an enhancement of the switching due to stochastic resonance was observed. Both the random fluctuations of the molecular levels and of the applied bias can affect the current passing through the system and both sources of stochasticity were addressed in Ref. [3], which forms the basis for all the material presented in Chapter 6 of this thesis.

To tackle the general problem of electron transport through a molecule with stochastic levels (applied bias), it is necessary to go beyond static transport schemes and use methods in which explicit time-dependence can be taken into account. A numerical propagation scheme based on NEGF has been used to study time-dependent (TD) transport through a single fluctuating level and analytic results were obtained for this system which confirm the numerics [211]. In this work, a stochastic resonance effect was observed in the current characteristics of a quantum dot system. In addition, a recent study investigated the problem of fluctuating site energies using a numerical time-stepping method based upon the NEGF formalism [243]. They compared numerical results of this TD-NEGF scheme with those obtained from the static LB formula (1.4.7), into which a ‘snapshot’ of the system parameters is substituted at each time step. As expected, they found that static ‘snapshot’ approaches to fast fluctuating systems cannot be accurate, because they omit non-adiabatic effects such as ultrafast dephasing due to the presence of transient modes, and changes in the amplification of the current response. A recent numerical work on noninteracting transport through a single fluctuating level [244] has recently made several questionable claims, e.g. the claim that colored noise fluctuations can be switched on and off but still affect the long time value of the current, thereby violating the Memory-loss Theorem discussed in Section 1.4.2. This controversy will be fully discussed and resolved in Chapter 6, where we can analytically study questions that were only considered with a numerical approach in Ref. [244].

1.4.2.4 Time and Frequency Dependent Quantum Noise

Due to the relative importance of the noise signal in nanojunctions discussed in Section 1.2.3, a theory of time-dependent fluctuations is essential for the design and control of these devices [252, 253]. Early theoretical studies chose the scattering potential to be static, but time-dependent scattering formalisms have been developed which enable the calculation of current and current noise in response to an AC potential in the leads [200, 254, 202], in both the adiabatic [200] and non-adiabatic [255, 256] regimes. These approaches make use of the Floquet theorem, as do

master equation approaches, which expand scattering states into a harmonic series [252, 257], generating functional approaches to the full counting statistics (FCS) [258] and reduced density matrix methods that make a perturbative expansion in the lead-molecule coupling [259]. In the theoretical literature, both symmetric [260, 147, 158, 257] and asymmetric [121, 261, 262] noise spectra have been classified and studied. The noise response to an AC field has been shown to carry information on the production of electron-hole pairs that does not appear in the noise response to a DC bias [263]. Moreover these electron-hole pairs are correlated and able to propagate through the molecular junction into separate terminals [264, 265]. In a generating functional approach to the full counting statistics of an AC-driven system, it was proven that a periodic Lorentzian voltage signal with quantized flux minimized the noise, i.e. it was reduced to the DC level [266, 267]. In recent experiments, these quantized voltage pulses, known as *levitons*, have been experimentally realized [268] and approximated by a biharmonic driving field [269]. Even given the restriction of periodic time-dependence, one can study the effects on the noise of a rich range of phenomena, such as photon-assisted tunneling (PAT) [270, 264, 257, 125], quantum pumping [271, 188], and the interplay of an external driving field parameters with Fabry-Pérot conductance oscillations in graphene nanoribbon (GNR) and carbon nanotube (CNT) systems [199].

There are key qualitative differences between the noise in the driven and static cases. In particular, whereas the noise in the static case depends only upon transmission probabilities, it has been found that in driven systems, the quantum noise will depend upon transmission probability amplitudes in a manner that cannot be reduced to probabilities alone [272, 273], unlike the static bias formulas in Eqs. (1.4.7) and (1.4.20). For a double-dot quantum pump, it is possible to tune the driving frequencies of the driving field so that the maximum DC current is obtained for a minimum of noise on the current signal [252]. Importantly, whereas Eq. (1.4.20) shows that the quantum noise vanishes in the limits of zero temperature and bias, this is not true of the noise in driven systems [252]. Recent calculations of transient noise characteristics have made use of the partitioned approach [209, 188, 274], and Ref. [4] contains the first calculations of the transient current noise arising from a partition-free switch on process. This will be useful within the field of fast noise calculations for real molecular junctions driven by ultrafast pulses [55, 275, 71], and reveals new physics arising from the time-resolved nanoelectronic response to these pulses that includes the effects of the initial coupling. These calculations are discussed in Chapter 5.

1.5 Nonequilibrium Green's Functions

1.5.1 Introduction to the Contour

The Kadanoff-Baym or Nonequilibrium Green's Function (NEGF) approach to electron transport is an exact method for the computation of time-dependent ensemble averages in many-electron subsystems open to an environment or bath, for both equilibrium and nonequilibrium states [174, 175, 176, 177, 178, 179, 180, 181, 128]. It has the particular advantages of exploiting a mathematical isomorphism between nonequilibrium and equilibrium ensemble averages, as well as automatically preserving all required conservation laws [177, 128]. Perhaps the most elegant representation of this equivalence comes with the introduction of the Konstantinov-Perel' contour, which provides a 'time' domain on which the initial preparation of the system in equilibrium together with its subsequent time evolution can be conveniently represented [176, 178].

Inserting (1.3.48) into the ensemble average for the operator $\hat{O}$ at time t returns the object

$$O(t) = Z^{-1} \text{Tr} \left[e^{-\beta \hat{H}^M} \hat{T}_C \left[e^{-i \int_C d\bar{t} \hat{H}(\bar{t})} \hat{O}(t) \right] \right] \quad (1.5.1)$$

where $\beta = 1/k_B T$ is the inverse temperature, $Z = \text{Tr} \left[e^{-\beta \hat{H}^M} \right]$ is the grand canonical partition function and we

use units in which $\hbar = 1$. In the expression (1.5.1), C refers to the Keldysh Contour, which is just the union of the two sets of points $C_- \equiv \{t_0 + i0, t + i0\}$ (the ‘upper’ branch), and $C_+ \equiv \{t - i0, t_0 - i0\}$ (the ‘lower’ branch), arranged so that points on C_+ are ‘below’ those on C_- in the complex time plane, i.e. $C = C_- \oplus C_+$ [176, 128]. $\hat{T}_C$ is the contour time-ordering operator, which orders times chronologically, with latest to the LHS on C_- , and which orders times with latest on the RHS on C_+ . One should remark that all times on C_+ are ordered as if they are later than any time on C_- . We can extend this contour if we note that

$$e^{-\beta \hat{H}^M} = e^{-i \int_{C_M} d\bar{t} \hat{H}^M}$$

where C_M is any contour in the complex plane between two points z_a, z_b , such that $z_b - z_a = -i\beta$. Usually one chooses $z_a = t_0$, and $z_b = t_0 - i\beta$, and adds a vertical path to the two horizontal branches of the Keldysh Contour, constructing the so-called Konstantinov-Perel’ Contour, $\gamma \equiv C_- \oplus C_+ \oplus C_M$ displayed on Fig. (1.5.1). On the vertical path, this contour can be used to describe a system in equilibrium, i.e. we think of averaging with respect to the equilibrium density matrix

$$\hat{\rho}(t = t_0) = \frac{\exp(-\beta \hat{H}^M)}{\text{Tr} [\exp(-\beta \hat{H}^M)]}$$

as a ‘propagation’ between the ‘times’ t_0 and $t_0 - i\beta$, where $\hat{H}^M$ governs the system ‘evolution’ along the vertical part of the Konstantinov-Perel’ contour. In this sense, the propagation in time of a quantum average along the imaginary time axis is isomorphic to a statistical averaging, and we can incorporate the complex time evolution into a formalism for contour evolution, provided that C_M is connected to $C_- \oplus C_+$, and that for any $z \in C_M$, $\hat{H}(z) = \hat{H}^M$. The points on the contour are ordered along the direction of this ‘propagation’, from $t_0 + i0$ to $t_0 - i0$ and then to $t_0 - i\beta$ as shown by the arrows in Fig. 1.5.1. The ensemble average for $\hat{O}(z)$ can finally be written in a manner which does not distinguish between values of z which correspond to equilibrium or nonequilibrium systems [128]:

$$O(z) = Z^{-1} \text{Tr} \left[\hat{T}_\gamma \left[e^{-i \int_\gamma d\bar{z} \hat{H}(\bar{z})} \hat{O}(z) \right] \right] \quad (1.5.2)$$

Here, $\hat{T}_\gamma$ is a generalized contour-ordering operator, and its action on a string of operators defined at times i , $\hat{O}_i$, is defined with the use of a sum over permutations of the time indices included in the string, denoted ‘ $\sum_P$ ’⁶:

$$\hat{T}_\gamma [\hat{O}_1 \dots \hat{O}_n] = \sum_P (\pm 1)^{\xi_P} \theta(t_{P_1}, t_{P_2}) \dots \vartheta(t_{P_{n-1}}, t_{P_n}) \hat{O}_{P_1} \dots \hat{O}_{P_n} \quad (1.5.4)$$

For $z \in C_M$,

$$O(z) = Z^{-1} \text{Tr} \left[e^{-i \int_{C_M} d\bar{z} \hat{H}^M} \hat{O} \hat{T}_\gamma \left[\hat{U}(t, t_0) \hat{U}^\dagger(t, t_0) \right] \right] \quad (1.5.5)$$

which by unitarity of the propagator is equal to the equilibrium ensemble average of $\hat{O}$. On the Konstantinov-Perel’ contour, the definition of the propagator is extended to the contour evolution operator between any pair of ‘times’ on γ :

⁶The step function θ is defined with respect to the contour, and has the following generic definition:

$$\theta(z_1, z_2) = \begin{cases} 1, & z_1 \in C_M, z_2 \in C_\pm \\ 0, & z_1 \in C_\pm, z_2 \in C_M \\ 1, & z_1 \in C_+, z_2 \in C_- \\ 0, & z_1 \in C_-, z_2 \in C_+ \\ \theta(t_1 - t_2) & z_1 = t_{1-}, z_2 = t_{2-} \\ \theta(t_2 - t_1) & z_1 = t_{1+}, z_2 = t_{2+} \\ \theta(\tau_1 - \tau_2) & z_1 = t_0 - i\tau_1, z_2 = t_0 - i\tau_2 \end{cases} \quad (1.5.3)$$

$$\hat{U}(z_2, z_1) = \begin{cases} \hat{T}_\gamma \left[e^{-i \int_{z_1}^{z_2} d\bar{z} \hat{H}(\bar{z})} \right] & z_2 >_\gamma z_1 \\ \tilde{T}_\gamma \left[e^{i \int_{z_2}^{z_1} d\bar{z} \hat{H}(\bar{z})} \right] & z_1 >_\gamma z_2 \end{cases} \quad (1.5.6)$$

Here $>_\gamma$ means ‘later on the contour’, and $\tilde{T}_\gamma$ orders operators defined on γ with ‘latest’ to the RHS. It should be noted that $\hat{U}(z_1, z_2)$ is unitary only when both $z_1, z_2 \in C_M$. Given systems prepared with the generic two-body Hamiltonian:

$$H^M = \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}) \langle \mathbf{x} | \hat{h}^M | \mathbf{x}' \rangle \hat{\psi}(\mathbf{x}') + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v^M(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}) \quad (1.5.7)$$

we can define the n -particle Green’s function:

$$G_n(1, \dots, n; 1', \dots, n') \equiv \frac{\text{Tr} \left[\hat{T}_\gamma \left[e^{-i \int_\gamma d\bar{z} \hat{H}(\bar{z})} \hat{\psi}(1) \dots \hat{\psi}(n) \hat{\psi}^\dagger(n') \dots \hat{\psi}^\dagger(1') \right] \right]}{\text{Tr} \left[\hat{T}_\gamma \left[e^{-i \int_\gamma d\bar{z} \hat{H}(\bar{z})} \right] \right]} \quad (1.5.8)$$

Here, $i \equiv (\mathbf{x}, t)$ denotes a space-spin-time index. It is shown in [128] that this object satisfies a set of integro-differential equations on γ , defining a hierarchy of nested n -particle Green’s Functions originally derived by Martin and Schwinger [175]:

$$\begin{aligned} \left[i \frac{d}{dz_k} - \hat{h}(k) \right] G_n(1, \dots, n; 1', \dots, n') &= \pm i \int_\gamma d\bar{1} v(k; \bar{1}) G_{n+1}(1, \dots, n, \bar{1}; 1', \dots, n', \bar{1}^+) \\ &+ \sum_{j=1}^n (\pm 1)^{k+j} \delta(k; j') G_{n-1}(1, \dots, k-1, k+1, \dots, n; 1', \dots, j'-1, j'+1, \dots, n') \end{aligned} \quad (1.5.9)$$

$$\begin{aligned} G_n(1, \dots, n; 1', \dots, n') \left[-i \frac{\overleftarrow{d}}{dz_2} - \hat{h}(k) \right] &= \pm i \int_\gamma d\bar{1} v(k'; \bar{1}) G_{n+1}(1, \dots, n, \bar{1}^-; 1', \dots, n', \bar{1}) \\ &+ \sum_{j=1}^n (\pm 1)^{k+j} \delta(j; k') G_{n-1}(1, \dots, k-1, k+1, \dots, n; 1', \dots, j'-1, j'+1, \dots, n') \end{aligned} \quad (1.5.10)$$

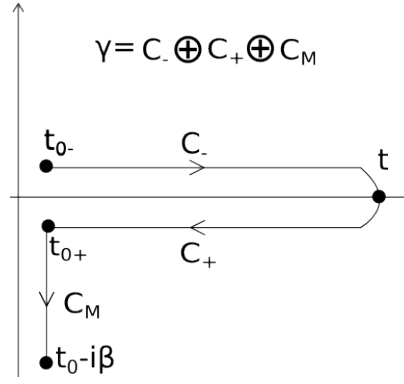
The signs ‘+’ and ‘-’ in (1.5.9) and (1.5.10) refer to bosonic and fermionic GFs, and from now we only consider the fermionic case. The solution for the GF must satisfy the Kubo-Martin-Schwinger (KMS) boundary conditions [128]:

$$\hat{G}(t_{0-}, z) = -\hat{G}(t_0 - i\beta, z) \quad (1.5.11)$$

$$\hat{G}(z, t_{0-}) = -\hat{G}(z, t_0 - i\beta) \quad (1.5.12)$$

We assume that the GF and self-energies are diagonal in spin space. Let G_{ij} , denote matrix elements of the full one-particle GF, where i and j may equal reservoir indices $k\alpha$, or those of the central region. Then the $i - j$ component of the Green’s Function operator is defined as:

$$G(z_1, z_2)_{ij} = -i \frac{\text{Tr} \left[e^{-\beta \hat{H}^M} \hat{T}_\gamma \left[\hat{d}_{i,H}(z_1) \hat{d}_{j,H}^\dagger(z_2) \right] \right]}{\text{Tr} \left[e^{-\beta \hat{H}^M} \right]} \quad (1.5.13)$$

Figure 1.5.1: The Konstantinov-Perel' Contour $\gamma \equiv C_- \oplus C_+ \oplus C_M$.

In (1.5.13), we denote the Heisenberg representation of the field operators,

$$\hat{d}_{i,H}(z) = \hat{U}(t_0, z) \hat{d}_i \hat{U}(z, t_0) \quad (1.5.14)$$

where $\hat{U}$ is the generalized contour evolution operator of Eq. (1.5.6). The EoM of the basis-independent single-particle GF operator (which we denote $\hat{G}$) can be used to define the many-body self-energy $\hat{\Sigma}_{MB}$:

$$\left[i \frac{d}{dz_1} - \hat{h}(z_1) \right] \hat{G}(z_1, z_2) = \delta(z_1, z_2) + \int_{\gamma} d\bar{z} \hat{\Sigma}_{MB}(z_1, \bar{z}) \hat{G}(\bar{z}, z_2) \quad (1.5.15)$$

$$\hat{G}(z_1, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \hat{h}(z_2) \right] = \delta(z_1, z_2) + \int_{\gamma} d\bar{z} \hat{G}(z_1, \bar{z}) \hat{\Sigma}_{MB}(\bar{z}, z_2) \quad (1.5.16)$$

Projecting this onto the position representation gives the following definition of the self-energies [128]:

$$\int_{\gamma} d3 \Sigma_{MB}(1; 3) G(3; 2) = -i \int_{\gamma} d3 v(1; 3) G_2(1, 3; 2, 3^+) \quad (1.5.17)$$

$$\int_{\gamma} d3 G(1; 3) \Sigma_{MB}(3; 2) = -i \int_{\gamma} d3 G_2(1, 3^-; 2, 3) v(3; 2) \quad (1.5.18)$$

These equations are true for any system; $\hat{\Sigma}$ is the full many-body self-energy and contains information on all scattering events which occur in the junction [180, 128]. In practice, the integrals on the right hand side of Eqs. (1.5.17) and (1.5.18) are evaluated by a diagrammatic expansion of the self-energies based on Wick's theorem [276], which is a rule for decomposing quantum statistical averages of even-numbered products of field operators into products of quantum statistical averages of pairs of field operators. The eigenmodes of this Hamiltonian have a finite lifetime associated with the imaginary part of the many-body self-energy, which is just the inverse of the electron scattering rate [132, 128]. However, in what follows we shall neglect two-body interactions, instead focusing on the effects on the dynamics of a small subsystem when it is *embedded* within a larger system. This leads to finite lifetimes in the eigenmodes of the embedded subsystem, in an analogous manner to the interaction-induced lifetimes arising from many-body interactions.

1.5.2 The Langreth Rules

The equations of motion (1.5.15) and (1.5.16) contain convolution integrals of functions along the entire Konstantinov-Perel' contour with the following structure:

$$\mathbf{C}(z_1, z_2) = \int_{\gamma} d\bar{z} \mathbf{A}(z_1, \bar{z}) \mathbf{B}(\bar{z}, z_2) \quad (1.5.19)$$

However, to calculate specific time-dependent quantum statistical variables, it is necessary to map integrals of this form onto real integrals which can actually be solved. First, we introduce the following notation conventions for integrals on the horizontal and vertical contour:

$$\mathbf{A} \cdot \mathbf{B}(z_1, z_2) \equiv \int_{t_0}^{\infty} d\bar{t} \mathbf{A}(z_1, \bar{t}) \mathbf{B}(\bar{t}, z_2) \quad (1.5.20)$$

$$\mathbf{A} \star \mathbf{B}(z_1, z_2) \equiv -i \int_0^{\beta} d\tau \mathbf{A}(z_1, \tau) \mathbf{B}(\tau, z_2) \quad (1.5.21)$$

Next, we re-write Eq. (1.5.19) in a matrix of ‘time blocks’, for example $\mathbf{A}^{-M}(z_1, \bar{z})$ corresponds to the ‘block’ of $\mathbf{A}$ with z_1 on C_- and $\bar{z}$ on C_M :

$$\mathbf{C}(z_1, z_2) = \int_{\gamma} d\bar{z} \begin{pmatrix} \mathbf{A}^{--}(z_1, \bar{z}) & \mathbf{A}^{-+}(z_1, \bar{z}) & \mathbf{A}^{-M}(z_1, \bar{z}) \\ \mathbf{A}^{+-}(z_1, \bar{z}) & \mathbf{A}^{++}(z_1, \bar{z}) & \mathbf{A}^{+M}(z_1, \bar{z}) \\ \mathbf{A}^{M-}(z_1, \bar{z}) & \mathbf{A}^{M+}(z_1, \bar{z}) & \mathbf{A}^{MM}(z_1, \bar{z}) \end{pmatrix} \begin{pmatrix} \mathbf{B}^{--}(\bar{z}, z_2) & \mathbf{B}^{-+}(\bar{z}, z_2) & \mathbf{B}^{-M}(\bar{z}, z_2) \\ \mathbf{B}^{+-}(\bar{z}, z_2) & \mathbf{B}^{++}(\bar{z}, z_2) & \mathbf{B}^{+M}(\bar{z}, z_2) \\ \mathbf{B}^{M-}(\bar{z}, z_2) & \mathbf{B}^{M+}(\bar{z}, z_2) & \mathbf{B}^{MM}(\bar{z}, z_2) \end{pmatrix} \quad (1.5.22)$$

Carrying out the matrix multiplication, we find for instance that the ‘ $-M$ ’ time block of $\mathbf{C}$ is given by

$$\mathbf{C}^{-M}(t_1, \tau_2) = [\mathbf{A}^{--} \cdot \mathbf{B}^{-M} - \mathbf{A}^{-+} \cdot \mathbf{B}^{+M} + \mathbf{A}^{-M} \star \mathbf{B}^{MM}](t_1, \tau_2) \quad (1.5.23)$$

where the minus sign in the second term arises from the fact that time runs antichronologically along C_+ . In similar fashion we find that the general rule for the ‘ $\mu\nu$ ’ time block may be written compactly:

$$\mathbf{C}^{\mu\nu}(z_1, z_2) = [\mathbf{A}^{\mu-} \cdot \mathbf{B}^{-\nu} - \mathbf{A}^{\mu+} \cdot \mathbf{B}^{+\nu} + \mathbf{A}^{\mu M} \star \mathbf{B}^{M\nu}](z_1, z_2) \quad (1.5.24)$$

The two-point correlators are matrices whose elements are structures of the form:

$$C(z_1, z_2) = \text{Tr} \left[\hat{\rho} \hat{T}_{\gamma} \left[\hat{O}_1(z_1) \hat{O}_2(z_2) \right] \right] \quad (1.5.25)$$

In Ref. [128], *Keldysh space* is introduced as the space of all two-point correlators which can be represented as a sum of singular, ‘greater’ and ‘lesser’ components:

$$C(z_1, z_2) = C^{\delta}(z_1) \delta(z_1, z_2) + \theta(z_1, z_2) C^{>}(z_1, z_2) + \theta(z_2, z_1) C^{<}(z_1, z_2) \quad (1.5.26)$$

In that book, the two-point correlator is also assumed to be defined with respect to a Hamiltonian that is the same on each of the two horizontal branches, that is:

$$C(z_1 \in C_-, z_2) = C(z_1 \in C_+, z_2) \quad (1.5.27)$$

$$C(z_1, z_2 \in C_-) = C(z_1, z_2 \in C_+) \quad (1.5.28)$$

This may not always be the case, and is an assumption that is violated by generating functional approaches to the quantum shot noise which use a branch-dependent auxiliary Hamiltonian [277]. Following the convention of Ref. [128] for the Dirac delta function, and using the generalized contour Heaviside definition in Eq. (1.5.3), we list the structures of each component:

$$C^{--}(t_1, t_2) = C^\delta(t_{1-}) \delta(t_1 - t_2) + \theta(t_1 - t_2) C^>(t_{1-}, t_{2-}) + \theta(t_2 - t_1) C^<(t_{1-}, t_{2-}) \quad (1.5.29)$$

$$C^{-+}(t_1, t_2) = C^<(t_{1-}, t_{2+}) \quad (1.5.30)$$

$$C^{+-}(t_1, t_2) = C^>(t_{1+}, t_{2-}) \quad (1.5.31)$$

$$C^{++}(t_1, t_2) = -C^\delta(t_{1+}) \delta(t_1 - t_2) + \theta(t_2 - t_1) C^>(t_{1+}, t_{2+}) + \theta(t_1 - t_2) C^<(t_{1+}, t_{2+}) \quad (1.5.32)$$

$$C^{-M}(t_1, \tau_2) = C^<(t_{1-}, t_0 - i\tau_2) \quad (1.5.33)$$

$$C^{+M}(t_1, \tau_2) = C^<(t_{1+}, t_0 - i\tau_2) \quad (1.5.34)$$

$$C^{M-}(\tau_1, t_2) = C^>(t_0 - i\tau_1, t_{2-}) \quad (1.5.35)$$

$$C^{M+}(\tau_1, t_2) = C^>(t_0 - i\tau_1, t_{2+}) \quad (1.5.36)$$

$$C^{MM}(\tau_1, \tau_2) = iC^\delta(t_0 - i\tau_1) \delta(\tau_1 - \tau_2) + \theta(\tau_1 - \tau_2) C^>(t_0 - i\tau_1, t_0 - i\tau_2) + \theta(\tau_2 - \tau_1) C^<(t_0 - i\tau_1, t_0 - i\tau_2) \quad (1.5.37)$$

The ‘greater’ and ‘lesser’ parts of this function therefore have a tridiagonal structure in the ‘time block’ representation:

$$C^>(t_1, t_2) = \begin{pmatrix} C^>(t_{1-}, t_{2-}) & 0 & 0 \\ C^>(t_{1+}, t_{2-}) & C^>(t_{1+}, t_{2+}) & 0 \\ C^>(t_0 - i\tau_1, t_{2-}) & C^>(t_0 - i\tau_1, t_{2+}) & C^>(t_0 - i\tau_1, t_0 - i\tau_2) \end{pmatrix} \quad (1.5.38)$$

$$C^<(t_1, t_2) = \begin{pmatrix} C^<(t_{1-}, t_{2-}) & C^<(t_{1-}, t_{2+}) & C^<(t_{1-}, t_0 - i\tau_2) \\ 0 & C^<(t_{1+}, t_{2+}) & C^<(t_{1+}, t_0 - i\tau_2) \\ 0 & 0 & C^<(t_0 - i\tau_1, t_0 - i\tau_2) \end{pmatrix} \quad (1.5.39)$$

When we assume a branch-independent Hamiltonian, the elements in these matrices with both times on $C_- \oplus C_+$ are given by an identical function, and we can make the identifications:

$$C^>(t_1, t_2) = C^{+-}(t_1, t_2) \quad (1.5.40)$$

$$C^<(t_1, t_2) = C^{+-}(t_1, t_2) \quad (1.5.41)$$

In this case, one can therefore talk of a single ‘greater’ or ‘lesser’ function without specifying the contour branches of the operators $\hat{O}_1(z_1)$, $\hat{O}_2(z_2)$ in Eq. (1.5.25). Similarly, we can talk of a single ‘right’ function

$$C^{\lrcorner}(t_1, \tau_2) = C^<(t_{1\pm}, t_0 - i\tau_2) \quad (1.5.42)$$

and a single ‘left’ function:

$$C^{\ulcorner}(\tau_1, t_2) = C^>(t_0 - i\tau_1, t_{2\pm}) \quad (1.5.43)$$

These functions are very important in the context of NEGF, and the physical meanings of the left and right Green’s functions will be discussed in Section 1.5.3. The ‘Matsubara’ component is then given by $C^M(\tau_1, \tau_2) \equiv C^{MM}(\tau_1, \tau_2)$, where we can now drop one of the ‘M’s for notational convenience. Since the greater and lesser functions now satisfy the properties (1.5.27) and (1.5.28), we can introduce the ‘retarded’ and ‘advanced’ functions of two real times:

$$C^r(t_1, t_2) = C^\delta(t_1) \delta(t_1 - t_2) + \theta(t_1 - t_2) [C^>(t_1, t_2) - C^<(t_1, t_2)] \quad (1.5.44)$$

$$C^a(t_1, t_2) = C^\delta(t_1) \delta(t_1 - t_2) - \theta(t_2 - t_1) [C^>(t_1, t_2) - C^<(t_1, t_2)] \quad (1.5.45)$$

Evidently, these functions satisfy the relation:

$$C^r(t_1, t_2) - C^a(t_1, t_2) = C^>(t_1, t_2) - C^<(t_1, t_2) \quad (1.5.46)$$

The greater, lesser, left, right, Matsubara, retarded and advanced components of a two-time correlator may be collectively referred to as the *Keldysh components*. The problem of deriving analogous expressions to Eq. (1.5.24) for the Keldysh components of $\mathbf{C}$ in terms of Keldysh components of $\mathbf{A}$ and $\mathbf{B}$ was solved by Langreth in [278, 179]. One can perform a quick derivation of these so-called *Langreth Rules* by noting the following:

$$\mathbf{C}^r(t_1, t_2) = \mathbf{C}^{+-}(t_1, t_2) - \mathbf{C}^{++}(t_1, t_2) = \mathbf{C}^{--}(t_1, t_2) - \mathbf{C}^{-+}(t_1, t_2) \quad (1.5.47)$$

$$\mathbf{C}^a(t_1, t_2) = \mathbf{C}^{-+}(t_1, t_2) - \mathbf{C}^{++}(t_1, t_2) = \mathbf{C}^{--}(t_1, t_2) - \mathbf{C}^{+-}(t_1, t_2) \quad (1.5.48)$$

We then use the identities (1.5.40), (1.5.41), (1.5.47) and (1.5.48) to get the Langreth Rule for the greater component directly as the ‘+−’ time block in Eq. (1.5.24):

$$\begin{aligned} \mathbf{C}^>(t_1, t_2) &= [\mathbf{A}^> \cdot (\mathbf{B}^< - \mathbf{B}^{++} + \mathbf{B}^>) - (\mathbf{A}^< - \mathbf{A}^{--} + \mathbf{A}^>) \cdot \mathbf{B}^> + \mathbf{A}^{\lrcorner} \star \mathbf{B}^{\ulcorner}] (t_1, t_2) \\ &= [\mathbf{A}^> \cdot \mathbf{B}^a + \mathbf{A}^r \cdot \mathbf{B}^> + \mathbf{A}^{\lrcorner} \star \mathbf{B}^{\ulcorner}] (t_1, t_2) \end{aligned} \quad (1.5.49)$$

We use Eqs. (1.5.47) and (1.5.24) to derive the retarded Langreth Rule:

$$\begin{aligned} \mathbf{C}^r(t_1, t_2) &= [\mathbf{A}^> \cdot (\mathbf{B}^{--} - \mathbf{B}^<) - \mathbf{A}^{++} \cdot (\mathbf{B}^> - \mathbf{B}^{++}) + \mathbf{A}^{\lrcorner} \star \mathbf{B}^{\ulcorner} - \mathbf{A}^{\lrcorner} \star \mathbf{B}^{\ulcorner}] (t_1, t_2) \\ &= [\mathbf{A}^r \cdot \mathbf{B}^r] (t_1, t_2) \end{aligned} \quad (1.5.50)$$

The right component is obtained from Eqs. (1.5.23), (1.5.42) and (1.5.47):

$$\begin{aligned}
\mathbf{C}^{\top}(t_1, \tau_2) &= [(\mathbf{A}^< - \mathbf{A}^{++} + \mathbf{A}^>) \cdot \mathbf{B}^{\top} - \mathbf{A}^< \cdot \mathbf{B}^{\top} + \mathbf{A}^{\top} \star \mathbf{B}^{\top}](t_1, \tau_2) \\
&= [\mathbf{A}^r \cdot \mathbf{B}^{\top} + \mathbf{A}^{\top} \star \mathbf{B}^M](t_1, \tau_2)
\end{aligned} \tag{1.5.51}$$

All the other Langreth Rules are similarly obtained, and we list them below for convenience:

$$\mathbf{C}^<(t_1, t_2) = [\mathbf{A}^< \cdot \mathbf{B}^a + \mathbf{A}^r \cdot \mathbf{B}^< + \mathbf{A}^{\top} \star \mathbf{B}^{\top}](t_1, t_2) \tag{1.5.52}$$

$$\mathbf{C}^a(t_1, t_2) = [\mathbf{A}^a \cdot \mathbf{B}^a](t_1, t_2) \tag{1.5.53}$$

$$\mathbf{C}^{\top}(\tau_1, t_2) = [\mathbf{A}^{\top} \cdot \mathbf{B}^a + \mathbf{A}^M \star \mathbf{B}^{\top}](\tau_1, t_2) \tag{1.5.54}$$

$$\mathbf{C}^M(\tau_1, \tau_2) = [\mathbf{A}^M \star \mathbf{B}^M](\tau_1, \tau_2) \tag{1.5.55}$$

These rules provide us with a concise means of writing down equations of motion for specific physical quantities that are described by parts of the full one-particle Green's Function. Usually they are derived in a much more tedious fashion, by fixing the time arguments of $\mathbf{C}$ to isolate one of the Keldysh components, then expanding the integral (1.5.19) into integrals along each of the three time branches of the Konstantinov-Perel' contour. When these rules are applied to the EoM (1.5.15), (1.5.16), one obtains a set of integro-differential equations known as the *Kadanoff-Baym equations* [177]. We will solve the Kadanoff-Baym equations for a specific Hamiltonian in Chapter 2; this will form the basis of most of the work in this thesis.

1.5.3 Green's Function Components and Their Physical Meaning

Different pairs of times in the one-particle Green's function correspond to different possible physical situations. For example, one is very often interested in calculating the ensemble average of the number operator, $N(t) = \left\langle \sum_n \hat{d}_n^{\dagger}(t) \hat{d}_n(t) \right\rangle$. Inspection of (1.5.13) shows that, if we can guarantee that z_2 appears later on the contour than z_1 , the time dependent number occupation of the i -th eigenstate can be obtained by choosing $z_1 = t_- \in C_-$, and $z_2 = t_+ \in C_+$, $n_i(t) = -iG_{ii}(t_-, t_+)$. This defines the *lesser Green's function*. Every combination of times defines a different GF, which are labelled according to the scheme introduced in Section 1.5.2. We now discuss the meaning of each function in more detail, reverting to the basis-independent representation of the Green's function operator $\hat{G}$.

Greater and Lesser These GFs are defined with both times on the horizontal part of the Konstantinov-Perel' contour:

$$\hat{G}^>(t_1, t_2) = \hat{G}(z_1, z_2), z_1 \in C_+, z_2 \in C_- \tag{1.5.56}$$

$$\hat{G}^<(t_1, t_2) = \hat{G}(z_1, z_2), z_1 \in C_-, z_2 \in C_+ \tag{1.5.57}$$

The physical meaning of the lesser Green's function has already been discussed. If one wishes to study the number density of electron holes in a material, one uses the greater Green's function, as the time ordering guarantees that

the annihilation operator sits to the left of the creation operator. The number of electron holes in the i -th eigenstate is given by $n_i^h(t) = iG_{ii}(t_+, t_-)$.

Right and Left These GFs have one argument on the horizontal part, and one argument on the vertical part of the contour:

$$\hat{G}^\top(t_1, \tau_2) = \hat{G}(z_1, z_2), \quad z_1 \in C_\pm, \quad z_2 = t_0 - i\tau_2 \in C_M \quad (1.5.58)$$

$$\hat{G}^\top(\tau_1, t_2) = \hat{G}(z_1, z_2), \quad z_1 = t_0 - i\tau_1 \in C_M, \quad z_2 \in C_\pm \quad (1.5.59)$$

Physically they correspond to an ensemble average taken over a pair of creation and annihilation events, one of which occurs when the system is in equilibrium, and the other which occurs after the system has begun to evolve after $t = t_0$.

Matsubara This GF was introduced by Matsubara in 1955, to facilitate the use of field-theoretic methods in calculating equilibrium properties of a many-body system [174]. It has both times on the vertical contour, and it is customarily introduced as a method for extending diagrammatic field theory methods to finite-temperature systems [131].

$$\hat{G}^M(\tau_1, \tau_2) = \hat{G}(z_1, z_2), \quad z_1 = t_0 - i\tau_1 \in C_M, \quad z_2 = t_0 - i\tau_2 \in C_M \quad (1.5.60)$$

Retarded and Advanced These GFs are defined in terms of the greater and lesser GFs ⁷:

$$\hat{G}^r(t_1, t_2) = \theta(t_1 - t_2) [\hat{G}^>(t_1, t_2) - \hat{G}^<(t_1, t_2)] \quad (1.5.64)$$

$$\hat{G}^a(t_1, t_2) = -\theta(t_2 - t_1) [\hat{G}^>(t_1, t_2) - \hat{G}^<(t_1, t_2)] \quad (1.5.65)$$

They are proportional to propagators between the two times t_1, t_2 , for which the ordering of these two times are fixed, unlike the generic propagator (1.5.6). For future reference, we summarize the definitions of all the GF components by the contour positions of the two times z_1, z_2 in Fig. 1.1.

Boundary Conditions It will not have escaped the reader that there appears to be some ambiguity in these definitions at the left-hand ‘corner’ of the contour, when both times in the full GF are equal to the initial value t_0 .

⁷The step function $\theta(x)$ is defined rigorously by:

$$\theta(x) \equiv i \int \frac{d\omega}{2\pi} \frac{e^{-i\omega x}}{\omega + i\eta} \quad (1.5.61)$$

which satisfies the properties:

$$\theta(x) = \begin{cases} 1, & x > 0 \\ \frac{1}{2}, & x = 0 \\ 0, & x < 0 \end{cases} \quad (1.5.62)$$

$$\theta(x) + \theta(-x) = 1, \quad \forall x \quad (1.5.63)$$

When implementing the step function numerically, we are therefore able to define it by (1.5.62), i.e. we make the half-maximum convention.

GF Component $\hat{G}(z_1, z_2)$	$z_1 \in$	$z_2 \in$
$\hat{G}^<(t_1, t_2)$ (Lesser)	C_-	C_+
$\hat{G}^>(t_1, t_2)$ (Greater)	C_+	C_-
$\hat{G}^\rceil(t_1, \tau_2)$ (Right)	$C_\pm$	C_M
$\hat{G}^\rfloor(\tau_1, t_2)$ (Left)	C_M	$C_\pm$
$\hat{G}^M(\tau_1, \tau_2)$ (Matsubara)	C_M	C_M

Table 1.1: Definition of Green's Function components.

In accordance with our definition of the greater and lesser GF, Fig. 1.5.1 indicates $\hat{G}^>(t_0, t_0) = \hat{G}(z_1, z_2)$, with $z_1 = t_0 + i0 \equiv t_{0-}$, and $z_2 = t_0 - i0 \equiv t_{0+}$, such that

$$\hat{G}^>(t_0, t_0) = \hat{G}(t_{0+}, t_{0-}) = \hat{G}^M(0^+, 0) \quad (1.5.66)$$

where $(0^+, 0)$ indicates that the first '0' is further down the vertical contour than the second, and therefore that the first argument is later than the second on the contour γ . Conversely,

$$\hat{G}^<(t_0, t_0) = \hat{G}(t_{0-}, t_{0+}) = \hat{G}^M(0, 0^+) \quad (1.5.67)$$

where once again $\tau = 0^+$ corresponds to the contour time $z = t_0 - i0^+$. This means that when integrating the equations of motion for the greater or lesser GFs, we can use the Matsubara GFs as boundary conditions [128], and thereby information on the system preparation is incorporated into a description of its dynamics. The boundary conditions for the right and left GFs follow from their definition, where we no longer have to worry about whether the real-time argument is on C_- or C_+ :

$$\hat{G}^\rceil(t_0, \tau) = \hat{G}^M(0^+, \tau) \quad (1.5.68)$$

$$\hat{G}^\rfloor(\tau, t_0) = \hat{G}^M(\tau, 0^+) \quad (1.5.69)$$

Here, the positive but small number 0^+ guarantees that the Matsubara GF retains the correct ordering of field operators at the point $\tau = 0$.

Chapter 2

Kadanoff-Baym Theory for Spatially Homogeneous Time-Dependent Fields

2.1 Introduction

In this Chapter, we use the general NEGF scheme developed in Section 1.5 to describe the time evolution of physical systems characterized by a particular kind of Hamiltonian with a spatially homogeneous but otherwise arbitrary time-dependence in both the leads and molecule of a molecular junction. The work follows the logic of the derivations published in Refs. [1, 3]. To be specific, we introduce the partition-free Hamiltonian on the contour in Section 2.2. Then the molecular ‘block’ of the system Green’s function is introduced in Section 2.3, along with the concept of an embedding self-energy, and the Kadanoff-Baym equations for lesser, greater, left, right, Matsubara, retarded and advanced Green’s functions are obtained. Next, we discuss the WBLA, and derive explicit formulas for the embedding self-energies within the WBLA. These simplify the Kadanoff-Baym equations so that the target function in each equation no longer appears both in a derivative on their left-hand side and in an integral on their right-hand side. Using similar analytic techniques as those used in Ref. [190, 128] for the derivation of a *single time* greater and lesser Green’s functions $\mathbf{G}_{CC}^{\gtrless}(t, t)$ in response to a *constant* bias switch-on process, we show in Sections 2.5.6 and 2.5.7 how to derive an exact formula for the *two-time* Green’s functions $\mathbf{G}_{CC}^{\gtrless}(t_1, t_2)$ in response to an arbitrary time-dependent bias switch-on process. This involves writing down the exact differential for these matrix functions, and then performing a line integral in the two-time plane. The resulting formula for these Green’s functions, Eq. (2.5.89) constitutes the central analytical result of this thesis. We next obtain expressions for the lesser and greater Green’s functions of the lead-molecule and lead-lead components of the greater and lesser Green’s functions, which will be used in the derivation of the current correlations in Chapter 3.

Once all the Green’s functions are obtained, it is possible to derive the *current* in each lead as the ensemble average of the derivative of the lead particle number. The compact formula for the current is presented in Eq. (2.6.11). Then, following a discussion from Ref. [2], we use the particle number to derive a continuity equation satisfied by the current in Section 2.7. Finally, in Section 2.8, we show that our generalized time-dependent bias Landauer-Büttiker formula for the current reproduces the result of Jauho et al. at long times [154], and it reproduces the result of Tuovinen et al. in the limit of a constant bias [190, 128].

2.2 Hamiltonian on the contour

The variable z will be used to indicate the ‘time’ along the contour, and the system Hamiltonian $\hat{H}(z)$ must be specified for all z . When used between z -variables, the symbols ‘ $>$ / ‘ $<$ ’ mean ‘later/earlier on the contour’, where z_1 is later than z_2 on the contour if a directed line drawn from the point t_{0-} to $t_0 - i\beta$ passes through z_2 before passing through z_1 . In general, the definition of the Hamiltonian will be different on different parts of the contour, containing both equilibrium and nonequilibrium parts; for instance, the non-equilibrium part contains the bias which is missing in $\hat{H}_0$ defined on the vertical track. For the typical set-up of a quantum transport problem, we therefore have the following Hamiltonian:

$$\hat{H}(z) = \sum_{k\alpha\sigma} \varepsilon_{k\alpha}(z) \hat{d}_{k\alpha\sigma}^\dagger \hat{d}_{k\alpha\sigma} + \sum_{mn\sigma} h_{mn}(z) \hat{d}_{m\sigma}^\dagger \hat{d}_{n\sigma} + \sum_{m,k\alpha\sigma} \left[T_{mk\alpha}(z) \hat{d}_{m\sigma}^\dagger \hat{d}_{k\alpha\sigma} + T_{k\alpha m}(z) \hat{d}_{k\alpha\sigma}^\dagger \hat{d}_{m\sigma} \right] \quad (2.2.1)$$

The first term in this expression corresponds to the sum of the Hamiltonians of the reservoirs/leads, where α labels the lead, and k labels the k -th eigenstate of this lead. The second term corresponds to the Hamiltonian of the central region C and hence refers to electron hopping events within this region with indices n and m labeling eigenstates there. Finally, the third term describes the coupling of the leads and the central system with the corresponding matrix elements $T_{m,k\alpha}$, and σ denotes the spin degree of freedom of the electrons. Correspondingly, $\hat{d}_{k\alpha\sigma}$, $\hat{d}_{m\sigma}$ and $\hat{d}_{k\alpha\sigma}^\dagger$, $\hat{d}_{m\sigma}^\dagger$ are destruction and creation operators of the leads and the central system.

In the following, bold letters will be used for matrices. We shall omit the spin index for simplicity of notation; it can be trivially introduced back in the final results if desired. It is useful at this point to introduce a matrix $\mathbf{h}(z)$, defined on the basis of the whole multi-terminal system, so that the Hamiltonian (2.2.1) can be rewritten simply as

$$\hat{H}(z) = \sum_{ij} h_{ij}(z) \hat{d}_i^\dagger \hat{d}_j \quad (2.2.2)$$

where we sum over all orbitals i, j of the leads and the central system, $h_{ij}(z)$ are elements of the matrix $\mathbf{h}(z)$, and d_i , $d_i^\dagger$ correspond to the operators of either the leads (if $i \equiv k\alpha$) or C (if $i \equiv n$). It is also convenient to introduce blocks of the matrix $\mathbf{h}(z)$, projected onto the molecule or reservoir subspaces, i.e. $\mathbf{h}_{\alpha\alpha'}(z)$ is the block of $\mathbf{h}(z)$ with matrix elements $[\mathbf{h}_{\alpha\alpha'}(z)]_{kk'} = \delta_{\alpha\alpha'} \delta_{kk'} \varepsilon_{k\alpha}(z)$ (note that there is no direct interaction between different leads, so that $\mathbf{h}_{\alpha\alpha'} = \delta_{\alpha\alpha'} \mathbf{h}_{\alpha\alpha}$), $\mathbf{h}_{\alpha C}(z)$ is the block of $\mathbf{h}(z)$ with matrix elements $[\mathbf{h}_{\alpha C}(z)]_{km} = T_{k\alpha m}(z)$, and $\mathbf{h}_{CC}(z)$ is the block of $\mathbf{h}(z)$ with matrix elements $[\mathbf{h}_{CC}(z)]_{mn} = T_{mn}(z)$. The Hamiltonian matrix thus has the structure:

$$\mathbf{h}(z) = \begin{pmatrix} \mathbf{h}_{11}(z) & 0 & \cdots & \mathbf{h}_{1C}(z) \\ 0 & \mathbf{h}_{22}(z) & \cdots & \mathbf{h}_{2C}(z) \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{h}_{C1}(z) & \mathbf{h}_{C2}(z) & \cdots & \mathbf{h}_{CC}(z) \end{pmatrix} \quad (2.2.3)$$

The contour formalism thus provides an elegant way of understanding the difference between partitioned and partition-free approaches: in the former, the lead-molecule ‘blocks’ $\mathbf{h}_{\alpha C}(z) = 0$ for all $z \in C_M$, whereas in the latter case it generally holds that for any z , $\mathbf{h}_{\alpha C}(z) \neq 0$. We assume that prior to the switch on at time t_0 the whole electronic system was in thermodynamic equilibrium characterised by the unique chemical potential μ and inverse temperature β . Then at t_0 the battery of the external circuit is used to subject an arbitrary time-dependent bias $V_\alpha(t)$ to each lead α . Our first modification to the Hamiltonian studied in [1] is to modify the molecular energy integrals by some time-independent shift,

$$\tilde{\mathbf{h}}_{CC} = \mathbf{h}_{CC} + \mathbf{u}_{CC} \quad (2.2.4)$$

This modification was considered in Ref. [172] to enable description of a switch-on of a static EM field in the central region, so we incorporate it here as a special case. In addition, we assume that the states of the molecule are all subject to a time-dependent perturbation that factorizes into a time-dependent scalar $V_C(t)$ and the identity matrix $\mathbf{I}_{CC}$, so that the matrix representation of the CC Hamiltonian following the switch-on is as follows:

$$\mathbf{h}_{CC}(t > t_0) = \tilde{\mathbf{h}}_{CC} + V_C(t) \mathbf{I}_{CC} \quad (2.2.5)$$

This is the second modification to the Hamiltonian studied in [1], and enables us to study a wide class of systems, such as molecules coupled to an external electric field. This type of modification of the molecular Hamiltonian was also considered in a recent model of a carbon nanotube quantum pump [109]. Such a system was considered in Ref. [279], where time-dependent modulation of the lead-dot coupling was also considered. We do not include the latter form of time dependence here, although it is certainly a possibility for future studies. We are interested in the most general models that can be treated analytically, and it should be emphasized that a great deal of physics can be realized in particular models that are special cases of the Hamiltonian considered here. Simulations of the current response to a stochastic bias in a single-electron transistor (SET) were performed in Ref. [244] which can be treated in our formalism by choosing $V_C(t)$ to be a stochastic process.

A full description of the dynamics subsequent to the switch-on requires a specification of $\mathbf{h}(z)$ at every contour time z :

$$[\mathbf{h}_{\alpha\alpha}(z)]_{kk'} = \begin{cases} (\varepsilon_{k\alpha} + V_\alpha(t)) \delta_{kk'}, & z \equiv t \in C_- \oplus C_+ \\ (\varepsilon_{k\alpha} - \mu) \delta_{kk'}, & z \in C_M \end{cases} \quad (2.2.6)$$

$$[\mathbf{h}_{C\alpha}(z)]_{mk} = T_{mk,\alpha}, \quad z \in \gamma \quad (2.2.7)$$

$$[\mathbf{h}_{CC}(z)]_{mn} = \begin{cases} h_{mn} + u_{mn} + V_C(t) \delta_{mn}, & z \in C_- \oplus C_+ \\ h_{mn} - \mu \delta_{mn}, & z \in C_M \end{cases} \quad (2.2.8)$$

This Hamiltonian corresponds to the switch-on of a spatially uniform bias in each reservoir, and a site-independent energy shift in the molecule. If we ignore all modifications to $\mathbf{h}_{CC}$, it differs from the Hamiltonian studied in [128] only through the explicit time-dependence in $V_\alpha(t)$.

One note is in order here. The experimentalist in such systems typically has control over the voltage passed across the nanojunction. At some initial time t_0 , the switch-on of a bias means that energy levels in lead α are shifted by some external bias, $V_\alpha(t)$. In general, an external field will cause a rearrangement of electrons in the junction and leads. In particular, the electrons in the conducting leads will screen the external field so that the electric field inside the conductor equals zero and its electric potential is uniform throughout. This leads to confinement of the drop in potential to the region C , and means that $V_\alpha(t)$ should not be interpreted as $eV(t)$, where $V(t)$ is the actual voltage across the whole macroscopic lead. Rather, it should be equal to the sum of $eV(t)$ and the screening potential induced by the switch-on [189]. However, the central region C can always be chosen sufficiently large that a part of each lead neighbouring C , which is mostly affected by the charge redistribution is incorporated into C , as discussed in [139]. In this case we may assume that the potential $V_\alpha(t)$ is uniform across the lead α and is equal to the bias voltage applied to this particular lead.

2.3 Green's Function Components

In the molecular basis, the ij -th component of the one-particle Green's function on the contour γ is defined as in (1.5.13). The elements G_{ij} of the Green's function form a matrix $\mathbf{G}$ defined on the whole space of orbitals of all leads and the central region; correspondingly, one can introduce diagonal, $\mathbf{G}_{CC}$ and $\mathbf{G}_{\alpha\alpha}$, as well as non-diagonal, $\mathbf{G}_{C\alpha}$ and $\mathbf{G}_{\alpha C}$, blocks of this matrix, as follows:

$$\mathbf{G}(z_1, z_2) = \begin{pmatrix} \mathbf{G}_{11}(z_1, z_2) & \mathbf{G}_{12}(z_1, z_2) & \cdots & \mathbf{G}_{1C}(z_1, z_2) \\ \mathbf{G}_{21}(z_1, z_2) & \mathbf{G}_{22}(z_1, z_2) & \cdots & \mathbf{G}_{2C}(z_1, z_2) \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{G}_{C1}(z_1, z_2) & \mathbf{G}_{C2}(z_1, z_2) & \cdots & \mathbf{G}_{CC}(z_1, z_2) \end{pmatrix} \quad (2.3.1)$$

Notice that in this matrix there are lead-lead coupling terms $\mathbf{G}_{\alpha\beta}$, where $\alpha \neq \beta$, unlike in the Hamiltonian matrix (2.2.3). This is because for all contour times z there will be $\alpha - C$ and $C - \beta$ terms in the Hamiltonian, so that there must exist a Green's Function describing a lead-to-lead hopping process that is mediated by the central region. We project the general equations of motion, Eqs. (1.5.15) and (1.5.16) onto the CC block to obtain corresponding equations of motion for the Green's function $\mathbf{G}_{CC}$ of the central region:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{CC}(z_1) \right] \mathbf{G}_{CC}(z_1, z_2) = \mathbf{I}_{CC} \delta(z_1, z_2) + \sum_{\alpha} \mathbf{h}_{\alpha C}(z_1) \mathbf{G}_{\alpha C}(z_1, z_2) \quad (2.3.2)$$

$$\mathbf{G}_{CC}(z_1, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \mathbf{h}_{CC}(z_2) \right] = \mathbf{I}_{CC} \delta(z_1, z_2) + \sum_{\alpha} \mathbf{G}_{C\alpha}(z_1, z_2) \mathbf{h}_{\alpha C}(z_2) \quad (2.3.3)$$

where $\mathbf{I}_{CC}$ is the unit matrix defined on the orbitals of C . In these equations, the many body self-energy $\Sigma_{MB} = 0$ due to the absence of interactions in the contour hamiltonian. We next seek to express the lead-molecule Green's functions appearing in Eqs. (2.3.2) and (2.3.3) in terms of calculable objects. To this end, we introduce $\mathbf{g}_{\alpha\alpha}(z_1, z_2)$ as the Green's function of an isolated lead α corresponding to the Hamiltonian with the matrix block $\mathbf{h}_{\alpha\alpha}(z)$; note that the latter contains the term with the time-dependent driving bias:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1) \right] \mathbf{g}_{\alpha\alpha}(z_1, z_2) = \mathbf{I}_{\alpha\alpha} \delta(z_1, z_2) \quad (2.3.4)$$

$$\mathbf{g}_{\alpha\alpha}(z_1, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \mathbf{h}_{\alpha\alpha}(z_2) \right] = \mathbf{I}_{\alpha\alpha} \delta(z_1, z_2) \quad (2.3.5)$$

where $\mathbf{I}_{\alpha\alpha}$ is the unit matrix projected onto the subspace of the lead labelled by α . The delta function on the Konstantinov-Perel' contour satisfies the identities:

$$\int_{\gamma} \mathbf{g}_{\alpha\alpha}^{-1}(z_1, \bar{z}) \mathbf{g}_{\alpha\alpha}(\bar{z}, z_2) = \mathbf{I}_{\alpha\alpha} \delta(z_1, z_2) = \int_{\gamma} \mathbf{g}_{\alpha\alpha}(z_1, \bar{z}) \mathbf{g}_{\alpha\alpha}^{-1}(\bar{z}, z_2) \quad (2.3.6)$$

$$\int_{\gamma} \left[i \frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1) \right] \delta(z_1, \bar{z}) \mathbf{g}_{\alpha\alpha}(\bar{z}, z_2) = \mathbf{I}_{\alpha\alpha} \delta(z_1, z_2) = \int_{\gamma} \mathbf{g}_{\alpha\alpha}(z_1, \bar{z}) \delta(\bar{z}, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \mathbf{h}_{\alpha\alpha}(z_2) \right] \quad (2.3.7)$$

It therefore follows that:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1) \right] \delta(z_1, z_2) = \mathbf{g}_{\alpha\alpha}^{-1}(z_1, z_2) = \delta(z_1, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \mathbf{h}_{\alpha\alpha}(z_2) \right] \quad (2.3.8)$$

Now, the equation of motion of the $\alpha - C$ and $C - \alpha$ Green's functions can be obtained by projecting Eqs. (2.3.2) and (2.3.3) onto the corresponding basis:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1) \right] \mathbf{G}_{\alpha C}(z_1, z_2) = \mathbf{h}_{\alpha C}(z_1) \mathbf{G}_{CC}(z_1, z_2) \quad (2.3.9)$$

$$\mathbf{G}_{C\alpha}(z_1, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \mathbf{h}_{\alpha\alpha}(z_2) \right] = \mathbf{G}_{CC}(z_1, z_2) \mathbf{h}_{C\alpha}(z_2) \quad (2.3.10)$$

Substituting Eq. (2.3.8) into Eqs. (2.3.9) and (2.3.10) leads to:

$$\int_{\gamma} d\bar{z} \mathbf{g}_{\alpha\alpha}^{-1}(z_1, \bar{z}) \mathbf{G}_{\alpha C}(\bar{z}, z_2) = \mathbf{h}_{\alpha C}(z_1) \mathbf{G}_{CC}(z_1, z_2) \quad (2.3.11)$$

$$\int_{\gamma} d\bar{z} \mathbf{G}_{C\alpha}(z_1, \bar{z}) \mathbf{g}_{\alpha\alpha}^{-1}(\bar{z}, z_2) = \mathbf{G}_{CC}(z_1, z_2) \mathbf{h}_{C\alpha}(z_2) \quad (2.3.12)$$

We multiply Eq. (2.3.11) from the left-hand side by $\mathbf{g}_{\alpha\alpha}(z_1, \bar{z}')$, integrate over the full Konstantinov-Perel' contour and use Eq. (2.3.6) to give:

$$\mathbf{G}_{\alpha C}(z_1, z_2) = \int_{\gamma} d\bar{z} \mathbf{g}_{\alpha\alpha}(z_1, \bar{z}) \mathbf{h}_{\alpha C}(\bar{z}) \mathbf{G}_{CC}(\bar{z}, z_2) \quad (2.3.13)$$

Similarly, we multiply Eq. (2.3.12) from the right-hand side by $\mathbf{g}_{\alpha\alpha}(\bar{z}', z_2)$, integrate over the full Konstantinov-Perel' contour and use Eq. (2.3.6) to give:

$$\mathbf{G}_{C\alpha}(z_1, z_2) = \int_{\gamma} d\bar{z} \mathbf{G}_{CC}(z_1, \bar{z}) \mathbf{h}_{C\alpha}(\bar{z}) \mathbf{g}_{\alpha\alpha}(\bar{z}, z_2) \quad (2.3.14)$$

Finally, we are able to substitute Eq. (2.3.13) into Eq. (2.3.2) and Eq. (2.3.14) into Eq. (2.3.3) to obtain the equations of motion for $\mathbf{G}_{CC}$ purely in terms of objects defined on the molecular region [128]:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{CC}(z_1) \right] \mathbf{G}_{CC}(z_1, z_2) = \mathbf{I}_{CC} \delta(z_1, z_2) + \int_{\gamma} d\bar{z} \mathbf{\Sigma}_{CC}(z_1, \bar{z}) \mathbf{G}_{CC}(\bar{z}, z_2) \quad (2.3.15)$$

$$\mathbf{G}_{CC}(z_1, z_2) \left[-i \frac{\overleftarrow{d}}{dz_2} - \mathbf{h}_{CC}(z_2) \right] = \mathbf{I}_{CC} \delta(z_1, z_2) + \int_{\gamma} d\bar{z} \mathbf{G}_{CC}(z_1, \bar{z}) \mathbf{\Sigma}_{CC}(\bar{z}, z_2) \quad (2.3.16)$$

where we define the so-called *embedding self-energy* as

$$\mathbf{\Sigma}_{CC}(z_1, z_2) = \sum_{\alpha} \mathbf{h}_{C\alpha}(z_1) \mathbf{g}_{\alpha\alpha}(z_1, z_2) \mathbf{h}_{\alpha C}(z_2) \quad (2.3.17)$$

It was mentioned above that the presence of the $\alpha - C$ coupling in the hamiltonian (2.2.3) for $z \in C_M$ distinguishes the partition-free approach from the partitioned. Eq. (2.3.17) implies that, in the partitioned approach, the embedding self-energy is always zero when one of z_1, z_2 lies on the vertical branch. This means that all terms involving $\mathbf{\Sigma}_{CC}^{M/\gamma/r}(z_1, z_2)$ must vanish in the partitioned approach.

As discussed in Sections 1.5.2 and 1.5.3, the retarded, advanced, lesser, greater, right, left and Matsubara components of $\mathbf{G}_{CC}(z_1, z_2)$ are defined by the choices of contour times given in Table 1.1. To fully define the mathematical problem of nonequilibrium transport through the molecule, one must map from the integro-differential equations (2.3.15), (2.3.16) defined on the Konstantinov-Perel' contour to the Kadanoff-Baym equations for the CC region. This is done by a simple application of the Langreth Rules (1.5.49)-(1.5.55) to (2.3.15) and (2.3.16); the resulting

GF Component	EoM
Retarded	$\left[i \frac{d}{dt_1} - \mathbf{h}_{CC}(t_1) \right] \mathbf{G}_{CC}^r(t_1, t_2) = \mathbf{I}_{CC} \delta(t_1 - t_2) + [\mathbf{\Sigma}_{CC}^r \cdot \mathbf{G}_{CC}^r](t_1, t_2)$
Advanced	$\mathbf{G}_{CC}^a(t_1, t_2) \left[-i \frac{d}{dt_2} - \mathbf{h}_{CC}(t_2) \right] = \mathbf{I}_{CC} \delta(t_1 - t_2) + [\mathbf{G}_{CC}^a \cdot \mathbf{\Sigma}_{CC}^a](t_1, t_2)$
Lesser	$\left[i \frac{d}{dt_1} - \mathbf{h}_{CC}(t_1) \right] \mathbf{G}_{CC}^<(t_1, t_2) = [\mathbf{\Sigma}_{CC}^< \cdot \mathbf{G}_{CC}^a + \mathbf{\Sigma}_{CC}^r \cdot \mathbf{G}_{CC}^< + \mathbf{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^\top](t_1, t_2)$ $\mathbf{G}_{CC}^<(t_1, t_2) \left[-i \frac{d}{dt_2} - \mathbf{h}_{CC}(t_2) \right] = [\mathbf{G}_{CC}^r \cdot \mathbf{\Sigma}_{CC}^< + \mathbf{G}_{CC}^< \cdot \mathbf{\Sigma}_{CC}^a + \mathbf{G}_{CC}^\top \star \mathbf{\Sigma}_{CC}^\top](t_1, t_2)$
Greater	$\left[i \frac{d}{dt_1} - \mathbf{h}_{CC}(t_1) \right] \mathbf{G}_{CC}^>(t_1, t_2) = [\mathbf{\Sigma}_{CC}^> \cdot \mathbf{G}_{CC}^a + \mathbf{\Sigma}_{CC}^r \cdot \mathbf{G}_{CC}^> + \mathbf{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^\top](t_1, t_2)$ $\mathbf{G}_{CC}^>(t_1, t_2) \left[-i \frac{d}{dt_2} - \mathbf{h}_{CC}(t_2) \right] = [\mathbf{G}_{CC}^r \cdot \mathbf{\Sigma}_{CC}^> + \mathbf{G}_{CC}^> \cdot \mathbf{\Sigma}_{CC}^a + \mathbf{G}_{CC}^\top \star \mathbf{\Sigma}_{CC}^\top](t_1, t_2)$
Right	$\left[i \frac{d}{dt_1} - \mathbf{h}_{CC}(t_1) \right] \mathbf{G}_{CC}^\top(t_1, \tau_2) = [\mathbf{\Sigma}_{CC}^r \cdot \mathbf{G}_{CC}^\top + \mathbf{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^M](t_1, \tau_2)$
Left	$\mathbf{G}_{CC}^\top(\tau_1, t_2) \left[-i \frac{d}{dt_2} - \mathbf{h}_{CC}(t_2) \right] = [\mathbf{G}_{CC}^\top \cdot \mathbf{\Sigma}_{CC}^a + \mathbf{G}_{CC}^M \star \mathbf{\Sigma}_{CC}^\top](\tau_1, t_2)$
Matsubara	$\left[-\frac{d}{d\tau_1} - \mathbf{h}_{CC}^M \right] \mathbf{G}_{CC}^M(\tau_1, \tau_2) = i \mathbf{I}_{CC} \delta(\tau_1 - \tau_2) + [\mathbf{\Sigma}_{CC}^M \star \mathbf{G}_{CC}^M](\tau_1, \tau_2)$ $\mathbf{G}_{CC}^M(\tau_1, \tau_2) \left[\frac{d}{d\tau_2} - \mathbf{h}_{CC}^M \right] = i \mathbf{I}_{CC} \delta(\tau_1 - \tau_2) + [\mathbf{G}_{CC}^M \star \mathbf{\Sigma}_{CC}^M](\tau_1, \tau_2)$

Table 2.1: Kadanoff-Baym Equations for the CC region with arbitrary self-energy.

set of coupled differential equations is listed in Table (2.1). We note in passing that a numerical approach to the solution of the embedded Kadanoff-Baym equations for systems that include an explicit electron-electron interaction term in their Hamiltonian within the Second Born (2B) and GW approximations has been recently developed [280, 281, 183, 186]. The latter approximations employ perturbative expansions of the exact many-body self-energy, and can therefore be used to correctly renormalize the molecular energy levels in a way that incorporates both polarization and intramolecular scattering effects into the switch-on problem. In a real system, these effects will alter the intrinsic relaxation time scales of the problem, and may prevent the formation of metastable states in the long-time limit [185]. The time-stepping approach developed for the interacting problem is also applicable to the non-interacting case with arbitrary embedding self-energy. Here we will not take this approach, and instead focus on an exactly solvable model for the self-energies, the so-called *wide-band limit approximation* or WBLA. This is detailed in Section 2.4.

2.4 Self-energies in the WBLA

Depending on where the two ‘time’ arguments in the self-energy $\mathbf{\Sigma}_{CC}(z_1, z_2)$ lie, various components of it can also be defined. These require calculation of the corresponding components of the Green’s function $\mathbf{g}_{\alpha\alpha}(z_1, z_2)$ of the isolated lead α . The time-dependent part, $\sum_k V_\alpha(t) \hat{N}_{k\alpha}$ (where $\hat{N}_{k\alpha} = \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha}$ is the number operator), in the Hamiltonian of the lead α commutes with the rest of its Hamiltonian and hence the contour time ordering can be omitted when calculating the corresponding evolution operator. Hence, the expressions for the creation and annihilation operators in the Heisenberg representation follow immediately: if $z \equiv t \in C_\pm$, then

$$\hat{d}_{k\alpha}(t) = \hat{d}_{k\alpha} e^{-i\phi_{k\alpha}(t, t_0)} = \left[\hat{d}_{k\alpha}^\dagger(t) \right]^\dagger \quad (2.4.1)$$

where it is convenient to introduce a function

$$\phi_{k\alpha}(t, t_0) = (t - t_0) \epsilon_{k\alpha} + \int_{t_0}^t V_\alpha(\tau) d\tau = (t - t_0) \epsilon_{k\alpha} + \psi_\alpha(t, t_0) ; \quad (2.4.2)$$

if $z = t_0 - i\tau \in C_M$, then the creation/annihilation operators are no longer Hermitian conjugates of each other:

$$\hat{d}_{k\alpha}(t_0 - i\tau) = \hat{d}_{k\alpha} e^{-(\varepsilon_{k\alpha} - \mu)\tau} \quad (2.4.3)$$

$$\hat{d}_{k\alpha}^\dagger(t_0 - i\tau) = \hat{d}_{k\alpha}^\dagger e^{(\varepsilon_{k\alpha} - \mu)\tau} \quad (2.4.4)$$

Using these operators and the definition of the Green's functions, we can obtain explicit formulae for the isolated α lead Green's functions:

$$[\mathbf{g}_{\alpha\alpha}^r(t_1, t_2)]_{kk'} = -i\theta(t_1 - t_2) \delta_{kk'} e^{-i\phi_{k\alpha}(t_1, t_2)} \quad (2.4.5)$$

$$[\mathbf{g}_{\alpha\alpha}^a(t_1, t_2)]_{kk'} = i\theta(t_2 - t_1) \delta_{kk'} e^{-i\phi_{k\alpha}(t_1, t_2)} \quad (2.4.6)$$

$$[\mathbf{g}_{\alpha\alpha}^<(t_1, t_2)]_{kk'} = i\delta_{kk'} f(\varepsilon_{k\alpha} - \mu) e^{-i\phi_{k\alpha}(t_1, t_2)} \quad (2.4.7)$$

$$[\mathbf{g}_{\alpha\alpha}^>(t_1, t_2)]_{kk'} = -i\delta_{kk'} [1 - f(\varepsilon_{k\alpha} - \mu)] e^{-i\phi_{k\alpha}(t_1, t_2)} \quad (2.4.8)$$

Here $f(\omega) = (e^{\beta\omega} + 1)^{-1}$ is the Fermi function. In the case of the Matsubara component, it is convenient to expand it into a Fourier series, exploiting the boundary conditions, $\mathbf{g}_{\alpha\alpha}^M(\tau, 0) = -\mathbf{g}_{\alpha\alpha}^M(\tau, \beta)$ and $\mathbf{g}_{\alpha\alpha}^M(0, \tau) = -\mathbf{g}_{\alpha\alpha}^M(\beta, \tau)$:

$$[\mathbf{g}_{\alpha\alpha}^M(\tau_1, \tau_2)]_{kk'} = \delta_{kk'} \frac{i}{\beta} \sum_q \frac{e^{-\omega_q(\tau_1 - \tau_2)}}{\omega_q - \varepsilon_{k\alpha} + \mu} \quad (2.4.9)$$

where $\omega_q = i\pi(2q + 1)/\beta$ are Matsubara frequencies and the q summation runs over all negative and positive integers. Then, the right and left components can also be written via the Matsubara sums:

$$[\mathbf{g}_{\alpha\alpha}^\top(t, \tau)]_{kk'} = [\mathbf{g}_{\alpha\alpha}^M(0, \tau)]_{kk'} e^{-i\phi_{k\alpha}(t, t_0)} = \delta_{kk'} \frac{i}{\beta} e^{-i\phi_{k\alpha}(t, t_0)} \sum_q \frac{e^{\omega_q \tau}}{\omega_q - \varepsilon_{k\alpha} + \mu} \quad (2.4.10)$$

$$[\mathbf{g}_{\alpha\alpha}^\top(\tau, t)]_{kk'} = [\mathbf{g}_{\alpha\alpha}^M(\tau, 0)]_{kk'} e^{i\phi_{k\alpha}(t, t_0)} = \delta_{kk'} \frac{i}{\beta} e^{i\phi_{k\alpha}(t, t_0)} \sum_q \frac{e^{-\omega_q \tau}}{\omega_q - \varepsilon_{k\alpha} + \mu} \quad (2.4.11)$$

All the components of the self-energy can now be obtained by substituting these expressions for the decoupled GFs into the embedded self-energy definition, Eq. (2.3.17). To obtain the retarded component, we shall Fourier transform that part of the expression which depends only on the time-difference $t_1 - t_2$:

$$\begin{aligned} [\Sigma_{CC}^r(t_1, t_2)]_{mn} &= \sum_\alpha e^{-i\psi_\alpha(t_1, t_2)} \int \frac{d\omega}{2\pi} e^{i\omega(t_1 - t_2)} \sum_k \frac{T_{m,k\alpha} T_{k\alpha,n}}{\omega + i0 - \varepsilon_{k\alpha}} \\ &= \sum_\alpha e^{-i\psi_\alpha(t_1, t_2)} \int \frac{d\omega}{2\pi} e^{i\omega(t_1 - t_2)} \left[\Lambda_{\alpha,mn}(\omega) - \frac{i}{2} \Gamma_{\alpha,mn}(\omega) \right] \end{aligned} \quad (2.4.12)$$

where (the symbol $\mathcal{P}$ corresponds to the Cauchy principal part):

$$\Lambda_{\alpha,mn}(\omega) = \mathcal{P} \int \frac{d\omega'}{2\pi} \frac{\Gamma_{\alpha,nm}(\omega')}{\omega - \omega'} \quad (2.4.13)$$

$$\Gamma_{\alpha,mn}(\omega) = 2\pi \sum_k T_{m,k\alpha} T_{k\alpha,n} \delta(\omega - \varepsilon_{k\alpha}) \quad (2.4.14)$$

As in the single-level case discussed in Section 1.4.1.2, the level-width $\Gamma_{\alpha,mn}(\omega) \simeq \Gamma_{\alpha,mn}$ loses its dependence on the energy within the WBLA, which means that it becomes localized in the time representation¹:

$$[\Sigma_{CC}^r(t_1, t_2)]_{mn} = -\frac{i}{2} \delta(t_1 - t_2) \Gamma_{mn} \quad (2.4.16)$$

¹Here we make use of the integral representation of the Dirac delta function:

$$[\Sigma_{CC}^a(t_1, t_2)]_{mn} = \frac{i}{2} \delta(t_1 - t_2) \Gamma_{mn} \quad (2.4.17)$$

A similar procedure is used to extract all other self-energy components, where a Fourier transform of the term multiplying $e^{i\psi_\alpha(t_1, t_2)}$ is made and the level width replaced with $2\pi \sum_{k, \alpha} T_{m, k\alpha} T_{k\alpha, n} \delta(\varepsilon_\alpha^F - \varepsilon_{k\alpha})$:

$$[\Sigma_{CC}^<(t_1, t_2)]_{mn} = i \left[\sum_{\alpha} \Gamma_{\alpha, mn} e^{-i\psi_\alpha(t_1, t_2)} \right] \int \frac{d\omega}{2\pi} f(\omega - \mu) e^{-i\omega(t_1 - t_2)} \quad (2.4.18)$$

$$[\Sigma_{CC}^>(t_1, t_2)]_{mn} = -i \left[\sum_{\alpha} \Gamma_{\alpha, mn} e^{-i\psi_\alpha(t_1, t_2)} \right] \int \frac{d\omega}{2\pi} [1 - f(\omega - \mu)] e^{-i\omega(t_1 - t_2)} \quad (2.4.19)$$

$$[\Sigma_{CC}^r(\tau, t)]_{mn} = \frac{i}{\beta} \left[\sum_{\alpha} \Gamma_{\alpha, mn} e^{i\psi_\alpha(t, t_0)} \right] \sum_q e^{-\omega_q \tau} \int \frac{d\omega}{2\pi} \frac{e^{i\omega(t - t_0)}}{\omega_q - \omega + \mu} \quad (2.4.20)$$

$$[\Sigma_{CC}^l(t, \tau)]_{mn} = \frac{i}{\beta} \left[\sum_{\alpha} \Gamma_{\alpha, mn} e^{-i\psi_\alpha(t, t_0)} \right] \sum_q e^{\omega_q \tau} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(t - t_0)}}{\omega_q - \omega + \mu} \quad (2.4.21)$$

The Matsubara self-energy is obtained similarly with the help of the identity

$$\int \frac{d\omega}{2\pi} \frac{1}{\omega_q - \omega + \mu} = \frac{i}{2} \xi_q \quad (2.4.22)$$

Here $\xi_q = +1$ when $\text{Im}(\omega_q) > 0$ and $\xi_q = -1$ when $\text{Im}(\omega_q) < 0$. This finally gives:

$$[\Sigma_{CC}^M(\tau_1, \tau_2)]_{mn} = -\frac{\Gamma_{mn}}{2\beta} \sum_q \xi_q e^{-\omega_q(\tau_1 - \tau_2)} \quad (2.4.23)$$

The WBLA is equivalent to the assumption that the energy range of the transmission channel in the leads is so wide that the coupling between every lead state and a given molecular orbital is independent of the energy of the lead state. This means that the ω dependence of the level width matrix $\Gamma_\alpha(\omega)$ can be neglected, $\Gamma_{\alpha, mn}(\omega) \simeq \Gamma_{\alpha, mn}(\varepsilon_\alpha^F)$, where ε_α^F is the equilibrium Fermi energy of lead α , such that the level shift matrix becomes exactly zero, $\Lambda_\alpha(\omega) = 0$. This is a good approximation in systems for which transport takes place at energies close to the Fermi level, and in cases where the matrices $\Lambda_\alpha(\omega)$ and $\Gamma_\alpha(\omega)$ vary slowly with ω . Detailed *ab initio* studies of the WBLA in transport calculations reveal that it compares favorably to fully self-consistent simulations for choices of the leads in which the density of states of the metal electrodes (DOS) are approximately constant (for example bulk gold) [139]. However, even in these systems it can lead to error in the estimation of the HOMO-LUMO gap from the transmission coefficient, and miscalculation of splittings in the transmission peaks when a bias is applied. It can also fail in 1D leads, where the DOS may exhibit van Hove singularities and step-like behaviour of the transmission at the band edges [139]. In the context of explicit time-dependence, we remark that transport calculations through 1D systems with an AC bias were performed numerically by Zhu *et al.*, who found that the WBLA leads to a ‘ringing’ signal on the current that is qualitatively different to the results of finite-band calculations [207]. The WBLA is, however, appropriate for transport calculations through large molecules, as in these cases the physical characteristics of the transport are dominated by the molecule and not the nature of its coupling to the leads. In

$$\delta(t_1 - t_2) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{\pm i\omega(t_1 - t_2)} \quad (2.4.15)$$

GF Component	EoM
Retarded	$\left[i\frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff}\right] \mathbf{G}_{CC}^r(t_1, t_2) = \mathbf{I}_{CC}\delta(t_1 - t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^r(t_1, t_2)$
Advanced	$\mathbf{G}_{CC}^a(t_1, t_2) \left[-i\frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger}\right] = \mathbf{I}_{CC}\delta(t_1 - t_2) + \mathbf{G}_{CC}^a(t_1, t_2) V_C(t_2) \mathbf{I}_{CC}$
Lesser	$\left[i\frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff}\right] \mathbf{G}_{CC}^<(t_1, t_2) = [\mathbf{\Sigma}_{CC}^< \cdot \mathbf{G}_{CC}^a + \mathbf{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^\top](t_1, t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^<(t_1, t_2)$ $\mathbf{G}_{CC}^<(t_1, t_2) \left[-i\frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger}(t_2)\right] = [\mathbf{G}_{CC}^r \cdot \mathbf{\Sigma}_{CC}^< + \mathbf{G}_{CC}^\top \star \mathbf{\Sigma}_{CC}^\top](t_1, t_2) + \mathbf{G}_{CC}^<(t_1, t_2) V_C(t_2) \mathbf{I}_{CC}$
Greater	$\left[i\frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff}(t_1)\right] \mathbf{G}_{CC}^>(t_1, t_2) = [\mathbf{\Sigma}_{CC}^> \cdot \mathbf{G}_{CC}^a + \mathbf{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^\top](t_1, t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^>(t_1, t_2)$ $\mathbf{G}_{CC}^>(t_1, t_2) \left[-i\frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger}(t_2)\right] = [\mathbf{G}_{CC}^r \cdot \mathbf{\Sigma}_{CC}^> + \mathbf{G}_{CC}^\top \star \mathbf{\Sigma}_{CC}^\top](t_1, t_2) + \mathbf{G}_{CC}^>(t_1, t_2) V_C(t_2) \mathbf{I}_{CC}$
Right	$\left[i\frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff}(t_1)\right] \mathbf{G}_{CC}^\top(t_1, t_2) = [\mathbf{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^M](t_1, t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^\top(t_1, t_2)$
Left	$\mathbf{G}_{CC}^\top(t_1, t_2) \left[-i\frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger}(t_2)\right] = [\mathbf{G}_{CC}^M \star \mathbf{\Sigma}_{CC}^\top](t_1, t_2) + \mathbf{G}_{CC}^\top(t_1, t_2) V_C(t_2) \mathbf{I}_{CC}$
Matsubara	$\left[-\frac{d}{d\tau_1} - \mathbf{h}_{CC}^M\right] \mathbf{G}_{CC}^M(\tau_1, \tau_2) = i\mathbf{I}_{CC}\delta(\tau_1 - \tau_2) + \mathbf{\Sigma}_{CC}^M \star \mathbf{G}_{CC}^M(\tau_1, \tau_2)$ $\mathbf{G}_{CC}^M(\tau_1, \tau_2) \left[\frac{d}{d\tau_2} - \mathbf{h}_{CC}^M\right] = i\mathbf{I}_{CC}\delta(\tau_1 - \tau_2) + \mathbf{G}_{CC}^M \star \mathbf{\Sigma}_{CC}^M(\tau_1, \tau_2)$

Table 2.2: Kadanoff-Baym Equations in the WBLA.

the context of NEGF, the WBLA finally gives a simple analytical result for the retarded self-energy:

$$[\mathbf{\Sigma}_{CC}^r(t_1, t_2)]_{mn} = -\frac{i}{2}\delta(t_1 - t_2)\Gamma_{mn} \quad (2.4.24)$$

where $\Gamma_{mn} = \sum_\alpha \Gamma_{\alpha, mn}$ is the total level width of the junction. Similarly,

$$[\mathbf{\Sigma}_{CC}^a(t_1, t_2)]_{mn} = \frac{i}{2}\delta(t_1 - t_2)\Gamma_{mn} \quad (2.4.25)$$

In the WBLA, the lesser, greater, right, left and Matsubara self-energy components are obtained in a similar manner, and are presented in Appendix A for completeness. One can see that expressions for the lesser, greater, right and left components of the self-energy differ from those obtained in [190, 128] for the case of the constant bias; the expressions for the Matsubara, advanced and retarded components remain the same.

To understand the significance of these expressions, one may note that the Kadanoff-Baym equation for each component of $\mathbf{G}_{CC}$ contains the target function convolved with one of $\mathbf{\Sigma}_{CC}^{r/a}$ on the right-hand side, as shown in Table 2.1. Formally, the effect of the WBLA is to localize $\mathbf{\Sigma}_{CC}^{r/a}(t_1, t_2)$ in time and remove the need for a self-consistent solution to (2.3.15), (2.3.16) while the eigenenergies of $\mathbf{h}_{CC}$ are simultaneously renormalized by a purely imaginary and energy-independent level-width matrix. In Table 2.2, the resulting Kadanoff-Baym (KB) equations are given in terms of $\tilde{\mathbf{h}}_{CC}^{eff} = \tilde{\mathbf{h}}_{CC} - i\frac{\mathbf{\Gamma}_{CC}}{2}$, the “effective” Hamiltonian of region C , where $\tilde{\mathbf{h}}_{CC}^{eff} \equiv \mathbf{h}_{CC}^{eff} + \mathbf{u}_{CC}$. Note the presence in these expressions of the ‘driving’ term $V_C(t_2) \mathbf{I}_{CC}$ to the right-hand side of each KB equation. This adds a level of mathematical complexity to the solution of these equations, which in Ref. [1] had no explicitly time-dependent driving. We shall give a complete overview of how to unpack and solve each of these equations in the following section.

2.5 Integration of the Kadanoff-Baym equations

2.5.1 Matsubara Green's function

Projecting Eq. (2.3.15) on the vertical track of the contour γ and applying the Langreth rules [278, 179], the corresponding equation of motion for the Matsubara Green's function $\mathbf{G}_{CC}^M(\tau_1, \tau_2)$ is obtained:

$$\left[-\frac{d}{d\tau_1} - \mathbf{h}_{CC}^M \right] \mathbf{G}_{CC}^M(\tau_1, \tau_2) = i\mathbf{I}_{CC}\delta(\tau_1 - \tau_2) + (\boldsymbol{\Sigma}_{CC}^M \star \mathbf{G}_{CC}^M)(\tau_1, \tau_2) \quad (2.5.1)$$

where $\mathbf{h}_{CC}^M = \mathbf{h}_{CC} - \mu\mathbf{I}_{CC}$ is the Hamiltonian matrix of the central region on the vertical track of the contour γ with $(\mathbf{h}_{CC})_{mn} = h_{mn}$, while the star in the last term corresponds to the imaginary time convolution integral defined in Eq. (1.5.21). Expanding the self-energy $\boldsymbol{\Sigma}_{CC}^M(\tau, \tau')$, the Green's function $\mathbf{G}_{CC}^M(\tau, \tau')$ and the delta function $\delta(\tau_1 - \tau_2)$ into the Matsubara sums² one immediately obtains [128]:

$$\mathbf{G}_{CC}^M(\tau_1, \tau_2) = \frac{i}{\beta} \sum_q e^{-\omega_q(\tau_1 - \tau_2)} \mathbf{G}_{CC}^M(\omega_q) \quad (2.5.2)$$

where we have defined:

$$\mathbf{G}_{CC}^M(\omega_q) = \begin{cases} \left[(\omega_q + \mu)\mathbf{I}_{CC} - \mathbf{h}_{CC}^{eff} \right]^{-1}, & \text{Im}(\omega_q) > 0 \\ \left[(\omega_q + \mu)\mathbf{I}_{CC} - (\mathbf{h}_{CC}^{eff})^\dagger \right]^{-1}, & \text{Im}(\omega_q) < 0 \end{cases} \quad (2.5.3)$$

The Matsubara Green's function is the same as in [190], where the problem of a constant bias switch-on in the partition-free approach was solved. This is to be expected as $\mathbf{G}_{CC}^M$ corresponds to the preparation of the system prior to the switch on of the bias, which is the same whether or not the bias switch on is time-dependent.

2.5.2 Right and left Green's functions

Projecting Eq. (2.3.15) on the right component (i.e. $t_1 \in C_- \oplus C_+$, $t_2 = t_0 - i\tau_2 \in C_M$) and using the Langreth rules again, the following equation of motion for the right Green's function is obtained:

$$\left[i\frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC} \right] \mathbf{G}_{CC}^\top(t_1, \tau_2) = (\boldsymbol{\Sigma}_{CC}^r \cdot \mathbf{G}_{CC}^\top + \boldsymbol{\Sigma}_{CC}^\top \star \mathbf{G}_{CC}^M)(t_1, \tau_2) + V_C(t_1)\mathbf{I}_{CC}\mathbf{G}_{CC}^\top(t_1, \tau_2)$$

²Note that the presence of the delta function in the equation 2.5.1 indicates the ambiguity of absolute time ordering on C_M in the times τ_1, τ_2 . The Dirac delta on C^M must satisfy the same antiperiodicity condition as the Matsubara GF, $\mathbf{G}_{CC}^M(\tau_1, \tau_2) = \frac{i}{\beta} \sum_{q=-\infty}^{\infty} e^{-\omega_q(\tau_1 - \tau_2)} \mathbf{G}_{CC}^M(\omega_q)$ whilst remaining periodic over the full range $[-\beta, \beta]$. This means it must be expanded in terms of the complex poles with odd indices, satisfying $e^{\beta\omega_q} = -1$. Also, due to the antiperiodicity condition, when integrating for the Fourier Series component we must include the point which is shifted by β from the spike of the delta function within the integral range:

$$\begin{aligned} \delta(\tau_1 - \tau_2) &= \frac{i}{\beta} \sum_{q=-\infty}^{\infty} e^{-\omega_q(\tau_1 - \tau_2)} \delta_q \\ \delta_q &= -\frac{i\beta}{2\beta} \int_{-\beta+\varepsilon}^{\beta+\varepsilon} d\tau e^{\omega_q\tau} \delta(\tau) = -\frac{i}{2} \left[\int_{-\beta+\varepsilon}^{\varepsilon} d\tau e^{\omega_q\tau} \delta(\tau) + \int_{\varepsilon}^{\beta+\varepsilon} d\tau e^{\omega_q\tau} \delta(\tau) \right] = -\frac{i}{2} \left[1 - \int_{\varepsilon}^{\beta+\varepsilon} d\tau e^{\omega_q\tau} \delta(\tau - \beta) \right] = -i \end{aligned}$$

This yields the integral representation of the delta function on C_M :

$$\delta(\tau_1 - \tau_2) = \frac{1}{\beta} \sum_{q=-\infty}^{\infty} e^{-\omega_q(\tau_1 - \tau_2)}$$

Using expression for the retarded self-energy (2.4.24), the equation of motion is manipulated into:

$$\left[i \frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff} \right] \mathbf{G}_{CC}^{\top} (t_1, \tau_2) = (\boldsymbol{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^M) (t_1, \tau_2) + V_C (t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^{\top} (t_1, \tau_2) \quad (2.5.4)$$

which can be solved for the right Green's function, if we make the substitution:

$$\mathbf{G}_{CC}^{\top} (t_1, \tau_2) \equiv e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} e^{-i\varphi_C(t_1,t_0)} \tilde{\mathbf{G}}_{CC}^{\top} (t_1, \tau_2) \quad (2.5.5)$$

Here we make the definition of the phase factor associated with the molecular time-dependence:

$$\varphi_C (t_1, t_2) \equiv \int_{t_2}^{t_1} d\tau V_C (\tau) \quad (2.5.6)$$

We can therefore obtain the following equation for the reduced object $\tilde{\mathbf{G}}_{CC}^{\top} (t_1, \tau_2)$:

$$\frac{d\tilde{\mathbf{G}}_{CC}^{\top} (t_1, \tau_2)}{dt_1} = -ie^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} e^{i\varphi_C(t_1,t_0)} (\boldsymbol{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^M) (t_1, \tau_2)$$

Taking into account the appropriate boundary conditions from Eq. (1.5.68),

$$\tilde{\mathbf{G}}_{CC}^{\top} (t_0, \tau_2) = \mathbf{G}_{CC}^{\top} (t_0, \tau_2) = \mathbf{G}_{CC}^M (0^+, \tau_2) \quad (2.5.7)$$

we can solve for the reduced GF and then map back to the full right component, which is sufficient for calculation of the lesser GF in Section (2.5.7):

$$\mathbf{G}_{CC}^{\top} (t_1, \tau_2) = e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} e^{-i\varphi_C(t_1,t_0)} \left[\mathbf{G}_{CC}^M (0^+, \tau_2) - i \int_{t_0}^{t_1} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t}-t_0)} e^{i\varphi_C(\bar{t},t_0)} (\boldsymbol{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^M) (\bar{t}, \tau_2) \right] \quad (2.5.8)$$

The projection onto the left component of the CC Green's function leads to the following equation of motion:

$$\mathbf{G}_{CC}^{\top} (\tau_1, t_2) \left[-i \frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger} (t_2) \right] = [\mathbf{G}_{CC}^M \star \boldsymbol{\Sigma}_{CC}^{\top}] (\tau_1, t_2) + \mathbf{G}_{CC}^{\top} (\tau_1, t_2) V_C (t_2) \mathbf{I}_{CC} \quad (2.5.9)$$

Once again we solve this by making an ansatz, this time of the form:

$$\mathbf{G}_{CC}^{\top} (\tau_1, t_2) \equiv \tilde{\mathbf{G}}_{CC}^{\top} (\tau_1, t_2) e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_2-t_0)} e^{i\varphi_C(t_2,t_0)} \quad (2.5.10)$$

This is substituted into (2.5.9) and combined with the initial condition implied by Eq. (1.5.69),

$$\tilde{\mathbf{G}}_{CC}^{\top} (\tau_1, t_0) = \mathbf{G}_{CC}^{\top} (\tau_1, t_0) = \mathbf{G}_{CC}^M (\tau_1, 0^+) \quad (2.5.11)$$

to give the following solution:

$$\mathbf{G}_{CC}^{\top} (\tau_1, t_2) = \left[\mathbf{G}_{CC}^M (\tau_1, 0^+) + i \int_{t_0}^{t_2} d\bar{t} (\mathbf{G}_{CC}^M \star \boldsymbol{\Sigma}_{CC}^{\top}) (\tau_1, \bar{t}) e^{-i(\tilde{\mathbf{h}}_{CC}^{eff})^{\dagger}(\bar{t}-t_0)} e^{-i\varphi_C(\bar{t},t_0)} \right] e^{i(\tilde{\mathbf{h}}_{CC}^{eff})^{\dagger}(t_2-t_0)} e^{i\varphi_C(t_2,t_0)} \quad (2.5.12)$$

Note that the obtained expressions contain exponential functions of the matrix $\tilde{\mathbf{h}}_{CC}^{eff}$. Formally the equations (2.5.8) and (2.5.12) for the right and left Green's functions in terms of different components are identical to those given in [128] for the constant bias switch-on case, with the addition of the φ_C phase factors. Note, however, that the

self-energies appearing in these formulae are also generalized versions of those published in [128].

2.5.3 Retarded and Advanced Green's functions

It is well known that for the case of the static bias the retarded and advanced Green's functions of the whole system still depend on the time difference as in the stationary case, and can be Fourier-transformed for a representation in terms of a single frequency. In the derivation of the generalized LB formalism given in [1], in which the bias applied to each lead is time-dependent, this property of these two Green's functions is still valid. However, contrary to suggestions there, it is not absolutely essential for our derivation that this property holds. This can be shown by first projecting Eq. (2.3.15) on the retarded subspace of the (z_1, z_2) plane and applying the Langreth rules, whilst setting $V_C(t) = 0$ and $\mathbf{T}_{CC} = 0$:

$$\left[i \frac{d}{dt_1} - \mathbf{h}_{CC} \right] \mathbf{G}_{CC}^r(t_1, t_2) = \mathbf{I}_{CC} \delta(t_1 - t_2) + (\boldsymbol{\Sigma}_{CC}^r \cdot \mathbf{G}_{CC}^r)_{(t_1, t_2)} \quad (2.5.13)$$

Using expression (2.4.24) for the retarded self-energy, the following equation of motion for the retarded Green's function $\mathbf{G}_{CC}^r(t_1, t_2)$ is obtained:

$$\left[i \frac{d}{dt_1} - \mathbf{h}_{CC}^{eff} \right] \mathbf{G}_{CC}^r(t_1, t_2) = \mathbf{I}_{CC} \delta(t_1 - t_2) \quad (2.5.14)$$

It immediately follows from this equation that the retarded Green's function, which is nothing but a propagator with fixed time-ordering, depends only on the time difference. Mathematically, this is a direct consequence of the fact that the retarded self-energy is proportional to the delta function. Physically it arises from the fact that the molecular region is propagated by a time-independent Hamiltonian, i.e. it does not see the time-varying field directly. Therefore, for this case one can introduce in the usual way the Fourier transform pair,

$$\mathbf{G}_{CC}^r(t_1, t_2) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t_1 - t_2)} \mathbf{G}_{CC}^r(\omega) \quad (2.5.15)$$

$$\mathbf{G}_{CC}^r(\omega) = \int_{-\infty}^{\infty} d(t_1 - t_2) e^{i\omega(t_1 - t_2)} \mathbf{G}_{CC}^r(t_1, t_2) \quad (2.5.16)$$

This definition of the Fourier transform pair will be used as the convention throughout this thesis. Substituting (2.5.15) into (2.5.14), one obtains:

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t_1 - t_2)} \left(\omega \mathbf{I}_{CC} - \mathbf{h}_{CC}^{eff} \right) \mathbf{G}_{CC}^r(\omega) = \mathbf{I}_{CC} \delta(t_1 - t_2) \quad (2.5.17)$$

The integral representation of the Dirac delta function Eq. (2.4.15) therefore implies:

$$\mathbf{G}_{CC}^r(\omega) = \left(\omega \mathbf{I}_{CC} - \mathbf{h}_{CC}^{eff} \right)^{-1} \quad (2.5.18)$$

The matrix $\mathbf{h}_{CC}^{eff}$ is not Hermitian; however, in numerical applications one can define its left and right eigenvectors which share the same eigenvalues [172]:

$$\mathbf{h}_{CC}^{eff} |\varphi_j^R\rangle = \bar{\varepsilon}_j |\varphi_j^R\rangle \text{ and } \langle \varphi_j^L | \mathbf{h}_{CC}^{eff} = \bar{\varepsilon}_j \langle \varphi_j^L | \quad (2.5.19)$$

The eigenenergies $\bar{\varepsilon}_j$ contain an imaginary part that is strictly negative (as $\mathbf{\Gamma}$ is positive-definite - see Ref. [194] for a detailed discussion of this point), and the same value of $\bar{\varepsilon}_j$ corresponds to each of the left and right eigenvectors. Using the idempotency property

$$\sum_j \frac{|\varphi_j^R\rangle \langle \varphi_j^L|}{\langle \varphi_j^L | \varphi_j^R \rangle} = \mathbf{I} = \sum_j \frac{|\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle}, \quad (2.5.20)$$

we obtain the corresponding spectral representation of Eq. (2.5.18),

$$\mathbf{G}_{CC}^r(\omega) = \sum_j \frac{|\varphi_j^R\rangle \langle \varphi_j^L|}{\langle \varphi_j^L | \varphi_j^R \rangle} \frac{1}{\omega - \bar{\varepsilon}_j} \quad (2.5.21)$$

and substitute into Eq. (2.5.15) before integrating over ω in the lower half of the complex frequency plane, so that the time representation of the retarded Green's function is obtained:

$$\mathbf{G}_{CC}^r(t_1, t_2) = -i\theta(t_1 - t_2) e^{-i\mathbf{h}_{CC}^{eff}(t_1 - t_2)} \quad (2.5.22)$$

A similar calculation for the advanced Green's function yields:

$$\mathbf{G}_{CC}^a(\omega) = \left(\omega \mathbf{I}_{CC} - \left(\mathbf{h}_{CC}^{eff} \right)^\dagger \right)^{-1} \quad (2.5.23)$$

$$\mathbf{G}_{CC}^a(t_1, t_2) = i\theta(t_2 - t_1) e^{-i(\mathbf{h}_{CC}^{eff})^\dagger(t_1 - t_2)} \quad (2.5.24)$$

As discussed, for example, in [207, 208], we see that even in the case of the variable bias the retarded and advanced functions do not depend on the bias in the WBLA and hence it is not surprising that they have exactly the same form as in [128]. Since the frequency-dependent retarded/advanced GFs arise only in the form (2.5.18) and (2.5.23) in what follows, we keep these expressions as the *definitions* of $\mathbf{G}_{CC}^{r/a}(\omega)$ in what follows, even though $\mathbf{G}_{CC}^{r/a}(t_1, t_2)$ will be allowed to take on different forms to (2.5.22) and (2.5.24). In particular, by inspection of (2.5.3), we can extract the following theorems of analytic continuation from this definition:

$$\mathbf{G}_{CC}^M(\omega + i0^+) = \mathbf{G}_{CC}^r(\omega + \mu) \quad (2.5.25)$$

$$\mathbf{G}_{CC}^M(\omega - i0^+) = \mathbf{G}_{CC}^a(\omega + \mu) \quad (2.5.26)$$

Now, with the modifications to the CC Hamiltonian in Equation (2.2.8), the Kadanoff-Baym equations for these components take the following form:

$$\left[i \frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff} \right] \mathbf{G}_{CC}^r(t_1, t_2) = \delta(t_1 - t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^r(t_1, t_2) \quad (2.5.27)$$

$$\mathbf{G}_{CC}^a(t_1, t_2) \left[-i \frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger} \right] = \delta(t_1 - t_2) + \mathbf{G}_{CC}^a(t_1, t_2) V_C(t_2) \mathbf{I}_{CC} \quad (2.5.28)$$

It can be shown that these have the general solutions:

$$\mathbf{G}_{CC}^r(t_1, t_2) = -i\theta(t_1 - t_2) e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_2)} e^{-i\varphi_C(t_1, t_2)} \quad (2.5.29)$$

$$\mathbf{G}_{CC}^a(t_1, t_2) = i\theta(t_2 - t_1) e^{-i(\tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t_1 - t_2)} e^{-i\varphi_C(t_1, t_2)} \quad (2.5.30)$$

These cannot be represented as functions of a single frequency in Fourier space, and we shall henceforth use these expressions in convolution integrals involving both time arguments.

2.5.4 Path Independence

A necessary and sufficient condition for the path-independence of a line integral $\int_L g(x, y)dx + h(x, y)dy$ on the (x, y) plane is $\partial g/\partial y = \partial h/\partial x$. This is equivalent to the statement that $df = gdx + hdy$ is an exact differential of some function $f(x, y)$. This condition corresponds to the symmetry of the second order mixed derivatives $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ of this function.

Green's functions are defined as functions of two contour times, i.e. the domain for integration of the Green's function is the set of points $\{\langle z_1, z_2 \rangle : z_1 \in \gamma \wedge z_2 \in \gamma\}$. We shall verify here that the mixed second derivatives of the Green's function $\mathbf{G}(z_1, z_2)$ are symmetric. We can write using the corresponding equations of motion:

$$\frac{\partial \mathbf{G}_{CC}(z_1, z_2)}{\partial z_1} = -i \left[\mathbf{h}_{CC}(z_1) \mathbf{G}_{CC}(z_1, z_2) + \mathbf{I}_{CC} \delta(z_1, z_2) + \int_\gamma d\bar{z} \mathbf{\Sigma}_{CC}(z_1, \bar{z}) \mathbf{G}_{CC}(\bar{z}, z_2) \right] \quad (2.5.31)$$

$$\frac{\partial \mathbf{G}_{CC}(z_1, z_2)}{\partial z_2} = i \left[\mathbf{G}_{CC}(z_1, z_2) \mathbf{h}_{CC}(z_2) + \mathbf{I}_{CC} \delta(z_1, z_2) + \int_\gamma d\bar{z} \mathbf{G}_{CC}(z_1, \bar{z}) \mathbf{\Sigma}_{CC}(\bar{z}, z_2) \right] \quad (2.5.32)$$

From the first of these:

$$\frac{\partial^2 \mathbf{G}_{CC}(z_1, z_2)}{\partial z_2 \partial z_1} = -i \left[\mathbf{h}_{CC}(z_1) \frac{\partial \mathbf{G}_{CC}(z_1, z_2)}{\partial z_2} + \mathbf{I}_{CC} \frac{\partial \delta(z_1, z_2)}{\partial z_2} + \int_\gamma d\bar{z} \mathbf{\Sigma}_{CC}(z_1, \bar{z}) \frac{\partial \mathbf{G}_{CC}(\bar{z}, z_2)}{\partial z_2} \right] \quad (2.5.33)$$

while from the second:

$$\frac{\partial^2 \mathbf{G}_{CC}(z_1, z_2)}{\partial z_1 \partial z_2} = i \left[\frac{\partial \mathbf{G}_{CC}(z_1, z_2)}{\partial z_1} \mathbf{h}_{CC}(z_2) + \mathbf{I}_{CC} \frac{\partial \delta(z_1, z_2)}{\partial z_1} + \int_\gamma d\bar{z} \frac{\partial \mathbf{G}_{CC}(z_1, \bar{z})}{\partial z_1} \mathbf{\Sigma}_{CC}(\bar{z}, z_2) \right] \quad (2.5.34)$$

Observe that due to the order in which the Green's functions and self-energy appear to the right hand side of the derivatives, one never needs to consider derivatives of the self-energy. Noting next that $\frac{\partial \delta(z_1, z_2)}{\partial z_2} = -\frac{\partial \delta(z_1, z_2)}{\partial z_1}$, and making use of the first derivatives written above, we obtain:

$$\frac{\partial^2 \mathbf{G}_{CC}(z_1, z_2)}{\partial z_2 \partial z_1} = \frac{\partial^2 \mathbf{G}_{CC}(z_1, z_2)}{\partial z_1 \partial z_2} \quad (2.5.35)$$

Given this identity, we can take the lesser part of the Green's function by setting $z_1 = t_1 \in C_-$ and $z_2 = t_2 \in C_+$, which results in the required symmetry of the second order mixed derivatives for the CC -component of the lesser Green's function. This fact can be used to demonstrate that the same property is satisfied by the objects

$$\tilde{\mathbf{G}}^{\leq}(t_1, t_2) \equiv e^{\mathbf{B}(t_1 - t_0)} \mathbf{G}_{CC}^{\leq}(t_1, t_2) e^{\mathbf{B}^\dagger(t_2 - t_0)} \quad (2.5.36)$$

where $\mathbf{B}$ is a square matrix, and therefore path independence of the line integral

$$\int_L d\tilde{\mathbf{G}}^{\leq} = \int_L \frac{\partial \tilde{\mathbf{G}}^{\leq}}{\partial t_1} dt_1 + \frac{\partial \tilde{\mathbf{G}}^{\leq}}{\partial t_2} dt_2 \quad (2.5.37)$$

is assured, as required.

2.5.5 Transformation for the lesser/greater Green's functions

Projecting Eqs. (2.3.15) and (2.3.16) onto the lesser and greater components, using the Langreth rules and the known expression for the retarded self-energy (2.4.24), the following equations of motion for these Green's functions are obtained:

$$\left[i \frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff} \right] \mathbf{G}_{CC}^<(t_1, t_2) = [\Sigma_{CC}^< \cdot \mathbf{G}_{CC}^a + \Sigma_{CC}^\top \star \mathbf{G}_{CC}^\top] (t_1, t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^<(t_1, t_2) \quad (2.5.38)$$

$$\mathbf{G}_{CC}^<(t_1, t_2) \left[-i \frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger} \right] = [\mathbf{G}_{CC}^r \cdot \Sigma_{CC}^< + \mathbf{G}_{CC}^\top \star \Sigma_{CC}^\top] (t_1, t_2) + \mathbf{G}_{CC}^<(t_1, t_2) V_C(t_2) \mathbf{I}_{CC} \quad (2.5.39)$$

$$\left[i \frac{d}{dt_1} - \tilde{\mathbf{h}}_{CC}^{eff} \right] \mathbf{G}_{CC}^>(t_1, t_2) = [\Sigma_{CC}^> \cdot \mathbf{G}_{CC}^a + \Sigma_{CC}^\top \star \mathbf{G}_{CC}^\top] (t_1, t_2) + V_C(t_1) \mathbf{I}_{CC} \mathbf{G}_{CC}^>(t_1, t_2) \quad (2.5.40)$$

$$\mathbf{G}_{CC}^>(t_1, t_2) \left[-i \frac{d}{dt_2} - \tilde{\mathbf{h}}_{CC}^{eff\dagger} \right] = [\mathbf{G}_{CC}^r \cdot \Sigma_{CC}^> + \mathbf{G}_{CC}^\top \star \Sigma_{CC}^\top] (t_1, t_2) + \mathbf{G}_{CC}^>(t_1, t_2) V_C(t_2) \mathbf{I}_{CC} \quad (2.5.41)$$

We now look to put the WBLA Kadanoff-Baym equations for the greater Green's Functions into a form suitable for the integration. This is done by introducing the “tilded” greater Green's Function $\tilde{\mathbf{G}}^>(t_1, t_2)$ via the following transformation (similar to the canonical transformation performed in [128] for the equal time case):

$$\mathbf{G}_{CC}^>(t_1, t_2) \equiv e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} \tilde{\mathbf{G}}_{CC}^>(t_1, t_2) e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_2-t_0)} e^{-i\varphi_C(t_1, t_2)} \quad (2.5.42)$$

This is substituted into the WBLA Kadanoff-Baym equations (2.5.40) and (2.5.41) to finally obtain integrable first order differential equations for $\tilde{\mathbf{G}}_{CC}^>(t_1, t_2)$:

$$\frac{\partial \tilde{\mathbf{G}}_{CC}^>(t_1, t_2)}{\partial t_1} = -ie^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} (\Sigma_{CC}^> \cdot \mathbf{G}_{CC}^a + \Sigma_{CC}^\top \star \mathbf{G}_{CC}^\top) (t_1, t_2) e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_2-t_0)} e^{i\varphi_C(t_1, t_2)} \equiv \mathbf{F}_{(1)}^>(t_1, t_2) \quad (2.5.43)$$

$$\frac{\partial \tilde{\mathbf{G}}_{CC}^>(t_1, t_2)}{\partial t_2} = ie^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} (\mathbf{G}_{CC}^r \cdot \Sigma_{CC}^> + \mathbf{G}_{CC}^\top \star \Sigma_{CC}^\top) (t_1, t_2) e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_2-t_0)} e^{i\varphi_C(t_1, t_2)} \equiv \mathbf{F}_{(2)}^>(t_1, t_2) \quad (2.5.44)$$

From the work done in Section 2.5.4, it is evident that

$$d\tilde{\mathbf{G}}_{CC}^> = \mathbf{F}_{(1)}^>(t_1, t_2) dt_1 + \mathbf{F}_{(2)}^>(t_1, t_2) dt_2 \quad (2.5.45)$$

and therefore the line integral in the two-time plane can be performed for the greater GF. When $\mathbf{G}_{CC}^>(t_1, t_2)$ is integrated for we take the following integral path:

$$(t_{0+}, t_{0-}) \rightarrow (t_{1+}, t_{0-}) \rightarrow (t_{1+}, t_{2-}) \quad (2.5.46)$$

Here $t_{0-} = t_0 + i0^+$ is the time t_0 on the upper horizontal part of the contour, while $t_{0+} = t_0 - i0^+$ is the later time lying on the lower horizontal track of γ . This guarantees the correct time ordering for the greater function. The line integral in the two-time plane has the structure:

$$\tilde{\mathbf{G}}_{CC}^>(t_1, t_2) = \int_L \mathbf{F}_{(1)}^>(t_1, t_2) dt_1 + \mathbf{F}_{(2)}^>(t_1, t_2) dt_2 \quad (2.5.47)$$

$$= \tilde{\mathbf{G}}^>(t_0, t_0) + \int_{t_0}^{t_1} d\bar{t} \mathbf{F}_{(1)}^>(\bar{t}, t_0^-) + \int_{t_0}^{t_2} d\bar{t} \mathbf{F}_{(2)}^>(t_1, \bar{t}) \quad (2.5.48)$$

Eq. (2.5.45) is an exact differential, and so, taking the integration path indicated above, we must perform the following integral to extract the greater GF:

$$\begin{aligned} \tilde{\mathbf{G}}_{CC}^>(t_1, t_2) - \tilde{\mathbf{G}}_{CC}^>(t_0, t_0) &= -i \int_{t_0}^{t_1} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t}-t_0)} [\Sigma_{CC}^> \cdot \mathbf{G}_{CC}^a + \Sigma_{CC}^\top \star \mathbf{G}_{CC}^r] (\bar{t}_+, t_{0-}) e^{i\varphi_C(\bar{t}, t_0)} \\ &+ i \int_{t_0}^{t_2} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-\bar{t}_0)} [\mathbf{G}_{CC}^r \cdot \Sigma_{CC}^> + \mathbf{G}_{CC}^\top \star \Sigma_{CC}^r] (t_{1+}, \bar{t}_-) e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_2-t_0)} e^{i\varphi_C(t_1, \bar{t})} \equiv \sum_{i=1}^4 \mathcal{G}_{(4)}^> \end{aligned} \quad (2.5.49)$$

The following formula, proven in Section A.1 is useful for evaluating the boundary condition $\tilde{\mathbf{G}}_{CC}^>(t_0, t_0) = \mathbf{G}_{CC}^M(0^+, 0)$

$$\frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{-\omega_n 0^+} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - f(\omega)) e^{-\omega 0^+} [Q(\omega^+) - Q(\omega^-)] \quad (2.5.50)$$

where we define $\omega^\pm = \omega \pm i0^+$. This lets us extract the functional form of the initial condition for the line integral in (2.5.49):

$$\begin{aligned} \mathbf{G}^>(t_0, t_0) &= \frac{i}{\beta} \sum_{q=-\infty}^{\infty} e^{-\omega_q 0^+} \mathbf{G}_{CC}^M(\omega_q) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{\beta\omega} f(\omega) [\mathbf{G}_{CC}^M(\omega^-) - \mathbf{G}_{CC}^M(\omega^+)] \\ &= -i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) \sum_{\alpha} \mathbf{A}_{\alpha}(\omega) \end{aligned} \quad (2.5.51)$$

Above, we have introduced the spectral function $\mathbf{A}_{\alpha}(\omega) = \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega)$ for the α lead. The final line of (2.5.51) follows from the identities (2.5.25) and (2.5.26). Details of the analytic evaluation of the convolution integrals $\mathcal{G}_{(i)}^>$ will be presented in Section (2.5.6).

Now we introduce the “tilded” lesser function $\tilde{\mathbf{G}}^<(t_1, t_2)$ via the following transformation:

$$\mathbf{G}_{CC}^<(t_1, t_2) = e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} \tilde{\mathbf{G}}_{CC}^<(t_1, t_2) e^{i(\tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t_2-t_0)} e^{-i\varphi_C(t_1, t_2)} \quad (2.5.52)$$

Differentiating both sides with respect to either t_1 or t_2 and using the above equations of motion (2.5.38) and (2.5.39), we can calculate the partial derivatives of the tilded function with respect to both times:

$$\frac{\partial \tilde{\mathbf{G}}_{CC}^<(t_1, t_2)}{\partial t_1} = -i e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} (\Sigma_{CC}^< \cdot \mathbf{G}_{CC}^a + \Sigma_{CC}^\top \star \mathbf{G}_{CC}^r) (t_1, t_2) e^{-i(\tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t_2-t_0)} e^{i\varphi_C(t_1, t_2)} \equiv \mathbf{F}_{(1)}^<(t_1, t_2) \quad (2.5.53)$$

$$\frac{\partial \tilde{\mathbf{G}}_{CC}^<(t_1, t_2)}{\partial t_2} = i e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} (\mathbf{G}_{CC}^r \cdot \Sigma_{CC}^< + \mathbf{G}_{CC}^\top \star \Sigma_{CC}^r) (t_1, t_2) e^{-i(\tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t_2-t_0)} e^{i\varphi_C(t_1, t_2)} \equiv \mathbf{F}_{(2)}^<(t_1, t_2) \quad (2.5.54)$$

We have explicitly proven in Section 2.5.4 that the mixed second derivatives of the tilded function do not depend on the order of differentiation. Therefore, one can introduce the exact differential

$$d\tilde{\mathbf{G}}_{CC}^<(t_1, t_2) = \mathbf{F}_{(1)}^<(t_1, t_2) dt_1 + \mathbf{F}_{(2)}^<(t_1, t_2) dt_2 \quad (2.5.55)$$

so that $\tilde{\mathbf{G}}_{CC}^<(t_1, t_2)$ can be calculated using a line integral taken along an arbitrary path connecting the initial, (t_0, t_0) , and the final, (t_1, t_2) , points in the two-dimensional (t_1, t_2) plane. The tilded Green’s function is calculated

using the line integral (2.5.37) taken along a particular path $(t_{0-}, t_{0+}) \longrightarrow (t_{1-}, t_{0+}) \longrightarrow (t_{1-}, t_{2+})$ on the (t_1, t_2) plane:

$$\begin{aligned}\tilde{\mathbf{G}}_{CC}^<(t_1, t_2) &= \int_L \mathbf{F}_{(1)}^<(t_1, t_2) dt_1 + \mathbf{F}_{(2)}^<(t_1, t_2) dt_2 \\ &= \tilde{\mathbf{G}}^<(t_0, t_0) + \int_{t_0}^{t_1} d\bar{t} \mathbf{F}_{(1)}^<(\bar{t}, t_0) + \int_{t_0}^{t_2} d\bar{t} \mathbf{F}_{(2)}^<(t_1, \bar{t})\end{aligned}\quad (2.5.56)$$

where the matrices $\mathbf{F}_{(1)}^<$ and $\mathbf{F}_{(2)}^<$ for both times are given by first derivatives of the tilded Green's function, Eqs. (2.5.53) and (2.5.54). Next we use the fact that the Matsubara Green's function provides the boundary conditions for the lesser Green's function at the special point (t_{0-}, t_{0+}) :

$$\tilde{\mathbf{G}}^<(t_0, t_0) = \mathbf{G}_{CC}^<(t_0, t_0) = \mathbf{G}_{CC}^M(0, 0^+) = \frac{i}{\beta} \sum_{q=-\infty}^{\infty} e^{\omega_q 0^+} \mathbf{G}_{CC}^M(\omega_q) \quad (2.5.57)$$

The sum over Matsubara frequencies is transformed using the well-known formula proven in Section A.1

$$\frac{i}{\beta} \sum_q Q(\omega_q) e^{\omega_q 0^+} = \int \frac{d\omega}{2\pi} f(\omega) [Q(\omega^-) - Q(\omega^+)] \quad (2.5.58)$$

Using then the relations (2.5.25) and (2.5.26), we find the following initial condition:

$$\tilde{\mathbf{G}}^<(t_0, t_0) = \int \frac{d\omega}{2\pi} f(\omega - \mu) [\mathbf{G}_{CC}^a(\omega) - \mathbf{G}_{CC}^r(\omega)] = i \sum_{\alpha} \int \frac{d\omega}{2\pi} f(\omega - \mu) \mathbf{A}_{\alpha}(\omega) \quad (2.5.59)$$

This incorporates information on the system preparation into a description of its dynamics. Hence, one can write:

$$\begin{aligned}\tilde{\mathbf{G}}_{CC}^<(t_1, t_2) - \mathbf{G}_{CC}^M(0, 0^+) &= -i \int_{t_0}^{t_1} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t}-t_0)} [\boldsymbol{\Sigma}_{CC}^< \cdot \mathbf{G}_{CC}^a + \boldsymbol{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^r] (\bar{t}_-, t_{0+}) e^{i\varphi_C(\bar{t}, t_0)} \\ &+ i \int_{t_0}^{t_2} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1-t_0)} [\mathbf{G}_{CC}^r \cdot \boldsymbol{\Sigma}_{CC}^< + \mathbf{G}_{CC}^{\top} \star \boldsymbol{\Sigma}_{CC}^r] (t_{1-}, \bar{t}_+) e^{-i(\tilde{\mathbf{h}}_{CC}^{eff})^{\dagger}(\bar{t}-t_0)} e^{i\varphi_C(t_1, \bar{t})} \equiv \sum_{i=1}^4 \mathcal{G}_{(i)}^<\end{aligned}\quad (2.5.60)$$

There are four terms here, $\mathcal{G}_{(i)}^<$ ($i = 1, \dots, 4$), two coming from each integral, and we shall evaluate them one at a time in Section (2.5.7).

2.5.6 Line Integral for the Greater GF

For completeness, we present here the derivation of the greater GF, which we shall use in Chapter 3 of this thesis. This derivation includes some details omitted from the published work [1, 3], and is based upon the similar derivation of [128] for the lesser Green's function of a single time. There are now four convolution integrals to perform. Firstly we can see that $\mathcal{G}_{(1)}^> = 0$ because

$$\boldsymbol{\Sigma}_{CC}^> \cdot \mathbf{G}_{CC}^a(\bar{t}, t_0) = \int_{t_0}^{\bar{t}} d\bar{t}' \boldsymbol{\Sigma}_{CC}^>(\bar{t}, \bar{t}') i\theta(t_0 - \bar{t}') e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t}-t_0)} e^{-i\varphi_C(\bar{t}, t_0)} = 0 \quad (2.5.61)$$

Next we must consider the object:

$$\begin{aligned}\Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^{\neg}(\bar{t}, t_0) &= \Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^M(\bar{t}, 0^+) + i \int_{t_0}^{t_0} d\bar{t}' (\Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^M \star \Sigma_{CC}^{\neg})(\bar{t}, \bar{t}') e^{-i(\tilde{\mathbf{h}}_{CC}^{eff})^{\dagger}(\bar{t}' - t_0)} e^{-i\varphi_C(\bar{t}', t_0)} \\ &= \Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^M(\bar{t}, 0^+)\end{aligned}\quad (2.5.62)$$

This follows from the integrated expression for the left Green's function, (2.5.12) and the boundary condition 1.5.69. From the exact expressions derived for the right self energy and Matsubara GFs, one obtains ³:

$$\Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^{\neg}(\bar{t}, t_0) = \frac{i}{\beta} \sum_{\alpha} \Gamma_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \sum_{q=-\infty}^{\infty} e^{-\omega_q 0^+} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(\bar{t}-t_0)}}{\omega_q - \omega + \mu} \mathbf{G}_{CC}^M(\omega_q) \quad (2.5.64)$$

Note that using the boundary condition Eq. (1.5.69) makes it unnecessary to introduce a regularization parameter into this expression by hand, as was done in Ref. [128]. Using Eq. (2.5.50), one obtains

$$\Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^{\neg}(\bar{t}, t_0) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(\bar{t}-t_0)} \sum_{\alpha} \Gamma_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \int \frac{d\omega'}{2\pi} e^{\beta\omega'} f(\omega') \left[\frac{\mathbf{G}_{CC}^M(\omega'^-)}{\omega'^- - \omega + \mu} - \frac{\mathbf{G}_{CC}^M(\omega'^+)}{\omega'^+ - \omega + \mu} \right] \quad (2.5.65)$$

If one now performs this integral by choosing the semi-circular contour in the lower-half plane about the simple pole at $\omega = \omega'^- + \mu$ [282], the following is obtained:

$$\begin{aligned}\Sigma_{CC}^{\neg} \star \mathbf{G}_{CC}^{\neg}(\bar{t}, t_0) &= -i \sum_{\alpha} \Gamma_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \int \frac{d\omega}{2\pi} e^{\beta(\omega-\mu)} f(\omega - \mu) e^{-i\omega(\bar{t}-t_0)} \mathbf{G}_{CC}^M(\omega - \mu) \\ &= -i \sum_{\alpha} \Gamma_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) e^{-i\omega(\bar{t}-t_0)} \mathbf{G}_{CC}^a(\omega)\end{aligned}\quad (2.5.66)$$

where the second line follows from the matching identity Eq. (2.5.26). The remaining part of the integral taken between t_0 and t_1 is therefore expressible as

$$\begin{aligned}\mathcal{G}_{(2)}^> &= - \int_{t_0}^{t_1} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t}-t_0)} e^{i\varphi_C(\bar{t}, t_0)} \sum_{\alpha} \Gamma_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) e^{-i\omega(\bar{t}-t_0)} \mathbf{G}_{CC}^a(\omega) \\ &= - \sum_{\alpha} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) \mathbf{K}_{\alpha}(t_1, t_0; \omega) \Gamma_{\alpha} \mathbf{G}_{CC}^a(\omega)\end{aligned}\quad (2.5.67)$$

³Here we make use of the identity

$$\int_0^{\beta} d\tau e^{(\omega_q - \omega_{q'})\tau} = \beta \delta_{q, q'} \quad (2.5.63)$$

where $\delta_{q, q'}$ is the Kronecker delta.

where we have defined the following matrix object for the α lead:

$$\mathbf{K}_\alpha(t, t_0; \omega) = \int_{t_0}^t d\bar{t} e^{-i(\omega \mathbf{1} - \tilde{\mathbf{h}}_{CC}^{eff})(\bar{t} - t_0)} e^{i(\varphi_C - \psi_\alpha)(\bar{t}, t_0)} \quad (2.5.68)$$

Note that this definition of the $\mathbf{K}_\alpha$ only differs from that given in [1] by the phase factor $e^{i\varphi_C(\bar{t}, t_0)}$ and the modified Hamiltonian $\tilde{\mathbf{h}}_{CC}$. The third convolution integral is given by:

$$\begin{aligned} \mathcal{G}_{(3)}^> &= i \int_{t_0}^{t_2} d\bar{t} e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_0)} \mathbf{G}_{CC}^r \cdot \Sigma_{CC}^>(t_1, \bar{t}) e^{-i\tilde{\mathbf{h}}_{CC}^{\dagger eff}(\bar{t} - t_0)} e^{i\varphi_C(t_1, \bar{t})} \\ &= -i \sum_\alpha \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) \int_{t_0}^{t_1} d\bar{t}' e^{-i\varphi_C(t_1, \bar{t}')} e^{-i(\omega - \tilde{\mathbf{h}}_{CC}^{eff})(\bar{t}' - t_0)} e^{-i\psi_\alpha(\bar{t}', t_0)} \Gamma_\alpha \int_{t_0}^{t_2} d\bar{t} e^{i(\omega - \tilde{\mathbf{h}}_{CC}^{\dagger eff})(\bar{t} - t_0)} e^{i\psi_\alpha(\bar{t}, t_0)} e^{i\varphi_C(t_1, \bar{t})} \\ &= -i \sum_\alpha \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) \mathbf{K}_\alpha(t_1, t_0; \omega) \Gamma_\alpha \mathbf{K}_\alpha^\dagger(t_2, t_0; \omega) \end{aligned} \quad (2.5.69)$$

We have in the final term the vertical contour convolution:

$$\mathbf{G}_{CC}^\top \star \Sigma_{CC}^\top(t_1, \bar{t}) = e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_0)} e^{-i\varphi_C(t_1, t_0)} \left[\mathbf{G}_{CC}^M \star \Sigma_{CC}^\top(0^+, \bar{t}) - i \int_{t_0}^{t_1} d\bar{t}' e^{i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t} - t_0)} e^{i\varphi_C(\bar{t}, t_0)} \Sigma_{CC}^\top \star \mathbf{G}_{CC}^M \star \Sigma_{CC}^\top(\bar{t}', \bar{t}) \right] \quad (2.5.70)$$

Above, in the second term we have a double convolution integral along the imaginary track. Using explicit expressions (2.4.21) and (2.4.20) for both self-energies and the expansion (2.5.2) for the Matsubara Green's function, this term is given by:

$$\begin{aligned} (\Sigma_{CC}^\top \star \mathbf{G}_{CC}^M \star \Sigma_{CC}^\top)(\bar{t}, \bar{t}') &= \frac{i}{\beta} \sum_q \left(\sum_\alpha \Gamma_\alpha e^{-i\psi_\alpha(\bar{t}, t_0)} \right) \mathbf{G}_{CC}^M(\omega_q) \left(\sum_{\alpha'} \Gamma_{\alpha'} e^{i\psi_{\alpha'}(\bar{t}', t_0)} \right) \\ &\quad \times \int \frac{d\omega_1}{2\pi} \frac{e^{-i\omega_1(\bar{t} - t_0)}}{\omega_q - \omega_1 + \mu} \int \frac{d\omega_2}{2\pi} \frac{e^{i\omega_2(\bar{t}' - t_0)}}{\omega_q - \omega_2 + \mu} = 0 \end{aligned} \quad (2.5.71)$$

The last line follows from the fact that the ω_1 integral is only non-vanishing when $\text{Im}(\omega_q) < 0$, while the ω_2 integral survives only when $\text{Im}(\omega_q) > 0$. We therefore get the following reduction:

$$\mathbf{G}_{CC}^\top \star \Sigma_{CC}^\top(t_1, \bar{t}) = e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_0)} e^{-i\varphi_C(t_1, t_0)} \mathbf{G}_{CC}^M \star \Sigma_{CC}^\top(0^+, \bar{t}) \quad (2.5.72)$$

So, after once again using the identity (2.5.63), we make use of Eq. (2.5.58) to obtain:

$$\begin{aligned} \mathbf{G}_{CC}^M \star \Sigma_{CC}^\top(0^+, \bar{t}) &= \frac{i}{\beta} \sum_{q=-\infty}^{\infty} \mathbf{G}_{CC}^M(\omega_q) \sum_\alpha \Gamma_\alpha e^{i\psi_\alpha(\bar{t}, t_0)} \int \frac{d\omega}{2\pi} \frac{e^{i\omega(\bar{t} - t_0)}}{\omega_q - \omega + \mu} e^{-\omega_q 0^+} \\ &= -\sum_\alpha \int \frac{d\omega}{2\pi} e^{i\omega(\bar{t} - t_0)} \int \frac{d\omega'}{2\pi} (1 - f(\omega')) \left[\frac{\mathbf{G}_{CC}^M(\omega'^-)}{\omega'^- - \omega + \mu} - \frac{\mathbf{G}_{CC}^M(\omega'^+)}{\omega'^+ - \omega + \mu} \right] \end{aligned} \quad (2.5.73)$$

Performing the contour integral about a semi-circular contour in the upper-half plane, we can use the matching identity Eq. (2.5.25) to obtain

$$\mathbf{G}_{CC}^M \star \mathbf{\Sigma}_{CC}^\Gamma (0^+, \bar{t}) = -i \sum_{\alpha} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) e^{i\omega(\bar{t}-t_0)} e^{i\psi_{\alpha}(\bar{t}, t_0)} \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\alpha} \quad (2.5.74)$$

From which it follows:

$$\mathcal{G}_{(4)}^> = \sum_{\alpha} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\alpha} \mathbf{K}_{\alpha}^{\dagger}(t_2, t_0; \omega) \quad (2.5.75)$$

Collecting all the terms together now, we map back from the transformation (2.5.42) and use the initial condition (2.5.51) to get the greater GF:

$$\begin{aligned} \mathbf{G}_{CC}^>(t_1, t_2) &= -e^{-i\varphi_C(t_1, t_0)} e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_0)} \sum_{\alpha} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) \\ &\times \sum_{\alpha} [\mathbf{K}_{\alpha}(t_1, t_0; \omega) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega) - \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\alpha} \mathbf{K}_{\alpha}^{\dagger}(t_2, t_0; \omega) \\ &+ i(\mathbf{K}_{\alpha}(t_1, t_0; \omega) \mathbf{\Gamma}_{\alpha} \mathbf{K}_{\alpha}^{\dagger}(t_2, t_0; \omega) + \mathbf{A}_{\alpha}(\omega))] e^{i\tilde{\mathbf{h}}_{CC}^{eff}(t_2 - t_0)} e^{i\varphi_C(t_2, t_0)} \end{aligned} \quad (2.5.76)$$

Note that all the information on the variable bias is contained in the $\mathbf{K}_{\alpha}$.

2.5.7 Line Integral for the Lesser GF

It is easily seen that the first term $\mathcal{G}_{(1)}^<$ in the first integral in the right hand side of Eq. (2.5.60) above is zero since

$$(\mathbf{\Sigma}_{CC}^< \cdot \mathbf{G}_{CC}^a)(\bar{t}, t_0) = \int_{t_0}^{\infty} dt' \mathbf{\Sigma}_{CC}^<(\bar{t}, t') \mathbf{G}_{CC}^a(t', t_0) \quad (2.5.77)$$

contains the advanced Green's function $\mathbf{G}_{CC}^a(t', t_0) \propto \theta(t_0 - t')$ for $t' > t_0$.

The second term $\mathcal{G}_{(2)}^<$ in the first integral in Eq. (2.5.60) includes the convolution integral $(\mathbf{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^{\Gamma})(\bar{t}, t_0)$. Using Eq. (2.5.12) for the left Green's function, we replace $\mathbf{G}_{CC}^{\Gamma}(\tau, t_0)$ in the convolution integral $(\mathbf{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^{\Gamma})(\bar{t}, t_0)$ with $\mathbf{G}_{CC}^M(\tau, 0^+)$. Using Eq. (2.4.20) for the left self-energy, expanding the Matsubara Green's function into the Fourier series (2.5.2) and integrating over τ , we obtain:

$$(\mathbf{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^{\Gamma})(\bar{t}, t_0) = \sum_{\alpha} \mathbf{\Gamma}_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \int \frac{d\omega'}{2\pi} e^{-i\omega'(\bar{t}-t_0)} \frac{i}{\beta} \sum_q \frac{\mathbf{G}_{CC}^M(\omega_q)}{\omega_q - \omega' + \mu} e^{\omega_q 0^+} \quad (2.5.78)$$

The sum over Matsubara frequencies is transformed using Eq. (A.1.7), so that the ω' -integration is easily performed in the complex plane to give:

$$(\mathbf{\Sigma}_{CC}^{\top} \star \mathbf{G}_{CC}^{\Gamma})(\bar{t}, t_0) = i \sum_{\alpha} \mathbf{\Gamma}_{\alpha} e^{-i\psi_{\alpha}(\bar{t}, t_0)} \int \frac{d\omega}{2\pi} f(\omega - \mu) e^{-i\omega(\bar{t}-t_0)} \mathbf{G}_{CC}^a(\omega) \quad (2.5.79)$$

for the second term in the first integral in Eq. (2.5.60):

$$\mathcal{G}_{(2)}^< = \int \frac{d\omega}{2\pi} f(\omega - \mu) \sum_{\alpha} \mathbf{K}_{\alpha}(t_1, t_0; \omega) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega) \quad (2.5.80)$$

where the $\mathbf{K}_{\alpha}$ matrix is given by Eq. (2.5.68) and we have used the formal identity (2.5.25).

The third contribution to the line integral coming from the term $(\mathbf{G}_{CC}^r \cdot \mathbf{\Sigma}_{CC}^<)(t_1, \bar{t})$ in the second integral in Eq.

(2.5.60) is obtained immediately owing to simple expressions (2.5.22) and (2.4.18) for the retarded Green's function and the lesser self-energy, respectively:

$$(\mathbf{G}_{CC}^r \cdot \Sigma_{CC}^<)(t_1, \bar{t}) = i \int \frac{d\omega}{2\pi} f(\omega - \mu) \sum_{\alpha} \int_{t_0}^{t_1} d\tau e^{-i\varphi_C(t_1, \tau)} e^{-i\tilde{\mathbf{h}}^{eff}(t_1 - \tau)} e^{-i\psi_{\alpha}(\tau, \bar{t})} e^{-i\omega(\tau - \bar{t})} \Gamma_{\alpha} \quad (2.5.81)$$

When this is substituted back into the line integral (2.5.60), it gives for the third contribution to the lesser 'tilded' Green's function:

$$\mathcal{G}_{(3)}^< = i \int \frac{d\omega}{2\pi} f(\omega - \mu) \sum_{\alpha} \mathbf{K}_{\alpha}(t_1; \omega) \Gamma_{\alpha} \mathbf{K}_{\alpha}^{\dagger}(t_2; \omega) \quad (2.5.82)$$

Finally, to calculate the last object $\mathcal{G}^{(4)}$ in the expression (2.5.60), one needs the term $(\mathbf{G}_{CC}^{\top} \star \Sigma_{CC}^{\top})(t_1, \bar{t})$ which is first manipulated into the expression

$$\begin{aligned} & (\mathbf{G}_{CC}^{\top} \star \Sigma_{CC}^{\top})(t_1, \bar{t}) = e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_0)} e^{-i\varphi_C(t_1, t_0)} \\ & \times \left[(\mathbf{G}_{CC}^M \star \Sigma_{CC}^{\top})(0^+, \bar{t}) - i \int_{t_0}^{t_1} d\bar{t}' e^{i\tilde{\mathbf{h}}_{CC}^{eff}(\bar{t}' - t_0)} e^{i\varphi_C(\bar{t}', t_0)} (\Sigma_{CC}^{\top} \star \mathbf{G}_{CC}^M \star \Sigma_{CC}^{\top})(\bar{t}', \bar{t}) \right] \end{aligned} \quad (2.5.83)$$

using the formula (2.5.8) for the right Green's function. In the above, the second term vanishes as

$$(\Sigma_{CC}^{\top} \star \mathbf{G}_{CC}^M \star \Sigma_{CC}^{\top})(\bar{t}', \bar{t}) = 0 \quad (2.5.84)$$

using the same steps as in the derivation of (2.5.71). We thus need only to calculate the following expression contained in the first term in (2.5.83):

$$(\mathbf{G}_{CC}^M \star \Sigma_{CC}^{\top})(0^+, \bar{t}) = \int \frac{d\omega}{2\pi} e^{i\omega(\bar{t} - t_0)} \frac{i}{\beta} \sum_q \frac{\mathbf{G}_{CC}^M(\omega_q)}{\omega_q - \omega + \mu} e^{\omega_q 0^+} \left(\sum_{\alpha} \Gamma_{\alpha} e^{i\psi_{\alpha}(\bar{t}, t_0)} \right) \quad (2.5.85)$$

Once again, we perform the summation over the Matsubara frequencies using formula (2.5.58) and then perform the ω integration in the complex plane, leading to the following result for the final contribution to the line integral:

$$\mathcal{G}_{(4)}^< = - \int \frac{d\omega}{2\pi} f(\omega - \mu) \mathbf{G}_{CC}^r(\omega) \sum_{\alpha} \Gamma_{\alpha} \mathbf{K}_{\alpha}^{\dagger}(t_2, t_0; \omega) \quad (2.5.86)$$

Summing up all four terms, and taking into account the initial condition of Eq. (2.5.59), we map back from the transformation (2.5.52) to obtain the following result:

$$\begin{aligned} \mathbf{G}_{CC}^<(t_1, t_2) = & e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t_1 - t_0)} e^{-i\varphi_C(t_1, t_0)} \int \frac{d\omega}{2\pi} f(\omega - \mu) \sum_{\gamma} [\mathbf{K}_{\gamma}(t_1, t_0; \omega) \Gamma_{\gamma} \mathbf{G}_{CC}^a(\omega) - \mathbf{G}_{CC}^r(\omega) \Gamma_{\gamma} \mathbf{K}_{\gamma}^{\dagger}(t_2, t_0; \omega) \\ & + i\mathbf{K}_{\gamma}(t_1, t_0; \omega) \Gamma_{\gamma} \mathbf{K}_{\gamma}^{\dagger}(t_2, t_0; \omega) + i\mathbf{A}_{\gamma}(\omega)] e^{i\varphi_C(t_2, t_0)} e^{i(\tilde{\mathbf{h}}_{CC}^{eff})^{\dagger}(t_2 - t_0)} \end{aligned} \quad (2.5.87)$$

The general result obtained for the lesser Green's function allows calculation of the current through any lead which will be done in the next section. It can also be used to extract the particle number of the central region via $\mathbf{N}_C(t) = -2i\text{Tr}_C[\mathbf{G}_{CC}^<(t, t)]$, where the factor of 2 accounts for spin degeneracy.

Note that in [128] only the equal time lesser Green's function was derived as this is sufficient to calculate the current in the WBLA. However, the two-time Green's function may be required for the calculation of other physical quantities, e.g. for the calculation of the quantum noise. A more compact notation can be used to represent the

lesser and greater GFs. Specifically, if we introduce the following matrix

$$\mathbf{S}_\alpha(t, t_0; \omega) \equiv e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t-t_0)} e^{-i\varphi_C(t, t_0)} [\mathbf{G}_{CC}^r(\omega) - i\mathbf{K}_\alpha(t, t_0; \omega)] \quad (2.5.88)$$

then the greater and lesser GFs can be expressed as follows:

$$\mathbf{G}_{CC}^{\gtrless}(t_1, t_2) = \mp i \int \frac{d\omega}{2\pi} f(\mp(\omega - \mu)) \sum_\gamma \mathbf{S}_\gamma(t_1, t_0; \omega) \mathbf{\Gamma}_\gamma \mathbf{S}_\gamma^\dagger(t_2, t_0; \omega) \quad (2.5.89)$$

We note in passing that the $\mathbf{S}_\gamma$, $\mathbf{S}_\gamma^\dagger$ matrices have the same units as retarded and advanced Green's functions, and so they may be regarded as propagators containing information on both the $t > t_0$ and $t < t_0$ regimes.

2.5.8 Lead-Molecule and Lead-Lead Coupling Terms

In this Section, we complete our solution of the Kadanoff-Baym equations by solving for the Green's functions of the lead-molecule and lead-lead 'blocks' of the Green's function matrix in Eq. (2.3.1). Specifically, we will compute the lesser and greater components of these functions, as these are sufficient for the calculation of the current in Section 2.6, and for simplifying the equations for the current-current correlator in Chapter 3. The Dyson equations for the full $\alpha - C$ and $C - \alpha$ Green's functions are given by Eq. (2.3.13) and (2.3.14), respectively. We use the notation ' (z_{1-}, z_{2+}) ' to denote that the first argument is always on the upper branch C_- of the Konstantinov-Perel' contour, and the second argument always on the lower branch C_+ , and therefore that the second argument is always 'later' on the contour than the first. ' (z_{1+}, z_{2-}) ' denotes the opposite ordering of contour positions, and retaining this ordering is necessary to obtain the correct initial conditions when the limit $t_1, t_2 \rightarrow t_0$ is taken. Next we apply the Langreth rules [278, 179] to Eqs. (2.3.13) and (2.3.14) to give:

$$\mathbf{G}_{\alpha C}^>(t_1, t_2) = [\mathbf{g}_{\alpha\alpha}^>\mathbf{h}_{\alpha C} \cdot \mathbf{G}_{CC}^a + \mathbf{g}_{\alpha\alpha}^r\mathbf{h}_{\alpha C} \cdot \mathbf{G}_{CC}^> + \mathbf{g}_{\alpha\alpha}^\top\mathbf{h}_{\alpha C} \star \mathbf{G}_{CC}^\top] (t_{1+}, t_{2-}) \quad (2.5.90)$$

$$\mathbf{G}_{\beta C}^<(t_2, t_1) = [\mathbf{g}_{\beta\beta}^<\mathbf{h}_{\beta C} \cdot \mathbf{G}_{CC}^a + \mathbf{g}_{\beta\beta}^r\mathbf{h}_{\beta C} \cdot \mathbf{G}_{CC}^< + \mathbf{g}_{\beta\beta}^\top\mathbf{h}_{\beta C} \star \mathbf{G}_{CC}^\top] (t_{2-}, t_{1+}) \quad (2.5.91)$$

$$\mathbf{G}_{C\beta}^>(t_1, t_2) = [\mathbf{G}_{CC}^> \cdot \mathbf{h}_{C\beta}\mathbf{g}_{\beta\beta}^a + \mathbf{G}_{CC}^r \cdot \mathbf{h}_{C\beta}\mathbf{g}_{\beta\beta}^> + \mathbf{G}_{CC}^\top \star \mathbf{h}_{C\beta}\mathbf{g}_{\beta\beta}^\top] (t_{1+}, t_{2-}) \quad (2.5.92)$$

$$\mathbf{G}_{C\alpha}^<(t_2, t_1) = [\mathbf{G}_{CC}^< \cdot \mathbf{h}_{C\alpha}\mathbf{g}_{\alpha\alpha}^a + \mathbf{G}_{CC}^r \cdot \mathbf{h}_{C\alpha}\mathbf{g}_{\alpha\alpha}^< + \mathbf{G}_{CC}^\top \star \mathbf{h}_{C\alpha}\mathbf{g}_{\alpha\alpha}^\top] (t_{2-}, t_{1+}) \quad (2.5.93)$$

Now we turn to the lead-lead matrix 'blocks' of the Green's function. First, the EoM for the full GF is projected onto the $\alpha\beta$ regions:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1) \right] \mathbf{G}_{\alpha\beta}(z_1, z_2) = \mathbf{I}_\alpha \delta_{\alpha\beta} \delta(z_1, z_2) + \mathbf{h}_{\alpha C}(z_1) \mathbf{G}_{C\beta}(z_1, z_2) \quad (2.5.94)$$

$$\mathbf{G}_{\alpha\beta}(z_1, z_2) \left[-i \frac{d}{dz_2} - \mathbf{h}_{\beta\beta}(z_2) \right] = \mathbf{I}_\alpha \delta_{\alpha\beta} \delta(z_1, z_2) + \mathbf{G}_{\alpha C}(z_1, z_2) \mathbf{h}_{C\beta}(z_2) \quad (2.5.95)$$

We insert the formulae (2.3.13) and (2.3.14) into these EoM to get:

$$\left[i \frac{d}{dz_1} - \mathbf{h}_{\alpha\alpha}(z_1) \right] \mathbf{G}_{\alpha\beta}(z_1, z_2) = \mathbf{I}_\alpha \delta_{\alpha\beta} \delta(z_1, z_2) + \int_\gamma d\bar{z} \mathbf{h}_{\alpha C}(z_1) \mathbf{G}_{CC}(z_1, \bar{z}) \mathbf{h}_{C\beta}(\bar{z}) \mathbf{g}_{\beta\beta}(\bar{z}, z_2) \quad (2.5.96)$$

$$\mathbf{G}_{\alpha\beta}(z_1, z_2) \left[-i \frac{d}{dz_2} - \mathbf{h}_{\beta\beta}(z_2) \right] = \mathbf{I}_\alpha \delta_{\alpha\beta} \delta(z_1, z_2) + \int_\gamma d\bar{z} \mathbf{g}_{\alpha\alpha}(z_1, \bar{z}) \mathbf{h}_{\alpha C}(\bar{z}) \mathbf{G}_{CC}(\bar{z}, z_2) \mathbf{h}_{C\beta}(z_2) \quad (2.5.97)$$

Using the Green's function of the bare leads defined in Eqs. (2.3.4) and (2.3.5), we can extract the desired Dyson equation:

$$\mathbf{G}_{\alpha\beta}(z_1, z_2) = \mathbf{g}_{\alpha\alpha}(z_1, z_2) \delta_{\alpha\beta} + \int_\gamma d\bar{z} d\bar{z}' \mathbf{g}_{\alpha\alpha}(z_1, \bar{z}) \mathbf{h}_{\alpha C}(\bar{z}) \mathbf{G}_{CC}(\bar{z}, \bar{z}') \mathbf{h}_{C\beta}(\bar{z}') \mathbf{g}_{\beta\beta}(\bar{z}', z_2) \quad (2.5.98)$$

Once more applying the Langreth rules, the greater and lesser GFs can then be found:

$$\begin{aligned} \mathbf{G}_{\alpha\beta}^>(t_1, t_2) &= \mathbf{g}_{\alpha\alpha}^>(t_1, t_2) \delta_{\alpha\beta} + \left[(\mathbf{g}_{\alpha\alpha}^> \mathbf{h}_{\alpha C} \cdot \mathbf{G}_{CC}^a + \mathbf{g}_{\alpha\alpha}^r \mathbf{h}_{\alpha C} \cdot \mathbf{G}_{CC}^> + \mathbf{g}_{\alpha\alpha}^\top \mathbf{h}_{\alpha C} \star \mathbf{G}_{CC}^\Gamma) \cdot \mathbf{h}_{C\beta} \mathbf{g}_{\beta\beta}^a \right. \\ &\quad \left. + \mathbf{g}_{\alpha\alpha}^r \mathbf{h}_{\alpha C} \cdot \mathbf{G}_{CC}^r \cdot \mathbf{h}_{C\beta} \mathbf{g}_{\beta\beta}^> + (\mathbf{g}_{\alpha\alpha}^r \mathbf{h}_{\alpha C} \cdot \mathbf{G}_{CC}^\top + \mathbf{g}_{\alpha\alpha}^\top \mathbf{h}_{\alpha C} \star \mathbf{G}_{CC}^M) \star \mathbf{h}_{C\beta} \mathbf{g}_{\beta\beta}^\Gamma \right] (t_{1+}, t_{2-}) \end{aligned} \quad (2.5.99)$$

$$\begin{aligned} \mathbf{G}_{\beta\alpha}^<(t_2, t_1) &= \mathbf{g}_{\alpha\alpha}^<(t_2, t_1) \delta_{\alpha\beta} + \left[(\mathbf{g}_{\beta\beta}^< \mathbf{h}_{\beta C} \cdot \mathbf{G}_{CC}^a + \mathbf{g}_{\beta\beta}^r \mathbf{h}_{\beta C} \cdot \mathbf{G}_{CC}^< + \mathbf{g}_{\beta\beta}^\top \mathbf{h}_{\beta C} \star \mathbf{G}_{CC}^\Gamma) \cdot \mathbf{h}_{C\alpha} \mathbf{g}_{\alpha\alpha}^a \right. \\ &\quad \left. + \mathbf{g}_{\beta\beta}^r \mathbf{h}_{\beta C} \cdot \mathbf{G}_{CC}^r \cdot \mathbf{h}_{C\alpha} \mathbf{g}_{\alpha\alpha}^< + (\mathbf{g}_{\beta\beta}^r \mathbf{h}_{\beta C} \cdot \mathbf{G}_{CC}^\top + \mathbf{g}_{\beta\beta}^\top \mathbf{h}_{\beta C} \star \mathbf{G}_{CC}^M) \star \mathbf{h}_{C\alpha} \mathbf{g}_{\alpha\alpha}^\Gamma \right] (t_{2-}, t_{1+}) \end{aligned} \quad (2.5.100)$$

2.6 The current

2.6.1 Generalized LB formula

The current in lead α is defined as the rate of increase of charge into that lead:

$$I_\alpha(t) = \left\langle \hat{I}_\alpha(t) \right\rangle \equiv q \left\langle \frac{d\hat{N}_\alpha(t)}{dt} \right\rangle \quad (2.6.1)$$

Here, $\hat{N}_\alpha(t) = 2 \times \sum_k \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha}$ is the number operator of this lead, where the factor of 2 accounts for spin degeneracy. Using the equation of motion for the number operator in the lead

$$\frac{d\hat{N}_\alpha(t)}{dt} = i [\hat{H}, \hat{N}_\alpha(t)] \quad (2.6.2)$$

, and the fact that the lead number operator commutes with terms (2.2.6) and (2.2.8) in the junction Hamiltonian, the time dependent current operator is given by

$$\hat{I}_\alpha(t) = 2iq \sum_{k,m} \left[T_{mk\alpha} \hat{d}_m^\dagger(t) \hat{d}_{k\alpha}(t) - T_{mk\alpha}^* \hat{d}_{k\alpha}^\dagger(t) \hat{d}_m(t) \right] \quad (2.6.3)$$

We then identify the Green's functions in the ensemble average of Eq. (2.6.3) using the definitions

$$[\mathbf{G}_{AB}^>(t_1, t_2)]_{kk'} = -i \left\langle \hat{d}_{kA}(t_1) \hat{d}_{k'B}^\dagger(t_2) \right\rangle \quad (2.6.4)$$

$$[\mathbf{G}_{AB}^<(t_1, t_2)]_{kk'} = i \left\langle \hat{d}_{k'B}^\dagger(t_2) \hat{d}_{kA}(t_1) \right\rangle \quad (2.6.5)$$

, so the simplified form of the current is given by the following expression [128]:

$$I_\alpha(t) = 4q\text{ReTr}_C [\mathbf{h}_{C\alpha} \mathbf{G}_{\alpha C}^<(t, t)] \quad (2.6.6)$$

One then uses Eq. (2.5.91) for the lesser Green's function coupling the lead to the molecule to obtain:

$$I_\alpha(t) = -4\text{ReTr}_C [(\Sigma_\alpha^< \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^< + \Sigma_\alpha^\top \star \mathbf{G}_{CC}^\top)(t, t)] \quad (2.6.7)$$

where the trace is taken with respect to the orbitals of the central region and we set the charge of an electron to $q = -1$. The right hand side of this expression contains the sum of three convolution integrals defined by Eqs. (1.5.20) and (1.5.21). Let us consider briefly the physical meaning of each term in this current formula. $\Sigma_\alpha^<$ is proportional to the decoupled lesser Green's function of the α lead, and therefore to the probability of finding an electron in the leads, whereas $\mathbf{G}_{CC}^a$ is a two-time propagator. So $\Sigma_\alpha^< \cdot \mathbf{G}_{CC}^a$ is interpreted as a 'source' term: it gives the current due to electrons tunneling from lead α into the central region [190]. The $\Sigma_\alpha^r \cdot \mathbf{G}_{CC}^<$ term, by contrast, is a 'sink' term: it contains $\mathbf{G}_{CC}^<$, which is proportional to the probability of occupation of the C region, and may therefore be attributed to the tunneling of electrons out from the central region [154, 190]. Finally, $\Sigma_\alpha^\top \star \mathbf{G}_{CC}^\top$ is a term containing information on the coupled system prior to the switch on time t_0 . As such, it vanishes in the partitioned approach, and the formula (2.6.7) reduces to the expression used in Ref. [154].

Within the WBLA, all functions of two times appearing in these convolution integrals are known, so that their functional form can be determined. Firstly, we find

$$\Sigma_\alpha^< \cdot \mathbf{G}_{CC}^a(t, t) = -\Gamma_\alpha \int \frac{d\omega}{2\pi} f(\omega - \mu) \mathbf{K}_\alpha^\dagger(t, t_0; \omega) e^{-i(\omega - \tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t-t_0)} e^{-i(\psi_\alpha - \varphi_C)(t, t_0)} \quad (2.6.8)$$

Where once again the $\mathbf{K}_\alpha$ matrix is defined as in (2.5.68). The final term to be evaluated can be done in similar fashion to the calculation for $\mathcal{G}_{(2)}^>$ above:

$$\begin{aligned} \Sigma_\alpha^\top \star \mathbf{G}_{CC}^\top(t, t) &= \Sigma_\alpha^\top \star \mathbf{G}_{CC}^M(t, 0^+) e^{i(\tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t-t_0)} e^{i\varphi_C(t, t_0)} \\ &= i\Gamma_\alpha e^{-i\psi_\alpha(t, t_0)} \int \frac{d\omega}{2\pi} f(\omega - \mu) e^{-i\omega(t-t_0)} \mathbf{G}_{CC}^a(\omega) e^{i\tilde{\mathbf{h}}_{CC}^{eff\dagger}(t-t_0)} e^{i\varphi_C(t, t_0)} \end{aligned} \quad (2.6.9)$$

Inserting these expressions, in addition to the lesser GF of equal times, $\mathbf{G}_{CC}^<(t, t)$, into (2.6.7), we obtain a generalized LB formula for the current:

$$\begin{aligned} I_\alpha(t) &= 2i \int \frac{d\omega}{2\pi} f(\omega - \mu) \text{Tr}_C \left\{ \Gamma_\alpha e^{i(\omega - \tilde{\mathbf{h}}_{CC}^{eff})(t-t_0)} e^{i(\psi_\alpha - \varphi_C)(t, t_0)} [\mathbf{G}_{CC}^r(\omega) - i\mathbf{K}_\alpha(t, t_0; \omega)] \right. \\ &\quad - \Gamma_\alpha [\mathbf{G}_{CC}^a(\omega) + i\mathbf{K}_\alpha^\dagger(t, t_0; \omega)] e^{-i(\omega - \tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t-t_0)} e^{-i(\psi_\alpha - \varphi_C)(t, t_0)} + \Gamma_\alpha e^{-i\tilde{\mathbf{h}}_{CC}^{eff}(t-t_0)} \sum_\gamma [i\mathbf{K}_\gamma(t, t_0; \omega) \Gamma_\gamma \mathbf{K}_\gamma^\dagger(t, t_0; \omega) \\ &\quad \left. + \mathbf{K}_\gamma(t, t_0; \omega) \Gamma_\gamma \mathbf{G}_{CC}^a(\omega) - \mathbf{G}_{CC}^r(\omega) \Gamma_\gamma \mathbf{K}_\gamma^\dagger(t, t_0; \omega) + i\mathbf{A}_\gamma(\omega)] e^{i(\tilde{\mathbf{h}}_{CC}^{eff})^\dagger(t-t_0)} \right\} \end{aligned} \quad (2.6.10)$$

We may also write down a compact formula for the current in terms of the $\mathbf{S}_\alpha$ matrix defined in (2.5.88):

$$I_\alpha(t) = \frac{1}{\pi} \int d\omega f(\omega - \mu) \text{Tr}_C \left[2\text{Re} \left[i\Gamma_\alpha e^{i\omega(t-t_0)} e^{i\psi_\alpha(t, t_0)} \mathbf{S}_\alpha(t, t_0; \omega) \right] - \Gamma_\alpha \sum_\gamma \mathbf{S}_\gamma(t, t_0; \omega) \Gamma_\gamma \mathbf{S}_\gamma^\dagger(t, t_0; \omega) \right] \quad (2.6.11)$$

This expression enables us to model electron transport in response to the switch-on of an arbitrary time-dependent bias in the leads, as well as a spatially homogeneous time-dependent perturbation in the molecule, within the

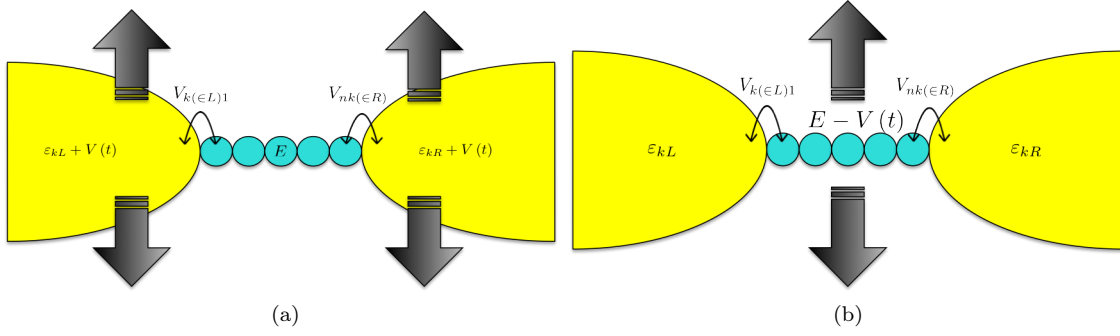


Figure 2.6.1: The physically equivalent cases of (a) $V_C(t) = 0$ and $\forall \alpha V_\alpha(t) = V(t)$ and (b) $V_C(t) = -V(t)$ and $\forall \alpha V_\alpha(t) = 0$.

WBLA. It represents progress on the work published in [1] because it enables us to study the interplay between the driving fields on the lead and molecular regions, and the current response is completely non-linear.

We note in this connection that if $V_\alpha(t) = V(t)$ is independent of the lead index α , and $V(t) = V_C(t)$, then $\psi_\alpha = \varphi_C$ and it follows (from the fact that the explicit time-dependence enters into (2.6.10) only in the form $e^{i(\psi_\alpha - \varphi_C)(t, t_0)}$) that the current is completely equivalent to that obtained in the static bias case. This is a rather intuitive result: it just means that if all energies in the system are simultaneously raised and lowered in the same way then there is no effect on the transport through the system; the transport is governed by energy *differences* only. We observe in Fig. 2.6.1 that it is physically equivalent to have a static molecule ($V_C(t) = 0$) and an identical time-dependent bias $V(t)$ in all leads (shown in Fig. 2.6.1 (a)) or static leads ($V_\alpha(t) = 0$) and an opposite-moving molecular time-dependence $V_C(t) = -V(t)$ (shown in Fig. 2.6.1 (b)). Thus, an identical perturbation across all the leads is equivalent to the negation of that perturbation in the CC region alone, and one has a freedom of choice in where to place the time-dependence when modelling such systems.

2.7 Charge Conservation and Continuity Equation

The physical system consisting of the molecule-plus-terminals is a closed quantum system, so that it does not exchange charge or energy with its environment. This implies that the total amount of electric charge in the molecular region plus that of all the leads is conserved; a condition automatically satisfied by the NEGF formalism [128]. However, if we focus on the molecular subsystem, we may regard the molecule as ‘open’ to the leads, which act as the molecular ‘environment’ consisting of a charge and energy reservoir. Therefore the local value of the charge sitting in the molecular region may vary in time. The condition required for *local charge conservation* is the following:

$$\sum_{\alpha} I_{\alpha}(t) = 0 \quad (2.7.1)$$

This condition states that the rate of charge entering the molecular region is balanced by the rate of charge leaving it, so that the sum of currents measured in the leads must be equal to zero. One should now recall that there is no direct coupling between leads, so that all charge transfer between leads is mediated by the central region, and also that the definition of the current in lead α was given as the rate of increase of charge in this lead. Eq. (2.7.1) is simply a statement of the condition that if charge increases in one lead connected to the molecule, then this increase is compensated exactly by a net decrease of charge from the other leads making up the junction. The total amount of charge in the molecular region at any given time is directly related to the lesser GF:

$$N_C(t) = -2i \text{Tr}_C [\mathbf{G}_{CC}^<(t, t)] = \frac{1}{\pi} \sum_{\gamma} \int d\omega f(\omega - \mu) \text{Tr}_C [\mathbf{S}_{\gamma}(t, t_0; \omega) \mathbf{\Gamma}_{\gamma} \mathbf{S}_{\gamma}^{\dagger}(t, t_0; \omega)] \quad (2.7.2)$$

The time derivative of the charge number $\frac{dN_C(t)}{dt}$ in the central region has been referred to as the *displacement current* in the literature [128]. To make precise the relation between this quantity and the currents measured in the leads, we take the time-derivatives of the matrix $\mathbf{S}_{\beta} \equiv \mathbf{S}_{\beta}(t, t_0; \omega)$ and its complex conjugate, e.g.

$$\frac{d\mathbf{S}_{\gamma}}{dt} = -i\mathbf{h}_{CC}^{eff} \mathbf{S}_{\gamma} - ie^{-i\omega(t-t_0)} e^{-i\psi_{\gamma}(t, t_0)} \quad (2.7.3)$$

This expression, along with its complex conjugate, is substituted into the derivative of N_C in Eq. (2.7.2) to give

$$\begin{aligned} \frac{dN_C(t)}{dt} &= \frac{1}{\pi} \sum_{\gamma} \int d\omega f(\omega - \mu) \text{Tr}_C \left\{ 2\text{Re} \left[ie^{i\omega(t-t_0)} e^{i\psi_{\gamma}(t, t_0)} \mathbf{S}_{\gamma} \mathbf{\Gamma}_{\gamma} \right] - i\mathbf{S}_{\gamma} \mathbf{\Gamma}_{\gamma} \mathbf{S}_{\gamma}^{\dagger} (\mathbf{h}_{CC}^{eff} - \mathbf{h}_{CC}^{eff\dagger}) \right\} \\ &= \frac{1}{\pi} \sum_{\alpha} \int d\omega f(\omega - \mu) \text{Tr}_C \left\{ 2\text{Re} \left[ie^{i\omega(t-t_0)} e^{i\psi_{\alpha}(t, t_0)} \mathbf{S}_{\alpha} \mathbf{\Gamma}_{\alpha} \right] - \sum_{\gamma} \mathbf{\Gamma}_{\alpha} \mathbf{S}_{\gamma} \mathbf{\Gamma}_{\gamma} \mathbf{S}_{\gamma}^{\dagger} \right\} \end{aligned} \quad (2.7.4)$$

where we use the fact that $\mathbf{h}_{CC}^{eff} - \mathbf{h}_{CC}^{eff\dagger} = -i\sum_{\alpha} \mathbf{\Gamma}_{\alpha} \equiv -i\mathbf{\Gamma}$, and exchange the summation index γ for α in the first term. If we then sum over lead indices in the expression (2.6.11), the following theorem is established:

$$\frac{dN_C(t)}{dt} = \sum_{\alpha} I_{\alpha}(t) \quad (2.7.5)$$

This is a statement of *global charge conservation* in the nanojunction. When the bias in every lead is constant, (2.7.2) reduces to the formula for the particle number given in [190]. In the long time limit the number of charges on the molecule is constant in time, i.e. an ideal stationary state is reached; hence the condition for local charge conservation (2.7.1) is trivially satisfied in this case. Although the condition of global charge conservation (2.7.5) is never violated, physical situations exist in which the condition of local charge conservation in the molecular (central) region of a nanojunction (2.7.1) is then violated, i.e. $dN_C(t)/dt \neq 0$.

2.8 Recovery of Known Results

2.8.1 Recovery of known results: asymptotics

Without making any assumptions on the shape of the bias, it is instructive to investigate the long time behaviour of the expression (2.6.10), which can be done by taking the limit $t_0 \rightarrow -\infty$, i.e. we shift the switch-on time to the distant past. We first note that, as $t_0 \rightarrow -\infty$, the asymptotic value of the ‘preparation’ term,

$$\Sigma_{\alpha}^{\top} \star \mathbf{G}_{CC}^{\top}(t, t) = i \int \frac{d\omega}{2\pi} f(\omega - \mu) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega) e^{-i(\omega - \mathbf{h}_{CC}^{eff})^{\dagger}(t-t_0)} \quad (2.8.1)$$

which contains the matrix function $e^{-i(\omega - \mathbf{h}_{CC}^{eff})^{\dagger}(t-t_0)} \propto e^{\Gamma t_0/2}$, is vanishing ($\Gamma > 0$), so that it has no effect on the steady state current. To investigate other objects associated with the system preparation, we consider those terms which result from vertical contour convolutions in $\mathbf{G}_{CC}^<$ (i.e. terms arising from $\mathcal{G}_{(2)}^<$ and $\mathcal{G}_{(4)}^<$ in Section 2.5.7):

$$\lim_{t_0 \rightarrow -\infty} \left[e^{-i\mathbf{h}_{CC}^{eff}(t-t_0)} (\mathbf{K}_{\alpha}(t, t_0; \omega) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega) - \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\alpha} \mathbf{K}_{\alpha}^{\dagger}(t, t_0; \omega)) e^{i(\mathbf{h}_{CC}^{eff})^{\dagger}(t-t_0)} \right] = 0 \quad (2.8.2)$$

This vanishes due to the two factors of $e^{\Gamma t_0/2}$ pre- and post- multiplying the bracketed expression; note that all times in the integral domain of $\mathbf{K}_\alpha$ are less than or equal to t . In addition, the term which arises from the initial condition for the integral of the lesser Green's function,

$$\lim_{t_0 \rightarrow -\infty} \left[e^{-i\mathbf{h}_{CC}^{eff}(t-t_0)} \mathbf{A}_\alpha(\omega) e^{i(\mathbf{h}_{CC}^{eff})^\dagger(t-t_0)} \right] = 0 \quad (2.8.3)$$

also vanishes in this limit as it also contains a similar exponential factor of $e^{\Gamma t_0}$. The asymptotic behaviour of the current for an arbitrary time-dependent bias is therefore given by:

$$\begin{aligned} \lim_{t_0 \rightarrow -\infty} I_\alpha(t) = \lim_{t_0 \rightarrow -\infty} 2 \int \frac{d\omega}{2\pi} f(\omega - \mu) \text{Tr}_C \left\{ \Gamma_\alpha \left(e^{i(\omega - \mathbf{h}_{CC}^{eff})(t-t_0)} e^{i\psi_\alpha(t, t_0)} \mathbf{K}_\alpha(t, t_0; \omega) \right. \right. \\ \left. \left. + \mathbf{K}_\alpha^\dagger(t, t_0; \omega) e^{-i(\omega \mathbf{1}_{CC} - \mathbf{h}_{CC}^{eff})^\dagger(t-t_0)} e^{-i\psi_\alpha(t, t_0)} - e^{-i\mathbf{h}_{CC}^{eff}(t-t_0)} \sum_\gamma \mathbf{K}_\gamma(t, t_0; \omega) \Gamma_\gamma \mathbf{K}_\gamma^\dagger(t, t_0; \omega) e^{i(\mathbf{h}_{CC}^{eff})^\dagger(t-t_0)} \right) \right\} \end{aligned} \quad (2.8.4)$$

where the limit remains on the right-hand side to account for the possibility of decaying terms once the bias has been specified, and we remark that in this limit the current remains a variable function of t .

In the formula (2.8.4), all terms resulting from either the equilibrium initial condition or from vertical contour convolutions have vanished. This tells us that the long-time limit of the current is independent of the way the system was prepared, and highlights the advantages of using a contour formalism, in which all preparation-dependent terms can be easily identified. Furthermore, with the exception of the initial condition term, every vanishing term includes a convolution with a left or right self-energy. In the partitioned approach to the transport problem, these quantities vanish, as one can see from the definition (2.3.17) and $\mathbf{h}_{C\alpha}(t_0 - i\tau) = 0$. So the formula (2.8.4) tells us that, at long times, the partitioned approach yields the same current as in the partition-free treatment. At this point, we can make a precise connection with the results of Jauho *et al.*, who considered the switch-on of a time-dependent bias taking place at $t_0 = -\infty$ within a partitioned approach [154]. They solved the Dyson equations on a two-branch contour running from $-\infty$ to t , before returning to $-\infty$ on a lower time branch, and obtained the following expression for the lesser Green's function of two times:

$$\mathbf{G}_{CC}^<(t_1, t_2) = \int_{-\infty}^t \int d\bar{t} d\bar{t}' \mathbf{G}_{CC}^r(t_1, \bar{t}) \Sigma_{CC}^<(\bar{t}, \bar{t}') \mathbf{G}_{CC}^a(\bar{t}', t_2) \quad (2.8.5)$$

where the functional form of the retarded/advanced Green's functions is identical to (2.5.22), (2.5.24). Working within the WBLA, and neglecting any time-dependence of the coupling, we can re-write this in the form:

$$\mathbf{G}_{CC}^<(t_1, t_2) = \lim_{t_0 \rightarrow -\infty} e^{-i\mathbf{h}_{CC}^{eff}(t_1-t_0)} \int \frac{d\omega}{2\pi} f(\omega - \mu) \sum_\gamma i\mathbf{K}_\gamma(t_1, t_0; \omega) \Gamma_\gamma \mathbf{K}_\gamma^\dagger(t_2, t_0; \omega) e^{i(\mathbf{h}_{CC}^{eff})^\dagger(t_2-t_0)} \quad (2.8.6)$$

Working on the Keldysh contour used by Jauho *et al.*, one neglects imaginary time convolutions when applying the Langreth Rules, to get instead of (2.6.10) the following expression for the current:

$$I_\alpha(t) = -4\text{Re Tr}_C \left[(\Sigma_\alpha^< \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^<) (t, t) \right] \quad (2.8.7)$$

where the real-time convolutions now extend from $-\infty$ up to t . Inserting (2.8.6) into (2.8.7) and working within the WBLA, one can easily show that the resulting formula is given exactly by (2.8.4). This discussion clearly shows that the formula derived in [154] is approximate as it is missing the terms related to the initial preparation of the system.

2.8.2 Recovery of known results: static bias

A second important check on the general formula (2.6.10) is that it reduces to known expressions for the time-dependent current in the case of a time-independent bias after the switch-on. When the bias V_α is static after the switch on, (2.6.10) can be evaluated purely in terms of the retarded/advanced Green's functions of the central region, as in this case,

$$\mathbf{K}_\alpha(t_1, t_0; \omega) = i\mathbf{G}_{CC}^r(\omega + V_\alpha) \left[e^{-i((\omega + V_\alpha) - \mathbf{h}_{CC}^{eff})(t_1 - t_0)} - 1 \right] \quad (2.8.8)$$

$$\mathbf{K}_\alpha^\dagger(t_2, t_0; \omega) = -i \left[e^{i((\omega + V_\alpha) - \mathbf{h}_{CC}^{eff})^\dagger(t_2, t_0)} - 1 \right] \mathbf{G}_{CC}^a(\omega + V_\alpha) \quad (2.8.9)$$

Substituting these expressions into Eq. (2.5.87), we use the identities (for scalar parameter A)

$$\mathbf{G}_{CC}^r(x + A) = \mathbf{G}_{CC}^r(x) - A\mathbf{G}_{CC}^r(x) \mathbf{G}_{CC}^r(x + A) \quad (2.8.10)$$

$$\mathbf{G}_{CC}^a(x + A) = \mathbf{G}_{CC}^a(x) - A\mathbf{G}_{CC}^a(x + A) \mathbf{G}_{CC}^a(x) \quad (2.8.11)$$

to show that it reduces to the following formula:

$$\begin{aligned} \mathbf{G}_{CC}^<(t_1, t_2) &= i \sum_\gamma \frac{d\omega}{2\pi} f(\omega - \mu) \left[\mathbf{A}_\gamma(\omega + V_\gamma) e^{-i(\omega + V_\gamma)(t_1 - t_2)} \right. \\ &+ V_\gamma \left(e^{-i\mathbf{h}_{CC}^{eff}(t_1 - t_0)} \mathbf{G}_{CC}^r(\omega) \mathbf{A}_\gamma(\omega + V_\gamma) e^{i(\omega + V_\gamma)(t_2 - t_0)} + e^{-i(\omega + V_\gamma)(t_1 - t_0)} \mathbf{A}_\gamma(\omega + V_\gamma) \mathbf{G}_{CC}^a(\omega) e^{i(\mathbf{h}_{CC}^{eff})^\dagger(t_2 - t_0)} \right) \\ &\left. + V_\gamma^2 e^{-i\mathbf{h}_{CC}^{eff}(t_1 - t_0)} \mathbf{G}_{CC}^r(\omega) \mathbf{A}_\gamma(\omega + V_\gamma) \mathbf{G}_{CC}^a(\omega) e^{i(\mathbf{h}_{CC}^{eff})^\dagger(t_2 - t_0)} \right] \end{aligned} \quad (2.8.12)$$

We remark that this expression is not, in general, a function of the time difference $\tau \equiv t_1 - t_2$. This property is satisfied only when both (a) $t_0 \rightarrow -\infty$ (or $t_1, t_2 \rightarrow \infty$) and (b) $\mathbf{h}_{CC}$ commutes with $\mathbf{\Gamma}_{CC}$, in which case the Fourier transform of (2.8.12) is a function of a single frequency. If one sets $t_1 = t_2$, (2.8.12) reduces to the expression published in Refs. [190, 128, 172] for the equal-time case.

The LB formalism was initially developed for the treatment of junctions having a static bias placed across them. If one replaces $\mathbf{K}_\alpha$, $\mathbf{K}_\alpha^\dagger$ in Eq. (2.6.11) with those given in Eqs. (2.8.8) and (2.8.9), one recovers the expression reported in [190]:

$$\begin{aligned} I_\alpha(t) &= \frac{1}{\pi} \int d\omega f(\omega - \mu) \sum_\gamma \text{Tr}_C [\mathbf{\Gamma}_\alpha \mathbf{G}^r(\omega + V_\alpha) \mathbf{\Gamma}_\gamma \mathbf{G}^a(\omega + V_\alpha) - \mathbf{\Gamma}_\alpha \mathbf{G}^r(\omega + V_\gamma) \mathbf{\Gamma}_\gamma \mathbf{G}^a(\omega + V_\gamma) \\ &- V_\gamma \left[\mathbf{\Gamma}_\alpha e^{i(\omega + V_\gamma - \mathbf{h}^{eff})(t - t_0)} \mathbf{G}^r(\omega) (-i\delta_{\alpha\gamma} \mathbf{G}^r(\omega + V_\gamma) + \mathbf{A}_\gamma(\omega + V_\gamma)) + h.c. \right] \\ &- V_\gamma^2 \mathbf{\Gamma}_\alpha e^{-i\mathbf{h}^{eff}(t - t_0)} \mathbf{G}^r(\omega) \mathbf{A}_\gamma(\omega + V_\gamma) \mathbf{G}^a(\omega) e^{i\mathbf{h}^{\dagger eff}(t - t_0)}] \end{aligned} \quad (2.8.13)$$

If one then inserts Eqs. (2.8.8) and (2.8.9) into (2.8.4) and takes the right-hand limit, or if the $t_0 \rightarrow -\infty$ limit is taken in Eq. (2.8.13), then a LB-type formula is obtained for the multi-terminal junction:

$$I_{\alpha}^{(LB)} = \lim_{t_0 \rightarrow -\infty} I_{\alpha}(t) = \frac{1}{\pi} \sum_{\gamma} \int d\omega [f(\omega - \mu - V_{\alpha}) - f(\omega - \mu - V_{\gamma})] T_{\alpha\gamma}(\omega) \quad (2.8.14)$$

Here we have defined the transmission function:

$$T_{\alpha}(\omega) \equiv \sum_{\gamma} \text{Tr}_C [\mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\gamma} \mathbf{G}_{CC}^a(\omega)] \equiv \sum_{\gamma} T_{\alpha\gamma}(\omega) \quad (2.8.15)$$

The lead-dependent parts of the transmission function are often written in the following way:

$$T_{\alpha\gamma}(\omega) = \text{Tr}_C [\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega)] \quad (2.8.16)$$

Where we have introduced the *transmission matrices* [113]:

$$\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \equiv [\mathbf{\Gamma}_{\alpha}]^{\frac{1}{2}} \mathbf{G}_{CC}^r(\omega) [\mathbf{\Gamma}_{\gamma}]^{\frac{1}{2}} \quad (2.8.17)$$

$$\mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \equiv [\mathbf{\Gamma}_{\gamma}]^{\frac{1}{2}} \mathbf{G}_{CC}^a(\omega) [\mathbf{\Gamma}_{\alpha}]^{\frac{1}{2}} \quad (2.8.18)$$

The formula (2.8.14) may be read physically as the rate at which electrons in lead α hop into β , minus the rate at which electrons in lead β hop into α , integrated over the energies of all states in the leads. The elements of the transmission matrices contain probability amplitudes for electrons travelling in conduction channels of lead β to be transmitted into conduction channels of lead α , and may also be computed within an S-matrix approach in terms of the probability amplitudes for incident waves to be transmitted or reflected when they propagate from the leads onto the molecule. Note also that Eq. (2.8.14) contains no dependence on t , and therefore describes transport in the ideal steady state, where the current has become an ideally stationary stochastic process.

If one specializes the discussion to that of resonant tunneling through a single-level quantum dot, coupled to just two leads, L and R, the Hamiltonian matrix $\mathbf{h}_{CC}$ of the central region is given by the scalar $h = \varepsilon_0$, and all other matrices defined on the central region also become scalars. Given that $\Gamma_L = x\Gamma$ for some real number x , and $\Gamma = \Gamma_L + \Gamma_R$, we find that (2.8.14) reduces to the simple form:

$$I_L^{(LB)} = \frac{x(1-x)\Gamma^2}{\pi} \int d\omega \frac{[f(\omega - V_L - \mu) - f(\omega - \mu - V_R)]}{(\omega - \varepsilon_0)^2 + (\Gamma/2)^2} \quad (2.8.19)$$

In the work which follows, this formula is principally used to guide our intuition about the qualitative physical behaviour we can expect from various molecular systems. It is exactly equivalent to Eq. (1.4.7) with the transmission function Eq. (1.4.13) given within the WBLA.

Chapter 3

Current-Current Correlations and the Quantum Noise

3.1 Introduction

The solutions of the Kadanoff-Baym equations derived in Chapter 2 led to new analytic formulas for the two-time lesser and greater Green's functions of the central region on a molecular junction, and consequently the current through the electrodes of the junction was derived. In the literature review of Chapter 1, the importance of the current fluctuations was emphasized as a key area of transport physics. Therefore in this Chapter we shall extend the formalism derived so far to include a partition-free theory of time-dependent current correlations, valid for an arbitrary time-dependent bias. This Chapter is organized as follows. In Section 3.2 we use Wick's theorem to derive a generic formulas for the current correlation as a function of two times t_1, t_2 for an arbitrary one-particle Hamiltonian. Then in Section 3.3 we specialize the system so that the WBLA is assumed with the same time-dependent noninteracting model considered in the previous Chapter. This enables us to express the two-time current correlation function in terms of the same $\mathbf{S}_\alpha$ matrices (defined in Eq. (2.5.88)) that were used to express the current in Eq. (2.6.11). We prove some symmetry properties satisfied by this two-time current correlation that may be used to numerically check the consistency of the formalism. By considering the steady-state behaviour of the $\mathbf{S}_\alpha$ matrices, we study the frequency-dependent quantum cross-lead correlations and autocorrelations in the limits of a static bias and at long times after the switch-on, $t_0 \rightarrow -\infty$, by taking a Fourier transform of the two time correlation with respect to the difference in time arguments, $\tau = t_1 - t_2$. The resulting formula is shown to reduce to previously published results when the molecule is assumed to be a quantum dot [274], but importantly, it generalizes these quantum dot formulas to the case of an arbitrarily large molecular region, thus making it useful for the study of noise in devices with far more complex electronic structures than the quantum dot. Finally, we consider the symmetrized current correlations originally studied by Büttiker et al. [147] in both the time and frequency domain. We demonstrate that in the limits of zero frequency and energy-independent transmission they reduce to well known expressions, and therefore conclude that this formalism contains many other published formalisms as special cases.

3.2 General Expressions from Wick's Theorem

Starting from the expression for the current operator in Eq. (2.6.3), we define the current deviation operator, Eq. (1.4.15), with a mean value of zero:

$$\Delta \hat{I}_\alpha(t) = 2iq \sum_{k,m} \left[T_{mk\alpha}(t) \left(\hat{d}_m^\dagger(t) \hat{d}_{k\alpha}(t) - \langle \hat{d}_m^\dagger(t) \hat{d}_{k\alpha}(t) \rangle \right) - T_{mk\alpha}^*(t) \left(\hat{d}_{k\alpha}^\dagger(t) \hat{d}_m(t) - \langle \hat{d}_{k\alpha}^\dagger(t) \hat{d}_m(t) \rangle \right) \right] \quad (3.2.1)$$

The two-time current correlator between leads α and β is then defined as:

$$C_{\alpha\beta}(t_1, t_2) \equiv \langle \Delta \hat{I}_\alpha(t_1) \Delta \hat{I}_\beta(t_2) \rangle \quad (3.2.2)$$

This correlator obviously satisfies the symmetry property:

$$C_{\alpha\beta}(t_1, t_2)^* = C_{\beta\alpha}(t_2, t_1) \quad (3.2.3)$$

Since $\Delta \hat{I}_\alpha(t_1)$ and $\Delta \hat{I}_\beta(t_2)$ do not commute in general, $C_{\alpha\beta}(t_1, t_2)$ is not guaranteed to be real and so in several studies the symmetrized correlation function, Eq. (1.4.16) is preferred [147, 158]:

$$P_{\alpha\beta}(t_1, t_2) \equiv \frac{1}{2} \langle \Delta \hat{I}_\alpha(t_1) \Delta \hat{I}_\beta(t_2) + \Delta \hat{I}_\beta(t_2) \Delta \hat{I}_\alpha(t_1) \rangle = \text{Re} [C_{\alpha\beta}(t_1, t_2)] \quad (3.2.4)$$

Since $P_{\alpha\beta}(t_1, t_2)$ is just the real part of $C_{\alpha\beta}(t_1, t_2)$, knowledge of the latter object is sufficient for a full characterization of the symmetric noise properties of the junction. The lack of two-particle interactions in the Hamiltonian (2.2.1) means that one can use Wick's Theorem to decompose quantum statistical averages of four field operators with the identity

$$\langle \hat{d}_\alpha^\dagger(t_1) \hat{d}_\beta(t_1) \hat{d}_\gamma^\dagger(t_2) \hat{d}_\delta(t_2) \rangle = \langle \hat{d}_\alpha^\dagger(t_1) \hat{d}_\beta(t_1) \rangle \langle \hat{d}_\gamma^\dagger(t_2) \hat{d}_\delta(t_2) \rangle + \langle \hat{d}_\alpha^\dagger(t_1) \hat{d}_\delta(t_2) \rangle \langle \hat{d}_\beta(t_1) \hat{d}_\gamma^\dagger(t_2) \rangle \quad (3.2.5)$$

where the indices $\alpha, \beta, \gamma, \delta$ can denote either lead or molecular orbitals. After some algebraic cancellations, one can simplify the non-symmetrized correlator to obtain:

$$\begin{aligned} C_{\alpha\beta}(t_1, t_2) = & -4q^2 \sum_{k,k',m,m'} \left[T_{mk\alpha}(t_1) T_{m'k'\beta}(t_2) \langle \hat{d}_m^\dagger(t_1) \hat{d}_{k'\beta}(t_2) \rangle \langle \hat{d}_{k\alpha}(t_1) \hat{d}_{m'}^\dagger(t_2) \rangle \right. \\ & - T_{mk\alpha}(t_1) T_{m'k'\beta}^*(t_2) \langle \hat{d}_m^\dagger(t_1) \hat{d}_{m'}(t_2) \rangle \langle \hat{d}_{k\alpha}(t_1) \hat{d}_{k'\beta}^\dagger(t_2) \rangle \\ & - T_{mk\alpha}^*(t_1) T_{m'k'\beta}(t_2) \langle \hat{d}_{k\alpha}^\dagger(t_1) \hat{d}_{k'\beta}(t_2) \rangle \langle \hat{d}_m(t_1) \hat{d}_{m'}^\dagger(t_2) \rangle \\ & \left. + T_{mk\alpha}^*(t_1) T_{m'k'\beta}^*(t_2) \langle \hat{d}_{k\alpha}^\dagger(t_1) \hat{d}_{m'}(t_2) \rangle \langle \hat{d}_m(t_1) \hat{d}_{k'\beta}^\dagger(t_2) \rangle \right] \quad (3.2.6) \end{aligned}$$

One identifies the Green's functions in this expression using Eqs. (2.6.4) and (2.6.5). It is then possible to rewrite Eq. (3.2.4) in the compact analytic form:

$$\begin{aligned} C_{\alpha\beta}(t_1, t_2) = & -4q^2 \text{Tr}_C \left[\mathbf{h}_{C\alpha}(t_1) \mathbf{G}_{\alpha C}^>(t_1, t_2) \mathbf{h}_{C\beta}(t_2) \mathbf{G}_{\beta C}^<(t_2, t_1) - \mathbf{h}_{C\alpha}(t_1) \mathbf{G}_{\alpha\beta}^>(t_1, t_2) \mathbf{h}_{\beta C}(t_2) \mathbf{G}_{CC}^<(t_2, t_1) \right. \\ & \left. - \mathbf{G}_{CC}^>(t_1, t_2) \mathbf{h}_{C\beta}(t_2) \mathbf{G}_{\beta\alpha}^<(t_2, t_1) \mathbf{h}_{\alpha C}(t_1) + \mathbf{G}_{C\beta}^>(t_1, t_2) \mathbf{h}_{\beta C}(t_2) \mathbf{G}_{C\alpha}^<(t_2, t_1) \mathbf{h}_{\alpha C}(t_1) \right] \quad (3.2.7) \end{aligned}$$

The expression in Eq. (3.2.7) is structurally identical to current correlation functions already in the literature [274, 71], but we emphasize that here the two time Green's functions appearing in Eq. (3.2.7) evolve in response to the switch-on of an arbitrary time-dependent bias in the partition-free approach, i.e. they contain convolution integrals taken along the vertical part of the Konstantinov-Perel' contour. Notice that, in addition to correlation functions describing particle hopping events between the leads and the molecule, Eq. (3.2.7) also contains information on lead-lead hopping events and on 'circular' [71] currents involving electronic transport processes within the molecular structure.

3.3 Current-current Correlations in the WBLA

In some work on the time-dependent noise, the two-time correlator was given as a function of a single time [209], but we emphasize that we need to solve the Kadanoff-Baym equations for all Green's functions 'blocks' in Eq. (2.3.1) in the two-time plane for a complete picture of current fluctuations. This was done in Section 2.5.8, and we combine Eqs. (2.5.90) - (2.5.93) with the definition of the embedding self-energy to give:

$$\begin{aligned} & \mathbf{h}_{C\alpha} \mathbf{G}_{\alpha C}^>(t_1, t_2) \mathbf{h}_{C\beta} \mathbf{G}_{\beta C}^<(t_2, t_1) + \mathbf{G}_{C\beta}^>(t_1, t_2) \mathbf{h}_{\beta C} \mathbf{G}_{C\alpha}^<(t_2, t_1) \mathbf{h}_{\alpha C} = \\ & [\Sigma_\alpha^> \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^> + \Sigma_\alpha^\neg \star \mathbf{G}_{CC}^\neg] (t_{1+}, t_{2-}) [\Sigma_\beta^< \cdot \mathbf{G}_{CC}^a + \Sigma_\beta^r \cdot \mathbf{G}_{CC}^< + \Sigma_\beta^\neg \star \mathbf{G}_{CC}^\neg] (t_{2-}, t_{1+}) \\ & + [\mathbf{G}_{CC}^> \cdot \Sigma_\beta^a + \mathbf{G}_{CC}^r \cdot \Sigma_\beta^> + \mathbf{G}_{CC}^\neg \star \Sigma_\beta^\neg] (t_{1+}, t_{2-}) [\mathbf{G}_{CC}^< \cdot \Sigma_\alpha^a + \mathbf{G}_{CC}^r \cdot \Sigma_\alpha^< + \mathbf{G}_{CC}^\neg \star \Sigma_\alpha^\neg] (t_{2-}, t_{1+}) \end{aligned} \quad (3.3.1)$$

Next, we use Eqs. (2.5.99) and (2.5.100) write the second and third terms in the correlation function (3.2.7) in terms of self energy and GF components:

$$\begin{aligned} \mathbf{h}_{C\alpha} \mathbf{G}_{\alpha\beta}^>(t_1, t_2) \mathbf{h}_{\beta C} &= \Sigma_\alpha^>(t_1, t_2) \delta_{\alpha\beta} + [(\Sigma_\alpha^> \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^> + \Sigma_\alpha^\neg \star \mathbf{G}_{CC}^\neg) \cdot \Sigma_\beta^a \\ &+ \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^r \cdot \Sigma_\beta^> + (\Sigma_\alpha^r \cdot \mathbf{G}_{CC}^\neg + \Sigma_\alpha^\neg \star \mathbf{G}_{CC}^M) \star \Sigma_\beta^\neg] (t_{1+}, t_{2-}) \end{aligned} \quad (3.3.2)$$

$$\begin{aligned} \mathbf{h}_{C\beta} \mathbf{G}_{\beta\alpha}^<(t_2, t_1) \mathbf{h}_{\alpha C} &= \Sigma_\alpha^<(t_2, t_1) \delta_{\alpha\beta} + [(\Sigma_\beta^< \cdot \mathbf{G}_{CC}^a + \Sigma_\beta^r \cdot \mathbf{G}_{CC}^< + \Sigma_\beta^\neg \star \mathbf{G}_{CC}^\neg) \cdot \Sigma_\alpha^a \\ &+ \Sigma_\beta^r \cdot \mathbf{G}_{CC}^r \cdot \Sigma_\alpha^< + (\Sigma_\beta^r \cdot \mathbf{G}_{CC}^\neg + \Sigma_\beta^\neg \star \mathbf{G}_{CC}^M) \star \Sigma_\alpha^\neg] (t_{2-}, t_{1+}) \end{aligned} \quad (3.3.3)$$

To simplify these expressions we use the identity (2.5.71) proven above. This enables us to neglect the terms in the correlation function arising from a double convolution on C_M in Eqs. (3.3.2) and (3.3.3). Taking Eq. (2.5.71) into account, the expressions (3.3.1), (3.3.2) and (3.3.3) are now inserted into Eq. (3.2.7), resulting in a sum of terms involving only self-energy components and components of the CC region Green's function:

$$\begin{aligned} C_{\alpha\beta}(t_1, t_2) &= 4q^2 \text{Tr}_C [(\Sigma_\alpha^>(t_1, t_2) \delta_{\alpha\beta} + [(\Sigma_\alpha^> \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^> + \Sigma_\alpha^\neg \star \mathbf{G}_{CC}^\neg) \cdot \Sigma_\beta^a \\ &+ \Sigma_\alpha^r \cdot (\mathbf{G}_{CC}^r \cdot \Sigma_\beta^> + \mathbf{G}_{CC}^\neg \star \Sigma_\beta^\neg)] (t_{1+}, t_{2-})) \mathbf{G}_{CC}^<(t_2, t_1) \end{aligned}$$

$$\begin{aligned}
& +\mathbf{G}_{CC}^>(t_1, t_2) \left(\Sigma_\alpha^<(t_2, t_1) \delta_{\alpha\beta} + \left[\left(\Sigma_\beta^< \cdot \mathbf{G}_{CC}^a + \Sigma_\beta^r \cdot \mathbf{G}_{CC}^< + \Sigma_\beta^\top \star \mathbf{G}_{CC}^\top \right) \cdot \Sigma_\alpha^a \right. \right. \\
& \quad \left. \left. + \Sigma_\beta^r \cdot \left(\mathbf{G}_{CC}^r \cdot \Sigma_\alpha^< + \mathbf{G}_{CC}^\top \star \Sigma_\alpha^\top \right) \right] (t_2-, t_1+) \right) \\
& - \left[\Sigma_\alpha^> \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^r \cdot \mathbf{G}_{CC}^> + \Sigma_\alpha^\top \star \mathbf{G}_{CC}^\top \right] (t_1+, t_2-) \left[\Sigma_\beta^< \cdot \mathbf{G}_{CC}^a + \Sigma_\beta^r \cdot \mathbf{G}_{CC}^< + \Sigma_\beta^\top \star \mathbf{G}_{CC}^\top \right] (t_2-, t_1+) \\
& - \left[\mathbf{G}_{CC}^> \cdot \Sigma_\beta^a + \mathbf{G}_{CC}^r \cdot \Sigma_\beta^> + \mathbf{G}_{CC}^\top \star \Sigma_\beta^\top \right] (t_1+, t_2-) \left[\mathbf{G}_{CC}^< \cdot \Sigma_\alpha^a + \mathbf{G}_{CC}^r \cdot \Sigma_\alpha^< + \mathbf{G}_{CC}^\top \star \Sigma_\alpha^\top \right] (t_2-, t_1+) \Big] \quad (3.3.4)
\end{aligned}$$

Here the sign subscripts indicate the contour position of each variable. So far, no assumptions have been made on the system Hamiltonian, i.e. we have not yet stated which regions are subject to a time-dependent perturbation, and neither have we made assumptions about the nature of the lead-molecule coupling. Up to this point, the derivation is completely algebraic, and so for noninteracting systems Eq. (3.3.4) is completely general.

Next, we assume that the leads satisfy the WBLA, i.e. we neglect the energy dependence of the lead-molecule coupling, as discussed in Chapter 2. The self-energy components for this problem derived in Section (2.4) for the WBLA enable us to derive a closed form for the current correlation function. We substitute the equations (2.4.16) and (2.4.17) for the retarded/advanced self energies into Eq. (3.3.4), which then reduces to a rather compact form:

$$\begin{aligned}
C_{\alpha\beta}(t_1, t_2) &= 4q^2 \text{Tr}_C \left[\delta_{\alpha\beta} \left(\Sigma_\alpha^>(t_1, t_2) \mathbf{G}_{CC}^<(t_2, t_1) + \mathbf{G}_{CC}^>(t_1, t_2) \Sigma_\alpha^<(t_2, t_1) \right) + \Gamma_\alpha \mathbf{G}_{CC}^>(t_1, t_2) \Gamma_\beta \mathbf{G}_{CC}^<(t_2, t_1) \right. \\
& \quad + i \mathbf{G}_{CC}^>(t_1, t_2) \left[\Lambda_\beta^+(t_2, t_1) \Gamma_\alpha + \Gamma_\beta \left(\Lambda_\alpha^+ \right)^\dagger(t_1, t_2) \right] + i \left[\Lambda_\alpha^-(t_1, t_2) \Gamma_\beta + \Gamma_\alpha \left(\Lambda_\beta^- \right)^\dagger(t_2, t_1) \right] \mathbf{G}_{CC}^<(t_2, t_1) \\
& \quad \left. - \Lambda_\beta^+(t_2, t_1) \Lambda_\alpha^-(t_1, t_2) - \left(\Lambda_\alpha^+ \right)^\dagger(t_1, t_2) \left(\Lambda_\beta^- \right)^\dagger(t_2, t_1) \right] \quad (3.3.5)
\end{aligned}$$

Here we have collected convolution integrals on the Konstantinov-Perel' contour into the objects $\Lambda_\alpha^\pm(t_1, t_2)$:

$$\Lambda_\beta^+(t_2, t_1) \equiv \left[\Sigma_\beta^< \cdot \mathbf{G}_{CC}^a + \Sigma_\beta^\top \star \mathbf{G}_{CC}^\top \right] (t_2-, t_1+) \quad (3.3.6)$$

$$\left(\Lambda_\alpha^+ \right)^\dagger(t_1, t_2) \equiv - \left[\mathbf{G}_{CC}^r \cdot \Sigma_\alpha^< + \mathbf{G}_{CC}^\top \star \Sigma_\alpha^\top \right] (t_2-, t_1+) \quad (3.3.7)$$

$$\Lambda_\alpha^-(t_1, t_2) \equiv \left[\Sigma_\alpha^> \cdot \mathbf{G}_{CC}^a + \Sigma_\alpha^\top \star \mathbf{G}_{CC}^\top \right] (t_1+, t_2-) \quad (3.3.8)$$

$$\left(\Lambda_\beta^- \right)^\dagger(t_2, t_1) \equiv - \left[\mathbf{G}_{CC}^r \cdot \Sigma_\beta^> + \mathbf{G}_{CC}^\top \star \Sigma_\beta^\top \right] (t_1+, t_2-) \quad (3.3.9)$$

We may now perform these convolution integrals using the formulas obtained for the self energies and GFs of the CC region obtained previously. Notice on the first line of Eq. (3.3.5) the presence of the following object:

$$4q^2 \text{Tr}_C \left[\Gamma_\alpha \mathbf{G}_{CC}^>(t_1, t_2) \Gamma_\beta \mathbf{G}_{CC}^<(t_2, t_1) \right] \quad (3.3.10)$$

In the single level case, all the terms inside the trace are replaced by scalars, and this object is equal to

$$q^2 \Gamma_\alpha \Gamma_\beta N_C(t) (1 - N_C(t)) \quad (3.3.11)$$

where the particle number on the molecular region is defined by Eq. (2.7.2). The time-dependence of this object is thus entirely due to the internal dynamics of electron and hole populations on sites of the molecule. This is in contrast to the current across the molecule, which from Eq. (2.6.6) is entirely due to electrons travelling from lead states to molecule states or vice versa [71]. The lead dependent matrices Λ_β^+ and Λ_α^- correspond physically to electrons propagating from lead β and positively charged holes propagating from lead α , respectively. We therefore interpret the two terms appearing on the second line of Eq. (3.3.5) as describing processes in which electrons in the leads interfere with holes in the molecular region, or holes in the leads interfere with electrons in the molecule. The terms on the third line of Eq. (3.3.5) are interpreted as cross-lead particle-hole interference terms.

The convolution integrals in $\Lambda^\pm$ are evaluated using the same methods of Refs. [1, 3], where the transformation from Matsubara summations to frequency integrals [128] is done taking account of the ordering of time-variables on the contour. This guarantees the linearity of each term in the fermion/hole distribution function $f(\pm(\omega - \mu))$, and results in the following pair of functional identities:

$$\Lambda_\beta^+(t_2, t_1) = ie^{-i\psi_\beta(t_2, t_0)} \int \frac{d\omega}{2\pi} f(\omega - \mu) e^{-i\omega(t_2 - t_0)} \Gamma_\beta \mathbf{S}_\beta^\dagger(t_1, t_0; \omega) \quad (3.3.12)$$

$$\Lambda_\alpha^-(t_1, t_2) = -ie^{-i\psi_\alpha(t_1, t_0)} \int \frac{d\omega}{2\pi} (1 - f(\omega - \mu)) e^{-i\omega(t_1 - t_0)} \Gamma_\alpha \mathbf{S}_\alpha^\dagger(t_2, t_0; \omega) \quad (3.3.13)$$

Here we have expressed $\Lambda_\alpha^\pm$ in terms of the matrix $\mathbf{S}_\alpha$ defined in Eq. (2.5.88). In [1, 3], the greater and lesser Green's functions were expressed in terms of the $\mathbf{S}_\alpha$ matrices following a line-integral of the Kadanoff Baym equations in the two-time plane, and these are given in Eq. (2.5.89). We thus have explicit formulas for all terms which appear in the two-time correlation function, which may be evaluated numerically in the (t_1, t_2) plane as follows:

$$\begin{aligned} C_{\alpha\beta}(t_1, t_2) = & 4q^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} (1 - f(\omega - \mu)) f(\omega' - \mu) \\ & \times \text{Tr}_C \left\{ \delta_{\alpha\beta} \sum_\gamma \left(\Gamma_\alpha e^{-i\psi_\alpha(t_1, t_2)} e^{-i\omega(t_1 - t_2)} \mathbf{S}_\gamma(t_2, t_0; \omega') \Gamma_\gamma \mathbf{S}_\gamma^\dagger(t_1, t_0; \omega') + h.c. \right) \right. \\ & + \sum_{\gamma, \gamma'} \Gamma_\alpha \mathbf{S}_\gamma(t_1, t_0; \omega) \Gamma_\gamma \mathbf{S}_\gamma^\dagger(t_2, t_0; \omega) \Gamma_\beta \mathbf{S}_{\gamma'}(t_2, t_0; \omega') \Gamma_{\gamma'} \mathbf{S}_{\gamma'}^\dagger(t_1, t_0; \omega') \\ & + i \sum_\gamma \left(\Gamma_\alpha \mathbf{S}_\gamma(t_1, t_0; \omega) \Gamma_\gamma \mathbf{S}_\gamma^\dagger(t_2, t_0; \omega) \Gamma_\beta \left(e^{-i\psi_\beta(t_2, t_0)} e^{-i\omega'(t_2 - t_0)} \mathbf{S}_\beta^\dagger(t_1, t_0; \omega') - e^{i\psi_\alpha(t_1, t_0)} e^{i\omega'(t_1 - t_0)} \mathbf{S}_\alpha(t_2, t_0; \omega') \right) \right) \\ & - \left(e^{-i\psi_\beta(t_2, t_0)} e^{-i\omega(t_2 - t_0)} \Gamma_\beta \mathbf{S}_\beta^\dagger(t_1, t_0; \omega) e^{-i\psi_\alpha(t_1, t_0)} e^{-i\omega'(t_1 - t_0)} \Gamma_\alpha \mathbf{S}_\alpha^\dagger(t_2, t_0; \omega') \right. \\ & \left. \left. + e^{i\psi_\alpha(t_1, t_0)} e^{i\omega(t_1 - t_0)} \mathbf{S}_\alpha(t_2, t_0; \omega) \Gamma_\alpha e^{i\psi_\beta(t_2, t_0)} e^{i\omega'(t_2 - t_0)} \mathbf{S}_\beta(t_1, t_0; \omega') \Gamma_\beta \right) \right\} \quad (3.3.14) \end{aligned}$$

This expression contains a great deal of information, and it is the central result of this Chapter. It is the two-time correlation function for a molecular junction connected to an arbitrary number of leads, through which time-

dependent voltages are passed. It contains transient parts which decay as $t_1, t_2 \rightarrow \infty$, while $\tau \equiv t_1 - t_2$ remains finite. It automatically enables evaluation of cross-correlation functions between different leads when $\alpha \neq \beta$, and the correlation between currents through the same lead when $\alpha = \beta$. It describes the noise on the current signal due to non-zero temperatures (the thermal noise), and due to a non-zero bias (the shot noise), as will be made clearer in the next section. The leads are assumed to satisfy the WBLA, and the additive contribution of the voltage to the lead state energies is assumed, but the approach is otherwise exact for electrons interacting at the mean field level [262]. Under close inspection, using the definition (2.5.88), we find that the explicit time-dependence enters into (3.3.14) only within structures of the form $e^{i(\psi_\alpha - \varphi_C)(t, t_0)}$, so that the noise does not distinguish between external fields that bias all leads identically ($V_\alpha(t) = V(t)$, for all α) or a gate voltage which moves energies in the negative energy direction ($V_C(t) = -V(t)$). This is also true for the current, as discussed in Section 2.6.1 The expression given in Eq. (3.3.14) will be used for the proof of analytic identities in Section 3.4, but it is not entirely convenient for numerical evaluation. Instead, we describe in Chapter 4 how to evaluate Eq. (3.3.5) directly.

3.4 Recovery of Known Results For a Static Bias

To parameterize our system with experimentally relevant variables, we work in the relative time coordinate system so that $t_1 = \tau + t$ and $t_2 = t$, where $\tau \equiv t_1 - t_2$ is the relative time that we wish to take a Fourier transform with respect to and t is the measurement time. Note that, to make the mapping to the Fourier space associated with τ , one needs τ to take on negative values. However, since both t_1 and t_2 must be times greater than t_0 , this means that τ is restricted to lie in the range $[-t + t_0, t - t_0]$, as was done in Ref. [187]. We define the Fourier transform of the correlation with respect to the time difference $\tau \equiv t_1 - t_2$, as a function of a single frequency and the measurement time t :

$$P_{\alpha\beta}(\Omega, t) \equiv \int_{-t+t_0}^{t-t_0} d\tau e^{i\Omega\tau} P_{\alpha\beta}(t + \tau, t) = \frac{1}{2} (C_{\alpha\beta}(\Omega, t) + C_{\alpha\beta}^*(-\Omega, t)) \quad (3.4.1)$$

where $C_{\alpha\beta}(\Omega, t)$ is the Fourier transform of $C_{\alpha\beta}(t + \tau, t)$ with respect to τ . Note that the relation

$$P_{\alpha\beta}^*(\Omega, t) = P_{\alpha\beta}(-\Omega, t) \quad (3.4.2)$$

immediately follows. In Section 3.2 we remarked that it is sufficient for knowledge of $P_{\alpha\beta}(t_1, t_2)$ to know the non-symmetrized function $C_{\alpha\beta}(t_1, t_2)$. In addition to the power spectrum, one can calculate several other useful quantities in terms of the $C_{\alpha\beta}$. For instance, in a two-lead junction, one may focus on the net current,

$$\hat{I}_{LR}^{(-)}(t) = \frac{1}{2} (\hat{I}_L(t) - \hat{I}_R(t)) \quad (3.4.3)$$

or on the sum of currents, which by the continuity equation is proportional to the rate of change of charge in the molecule [2]:

$$\hat{I}_{LR}^{(+)}(t) = \frac{1}{2} (\hat{I}_L(t) + \hat{I}_R(t)) \quad (3.4.4)$$

The time-dependent noise spectra of these objects can be written:

$$C^{(-)}(\Omega, t) = \int d\tau e^{i\Omega\tau} \langle \Delta \hat{I}_{LR}^{(-)}(t + \tau) \Delta \hat{I}_{LR}^{(-)}(t) \rangle = \frac{1}{2} (C^{(auto)}(\Omega, t) - C^{(\times)}(\Omega, t)) \quad (3.4.5)$$

$$C^{(+)}(\Omega, t) = \int d\tau e^{i\Omega\tau} \left\langle \Delta \hat{I}_{LR}^{(+)}(t+\tau) \Delta \hat{I}_{LR}^{(+)}(t) \right\rangle = \frac{1}{2} \left(C^{(auto)}(\Omega, t) + C^{(\times)}(\Omega, t) \right) \quad (3.4.6)$$

Where we have defined Fourier transforms of the *average* autocorrelation and cross-correlations:

$$C^{(auto)}(t+\tau, t) \equiv \frac{1}{2} (C_{LL}(t+\tau, t) + C_{RR}(t+\tau, t)) \quad (3.4.7)$$

$$C^{(\times)}(t+\tau, t) \equiv \frac{1}{2} (C_{LR}(t+\tau, t) + C_{RL}(t+\tau, t)) \quad (3.4.8)$$

In general, $C^{(auto)}$ and $C^{(\times)}$ are complex quantities and so cannot be observed. However, due to the symmetry property (3.2.3), they are both real at the equal observation time point $\tau = 0$. This fact was exploited in Ref. [209], where the equal time autocorrelation in the left lead, $C_{LL}(t, t)$, was studied in the time domain. Using the identity (3.2.3), one can show that the real parts of these functions are always *symmetric* in the $\tau = 0$ line:

$$\text{Re} \left[C^{(auto)}(t+\tau, t) \right] = \text{Re} \left[C^{(auto)}(t, t+\tau) \right] \quad (3.4.9)$$

$$\text{Re} \left[C^{(\times)}(t+\tau, t) \right] = \text{Re} \left[C^{(\times)}(t, t+\tau) \right] \quad (3.4.10)$$

, whereas the imaginary parts are always *antisymmetric* about this line:

$$\text{Im} \left[C^{(auto)}(t+\tau, t) \right] = -\text{Im} \left[C^{(auto)}(t, t+\tau) \right] \quad (3.4.11)$$

$$\text{Im} \left[C^{(\times)}(t+\tau, t) \right] = -\text{Im} \left[C^{(\times)}(t, t+\tau) \right] \quad (3.4.12)$$

To check the validity of our theory, we must confirm that it reduces to known expressions in the long time and static bias limits, which was already demonstrated for the current in Ref. [1]. We shall assume that the bias is applied only to the leads ($\varphi_C(t_1, t_2) \equiv 0$), that the equilibrium and nonequilibrium effective molecular hamiltonians are identical ($\tilde{\mathbf{h}}_{CC}^{eff} = \mathbf{h}_{CC}^{eff}$), and that $V_\alpha(t) = V_\alpha$ is constant in time. In this case the $\mathbf{S}_\alpha$ defined in Eq. (2.5.88) can be evaluated explicitly, and in the $t_0 \rightarrow -\infty$ limit we obtain

$$\mathbf{S}_\gamma(t_1, t_0; \omega) \mathbf{\Gamma}_\gamma \mathbf{S}_\gamma^\dagger(t_2, t_0; \omega) \xrightarrow{t_0 \rightarrow -\infty} e^{-i(\omega+V_\gamma)(t_1-t_2)} \mathbf{A}_\gamma(\omega+V_\gamma) \quad (3.4.13)$$

where $\mathbf{A}_\gamma(\omega) \equiv \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_\gamma \mathbf{G}_{CC}^a(\omega)$. Other expressions appearing in the generalized two-time correlation function can be worked out in a similar way, for instance:

$$e^{-i\psi_\beta(t_2, t_0)} e^{-i\omega'(t_2-t_0)} \mathbf{S}_\beta^\dagger(t_1, t_0; \omega') \xrightarrow{t_0 \rightarrow -\infty} \mathbf{G}_{CC}^a(\omega'+V_\beta) e^{i(\omega'+V_\beta)\tau} \quad (3.4.14)$$

The $\mathbf{S}_\alpha$ matrices enter into the general expression (3.3.14) only in the form of structures like (3.4.13) and (3.4.14), so we easily conclude that the power spectrum is a function of τ and hence the current becomes a stationary stochastic process under the conditions that the bias is static and that the switch-on time is relegated to the distant past. This is implied by the fact that the current itself is simply the steady-state LB formula in this case, as proven in [128, 1].

In studies of high-frequency shot noise for a static bias, the interesting physical observable is usually the static non-

symmetrized power spectrum [122, 126], which is the regular Fourier transform of $C_{\alpha\beta}(\tau) \equiv \lim_{t_0 \rightarrow -\infty} C_{\alpha\beta}(t + \tau, t)$:

$$C_{\alpha\beta}(\Omega) \equiv \lim_{t_0 \rightarrow -\infty} C_{\alpha\beta}(\Omega, t) = \int_{-\infty}^{\infty} d\tau e^{i\Omega\tau} C_{\alpha\beta}(\tau) \equiv \mathcal{F}[C_{\alpha\beta}(\tau); \Omega] \quad (3.4.15)$$

Taking the Fourier transform of the relation (3.2.3), we have

$$\mathcal{F}^*[C_{\alpha\beta}(\tau); -\Omega] = \mathcal{F}[C_{\beta\alpha}(-\tau); \Omega] \quad (3.4.16)$$

, which is another way of writing $C_{\alpha\beta}^*(-\Omega) = C_{\beta\alpha}(-\Omega)$. Therefore, as pointed out in Ref. [283], this quantity also satisfies the relation

$$C_{\alpha\beta}^*(\Omega) = C_{\beta\alpha}(\Omega)$$

For those experiments which do distinguish between absorption and emission processes, the quantity of interest is most often $C_{\alpha\alpha}(\Omega)$, which in general satisfies the inequality $C_{\alpha\alpha}(\Omega) \neq C_{\alpha\alpha}(-\Omega)$. $C_{\alpha\alpha}(\Omega)$ can therefore be used to describe measurements in which a quantum of energy $\hbar\Omega$ is transferred from the measuring device to the system. By contrast, the symmetrized spectrum obeys $P_{\alpha\alpha}(\Omega, t) = P_{\alpha\alpha}(-\Omega, t)$, i.e. it does not distinguish between emission and absorption processes. Moreover, in recently published work [274], a master equation formalism was used to derive an exact formula for the frequency-dependent autocorrelation and cross-lead current correlations in a nanojunction composed of a quantum dot coupled to two leads, which were treated within the WBLA. In the limits of long time and static bias, the general WBLA formula for the two-time correlation given in Eq. (3.3.5) may be mapped to the frequency domain as a summation over five terms:

$$C_{\alpha\beta}(\Omega) = \sum_{i=1}^5 C_{\alpha\beta}^{(i)}(\Omega) \quad (3.4.17)$$

The first term is nonzero only when $\alpha = \beta$

$$\begin{aligned} C_{\alpha\beta}^{(1)}(\Omega) &= \lim_{t_0 \rightarrow -\infty, V_\alpha(t) \rightarrow V_\alpha} \int d\tau e^{i\Omega\tau} \delta_{\alpha\beta} 4q^2 \text{Tr}_C [\Sigma_\alpha^>(t_1, t_2) \mathbf{G}_{CC}^<(t_2, t_1) + \mathbf{G}_{CC}^>(t_1, t_2) \Sigma_\alpha^<(t_2, t_1)] \\ &= \delta_{\alpha\beta} 4q^2 \sum_\gamma \int \frac{d\omega}{2\pi} [(1 - f_\alpha(\omega + \Omega - \mu)) f_\gamma(\omega - \mu) + (1 - f_\gamma(\omega - \mu)) f_\alpha(\omega - \Omega - \mu)] T_{\gamma\alpha}(\omega) \end{aligned} \quad (3.4.18)$$

where we have the transmission probability $T_{\gamma\alpha}(\omega)$ defined in Eq. (2.8.16). Following the interpretative scheme of Refs. [125, 126], we identify the physical origin of this term in processes involving the excitation and propagation of a quasiparticle electron-hole pair, one of which is excited by an energy of $\hbar\Omega$ with respect to the other. These electron-hole pair excitations arise from thermal fluctuations of the particle number, as discussed at length in Ref. [114]. There are similar terms in all the other $C_{\alpha\beta}^{(i)}(\Omega)$, corresponding to different combinations of transmission and reflection events in the molecule. These may include, for instance, the propagation of entangled electron-hole pairs where the electron is scattered into a different lead to that of the hole [264]. We list all the terms explicitly below:

$$\begin{aligned} C_{\alpha\beta}^{(2)}(\Omega) &= \lim_{t_0 \rightarrow -\infty, V_\alpha(t) \rightarrow V_\alpha} \int d\tau e^{i\Omega\tau} 4q^2 \text{Tr}_C [\mathbf{\Gamma}_\alpha \mathbf{G}_{CC}^>(t + \tau, t) \mathbf{\Gamma}_\beta \mathbf{G}_{CC}^<(t, t + \tau)] \\ &= 4q^2 \sum_{\gamma, \gamma'} \int \frac{d\omega}{2\pi} (1 - f_\gamma(\omega - \mu)) f_{\gamma'}(\omega - \Omega - \mu) \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\beta\gamma)}(\omega) \mathbf{T}_{CC}^{(\beta\gamma')}(\omega - \Omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma')}(\omega - \Omega) \right] \end{aligned} \quad (3.4.19)$$

$$\begin{aligned}
C_{\alpha\beta}^{(3)}(\Omega) &= \lim_{t_0 \rightarrow -\infty, V_\alpha(t) \rightarrow V_\alpha} \int d\tau e^{i\Omega\tau} i4q^2 \text{Tr}_C \left[\mathbf{G}_{CC}^>(t+\tau, t) \left[\mathbf{\Lambda}_\beta^+(t, t+\tau) \mathbf{\Gamma}_\alpha + \mathbf{\Gamma}_\beta (\mathbf{\Lambda}_\alpha^+)^{\dagger}(t+\tau, t) \right] \right] \\
&= i4q^2 \sum_{\gamma} \int \frac{d\omega}{2\pi} \text{Tr}_C [(1 - f_{\gamma}(\omega - \mu)) f_{\beta}(\omega - \Omega - \mu) \mathbf{A}_{\gamma}(\omega) \mathbf{\Gamma}_{\beta} \mathbf{G}_{CC}^a(\omega - \Omega) \mathbf{\Gamma}_{\alpha} \\
&\quad - (1 - f_{\gamma}(\omega - \mu)) f_{\alpha}(\omega - \Omega - \mu) \mathbf{A}_{\gamma}(\omega) \mathbf{\Gamma}_{\beta} \mathbf{G}_{CC}^r(\omega - \Omega) \mathbf{\Gamma}_{\alpha}]
\end{aligned} \tag{3.4.20}$$

$$\begin{aligned}
C_{\alpha\beta}^{(4)}(\Omega) &= \lim_{t_0 \rightarrow -\infty, V_\alpha(t) \rightarrow V_\alpha} \int d\tau e^{i\Omega\tau} i4q^2 \text{Tr}_C \left[\left[\mathbf{\Lambda}_{\alpha}^-(t+\tau, t) \mathbf{\Gamma}_{\beta} + \mathbf{\Gamma}_{\alpha} (\mathbf{\Lambda}_{\beta}^-)^{\dagger}(t, t+\tau) \right] \mathbf{G}_{CC}^<(t, t+\tau) \right] \\
&= i4q^2 \sum_{\gamma} \int \frac{d\omega}{2\pi} \text{Tr}_C [(1 - f_{\alpha}(\omega - \mu)) f_{\gamma}(\omega - \Omega - \mu) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega) \mathbf{\Gamma}_{\beta} \mathbf{A}_{\gamma}(\omega - \Omega) \\
&\quad - (1 - f_{\beta}(\omega - \mu)) f_{\gamma}(\omega - \Omega - \mu) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\beta} \mathbf{A}_{\gamma}(\omega - \Omega)]
\end{aligned} \tag{3.4.21}$$

$$\begin{aligned}
C_{\alpha\beta}^{(5)}(\Omega) &= \lim_{t_0 \rightarrow -\infty, V_\alpha(t) \rightarrow V_\alpha} - \int d\tau e^{i\Omega\tau} i4q^2 \text{Tr}_C \left[\mathbf{\Lambda}_{\beta}^+(t, t+\tau) \mathbf{\Lambda}_{\alpha}^-(t+\tau, t) + (\mathbf{\Lambda}_{\alpha}^+)^{\dagger}(t+\tau, t) (\mathbf{\Lambda}_{\beta}^-)^{\dagger}(t, t+\tau) \right] \\
&= -4q^2 \sum_{\gamma} \int \frac{d\omega}{2\pi} \text{Tr}_C [f_{\beta}(\omega - \Omega - \mu) (1 - f_{\alpha}(\omega - \mu)) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^a(\omega) \mathbf{\Gamma}_{\beta} \mathbf{G}_{CC}^a(\omega - \Omega) \\
&\quad + f_{\alpha}(\omega - \Omega - \mu) (1 - f_{\beta}(\omega - \mu)) \mathbf{\Gamma}_{\alpha} \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\beta} \mathbf{G}_{CC}^r(\omega - \Omega)]
\end{aligned} \tag{3.4.22}$$

These formulas are then substituted into Eq. (3.4.17). If we restrict the discussion to a molecule coupled to left and right leads, L, R , we can use the identities (2.8.10) and (2.8.11) to show (after some lengthy algebra) that the non-symmetrized autocorrelation associated with a single lead is given by

$$\begin{aligned}
C_{\alpha\alpha}(\Omega) &= 4q^2 \int \frac{d\omega}{2\pi} \text{Tr}_C \left[(1 - f_{\alpha}(\omega + \Omega - \mu)) f_{\bar{\alpha}}(\omega - \mu) \mathbf{T}_{CC}^{(\alpha\bar{\alpha})}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\bar{\alpha})}(\omega) \right. \\
&\quad \left. + (1 - f_{\bar{\alpha}}(\omega + \Omega - \mu)) f_{\alpha}(\omega - \mu) \mathbf{T}_{CC}^{(\alpha\bar{\alpha})}(\omega + \Omega) \mathbf{T}_{CC}^{\dagger(\alpha\bar{\alpha})}(\omega + \Omega) \right. \\
&\quad \left. - (f_{\alpha}(\omega - \mu) - f_{\bar{\alpha}}(\omega - \mu)) (f_{\alpha}(\omega + \Omega - \mu) - f_{\bar{\alpha}}(\omega + \Omega - \mu)) \mathbf{T}_{CC}^{(\alpha\bar{\alpha})}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\bar{\alpha})}(\omega) \mathbf{T}_{CC}^{(\alpha\bar{\alpha})}(\omega + \Omega) \mathbf{T}_{CC}^{\dagger(\alpha\bar{\alpha})}(\omega + \Omega) \right. \\
&\quad \left. - \Omega^2 (1 - f_{\alpha}(\omega + \Omega - \mu)) f_{\alpha}(\omega - \mu) \mathbf{\Gamma}_{\alpha} \mathbf{G}^r(\omega) \mathbf{A}_{\alpha}(\omega + \Omega) \mathbf{G}^a(\omega) \right]
\end{aligned} \tag{3.4.23}$$

where $\bar{\alpha} \neq \alpha$, and we have defined the *transmission matrices* as in Eqs. (2.8.17) and (2.8.18). Physically, the eigenvalues of $\mathbf{T}_{CC}^{(\alpha\bar{\alpha})}(\omega)$ may be interpreted as probability amplitudes for electron scattering events between the α and β leads. Eq. (3.4.23) gives the analytic behaviour of a function which should be accessible to the experimentalist - it is a power spectrum for current measurements carried out with arbitrary detection frequency, taken at long times after the switch-on of a constant bias. It is expressed in terms of the transmission matrices, which depend on the molecular Hamiltonian and on the coupling of the molecule to the leads. We remark that if one restricts the CC

region to a single energy level, and replaces $\Omega \rightarrow -\Omega$ on the right-hand side, then Eq. (3.4.23) is exactly equivalent to the expression found in Ref. [274] (there the Fourier transform was taken with a phase of $-i\Omega\tau$). Note that, unlike the steady-state formula in Eq. (1.4.20) of Chapter 1, Eq. (3.4.23) cannot be expressed purely in terms of transmission probabilities, due to the final term (proportional to Ω^2). When $\Omega = 0$, this is no longer the case.

From Eqs. (3.3.14) and (3.2.4) one obtains the symmetrized two-time correlation function:

$$\begin{aligned}
P_{\alpha\beta}(t_1, t_2) = & 2q^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} F(\omega, \omega') \text{Tr}_C \left\{ \delta_{\alpha\beta} \sum_{\gamma} \left(\mathbf{\Gamma}_{\alpha} e^{-i\psi_{\alpha}(t_1, t_2)} e^{-i\omega(t_1 - t_2)} \mathbf{S}_{\gamma}(t_2, t_0; \omega') \mathbf{\Gamma}_{\gamma} \mathbf{S}_{\gamma}^{\dagger}(t_1, t_0; \omega') + h.c \right) \right. \\
& + \sum_{\gamma, \gamma'} \mathbf{\Gamma}_{\alpha} \mathbf{S}_{\gamma}(t_1, t_0; \omega) \mathbf{\Gamma}_{\gamma} \mathbf{S}_{\gamma}^{\dagger}(t_2, t_0; \omega) \mathbf{\Gamma}_{\beta} \mathbf{S}_{\gamma'}(t_2, t_0; \omega') \mathbf{\Gamma}_{\gamma'} \mathbf{S}_{\gamma'}^{\dagger}(t_1, t_0; \omega') \\
& + i \sum_{\gamma} \left(\mathbf{\Gamma}_{\alpha} \mathbf{S}_{\gamma}(t_1, t_0; \omega) \mathbf{\Gamma}_{\gamma} \mathbf{S}_{\gamma}^{\dagger}(t_2, t_0; \omega) \mathbf{\Gamma}_{\beta} \left(e^{-i\psi_{\beta}(t_2, t_0)} e^{-i\omega'(t_2 - t_0)} \mathbf{S}_{\beta}^{\dagger}(t_1, t_0; \omega') - e^{i\psi_{\alpha}(t_1, t_0)} e^{i\omega'(t_1 - t_0)} \mathbf{S}_{\alpha}(t_2, t_0; \omega') \right) + h.c \right) \\
& \left. - \left(e^{-i\psi_{\beta}(t_2, t_0)} e^{-i\omega(t_2 - t_0)} \mathbf{\Gamma}_{\beta} \mathbf{S}_{\beta}^{\dagger}(t_1, t_0; \omega) e^{-i\psi_{\alpha}(t_1, t_0)} e^{-i\omega'(t_1 - t_0)} \mathbf{\Gamma}_{\alpha} \mathbf{S}_{\alpha}^{\dagger}(t_2, t_0; \omega') + h.c \right) \right\} \quad (3.4.24)
\end{aligned}$$

where we define the combination of electron-hole distribution functions:

$$F(\omega, \omega') \equiv (1 - f(\omega - \mu)) f(\omega' - \mu) + (1 - f(\omega' - \mu)) f(\omega - \mu) \quad (3.4.25)$$

The steady-state symmetrized power spectrum can then be obtained either by substituting the long time formulas (3.4.13) and (3.4.14) into Eq. (3.4.24) and taking the Fourier Transform, or simply by substituting the expression for $C_{\alpha\beta}(\Omega)$ into (3.4.1):

$$\begin{aligned}
P_{\alpha\beta}(\Omega) \equiv \lim_{t_0 \rightarrow -\infty} P_{\alpha\beta}(\Omega, t) = & 2q^2 \int \frac{d\omega}{2\pi} \left\{ \delta_{\alpha\beta} \sum_{\gamma} \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \right] (F_{\alpha\gamma}(\omega + \Omega, \omega) + F_{\alpha\gamma}(\omega - \Omega, \omega)) \right. \\
& + \sum_{\gamma, \gamma'} F_{\gamma\gamma'}(\omega, \omega - \Omega) \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\beta\gamma)}(\omega) \mathbf{T}_{CC}^{(\beta\gamma')}(\omega - \Omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma')}(\omega - \Omega) \right] \\
& + i \sum_{\gamma} \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\beta\gamma)}(\omega) \left(F_{\gamma\beta}(\omega, \omega - \Omega) \mathbf{T}_{CC}^{\dagger(\alpha\beta)}(\omega - \Omega) - F_{\gamma\alpha}(\omega, \omega - \Omega) \mathbf{T}_{CC}^{(\beta\alpha)}(\omega - \Omega) \right) \right. \\
& \left. + \mathbf{T}_{CC}^{(\beta\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \left(F_{\gamma\alpha}(\omega, \omega + \Omega) \mathbf{T}_{CC}^{\dagger(\beta\alpha)}(\omega + \Omega) - F_{\gamma\beta}(\omega, \omega + \Omega) \mathbf{T}_{CC}^{(\alpha\beta)}(\omega + \Omega) \right) \right] \\
& \left. - \text{Tr}_C \left[F_{\alpha\beta}(\omega, \omega - \Omega) \mathbf{T}_{CC}^{\dagger(\alpha\beta)}(\omega - \Omega) \mathbf{T}_{CC}^{\dagger(\beta\alpha)}(\omega) + F_{\alpha\beta}(\omega, \omega + \Omega) \mathbf{T}_{CC}^{(\alpha\beta)}(\omega + \Omega) \mathbf{T}_{CC}^{(\beta\alpha)}(\omega) \right] \right\} \quad (3.4.26)
\end{aligned}$$

where we introduce $f_{\alpha}(x) \equiv f(x - V_{\alpha})$, and make the definition:

$$F_{\alpha\beta}(\omega, \omega') \equiv (1 - f_{\alpha}(\omega - \mu)) f_{\beta}(\omega' - \mu) + (1 - f_{\beta}(\omega' - \mu)) f_{\alpha}(\omega - \mu) = F_{\beta\alpha}(\omega', \omega) \quad (3.4.27)$$

It is instructive to compare this formula with the finite frequency power spectrum derived by Büttiker and Yang

[147, 158, 260, 202] within an S-matrix approach. In particular, when one assumes the CC region to be a single level, and a Breit-Wigner resonance in the scattering matrix amplitudes with energy-independent resonance widths [121, 261, 125], the LB formalism is exactly equivalent to ours.

It is common practice [260, 113] to neglect the frequency-dependence of the transmission functions, $\mathbf{T}_{CC}(\omega) \sim \mathbf{T}_{CC}$ in Eq. (3.4.26), which allows for the trivial removal of all frequency integrals via the identity

$$\int_{-\infty}^{\infty} dx F_{\alpha\beta}(x, x+A) = (V_{\alpha} - V_{\beta} + A) \coth\left(\frac{V_{\alpha} - V_{\beta} + A}{2k_B T}\right) \quad (3.4.28)$$

This puts the power spectrum into the form:

$$\begin{aligned} P_{\alpha\beta}(\Omega) = & \frac{q^2}{\pi} \left\{ \delta_{\alpha\beta} \sum_{\gamma} \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)} \mathbf{T}_{CC}^{\dagger(\alpha\gamma)} \right] \left((V_{\alpha} - V_{\gamma} - \Omega) \coth\left(\frac{V_{\alpha} - V_{\gamma} - \Omega}{2k_B T}\right) + (V_{\alpha} - V_{\gamma} + \Omega) \coth\left(\frac{V_{\alpha} - V_{\gamma} + \Omega}{2k_B T}\right) \right) \right. \\ & + \sum_{\gamma, \gamma'} \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)} \mathbf{T}_{CC}^{\dagger(\beta\gamma)} \mathbf{T}_{CC}^{(\beta\gamma')} \mathbf{T}_{CC}^{\dagger(\alpha\gamma')} \right] (V_{\gamma} - V_{\gamma'} - \Omega) \coth\left(\frac{V_{\gamma} - V_{\gamma'} - \Omega}{2k_B T}\right) \\ & + i \sum_{\gamma} \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)} \mathbf{T}_{CC}^{\dagger(\beta\gamma)} \left(\mathbf{T}_{CC}^{\dagger(\beta\alpha)} (V_{\gamma} - V_{\beta} - \Omega) \coth\left(\frac{V_{\gamma} - V_{\beta} - \Omega}{2k_B T}\right) - \mathbf{T}_{CC}^{(\beta\alpha)} (V_{\gamma} - V_{\alpha} - \Omega) \coth\left(\frac{V_{\gamma} - V_{\alpha} - \Omega}{2k_B T}\right) \right) \right. \\ & \left. + \mathbf{T}_{CC}^{(\beta\gamma)} \mathbf{T}_{CC}^{\dagger(\alpha\gamma)} \left(\mathbf{T}_{CC}^{\dagger(\beta\alpha)} (V_{\gamma} - V_{\beta} + \Omega) \coth\left(\frac{V_{\gamma} - V_{\beta} + \Omega}{2k_B T}\right) - \mathbf{T}_{CC}^{(\alpha\beta)} (V_{\gamma} - V_{\alpha} + \Omega) \coth\left(\frac{V_{\gamma} - V_{\alpha} + \Omega}{2k_B T}\right) \right) \right] \\ & \left. - \text{Tr}_C \left[\mathbf{T}_{CC}^{\dagger(\alpha\beta)} \mathbf{T}_{CC}^{\dagger(\beta\alpha)} (V_{\alpha} - V_{\beta} - \Omega) \coth\left(\frac{V_{\alpha} - V_{\beta} - \Omega}{2k_B T}\right) + \mathbf{T}_{CC}^{(\alpha\beta)} \mathbf{T}_{CC}^{(\beta\alpha)} (V_{\alpha} - V_{\beta} + \Omega) \coth\left(\frac{V_{\alpha} - V_{\beta} + \Omega}{2k_B T}\right) \right] \right\} \quad (3.4.29) \end{aligned}$$

It is then simple to show that the LL component of this reduces to the well-known expression:

$$\begin{aligned} P_{LL}(\Omega) = & \frac{q^2}{\pi} \left\{ \text{Tr}_C \left[\mathbf{T}_{CC}^{(LR)} \mathbf{T}_{CC}^{\dagger(LR)} \mathbf{T}_{CC}^{(LR)} \mathbf{T}_{CC}^{\dagger(LR)} \right] 2\Omega \coth\left(\frac{\Omega}{2k_B T}\right) \right. \\ & \left. + \text{Tr}_C \left[\mathbf{T}_{CC}^{(LR)} \mathbf{T}_{CC}^{\dagger(LR)} \left(1 - \mathbf{T}_{CC}^{(LR)} \mathbf{T}_{CC}^{\dagger(LR)} \right) \right] \left((V_L - V_R - \Omega) \coth\left(\frac{V_L - V_R - \Omega}{2k_B T}\right) + (V_L - V_R + \Omega) \coth\left(\frac{V_L - V_R + \Omega}{2k_B T}\right) \right) \right\} \quad (3.4.30) \end{aligned}$$

This formula expresses the interplay of the shot noise, Nyquist noise and quantum vacuum fluctuations in a conductor, and moreover has been verified experimentally for a wide range of mesoscale conductors [163, 284].

In many experiments, the quantity (3.4.26) is measured in the *zero-frequency limit* i.e. when the time separating measurements is much longer than the timescale over which the current fluctuates [164]. Taking this limit, and using the identity:

$$\mathbf{G}_{CC}^r(\omega) = \mathbf{G}_{CC}^a(\omega) - i \sum_{\gamma} \mathbf{G}_{CC}^r(\omega) \mathbf{\Gamma}_{\gamma} \mathbf{G}_{CC}^a(\omega) \quad (3.4.31)$$

we obtain the zero-frequency power spectrum as:

$$\begin{aligned}
\lim_{\Omega \rightarrow 0} P_{\alpha\beta}(\Omega) &= 2q^2 \int \frac{d\omega}{2\pi} \left\{ 2\delta_{\alpha\beta} \sum_{\gamma} F_{\alpha\gamma}(\omega, \omega) \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \right] \right. \\
&\quad \left. - F_{\alpha\beta}(\omega, \omega) \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\beta)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\beta)}(\omega) + \mathbf{T}_{CC}^{(\beta\alpha)}(\omega) \mathbf{T}_{CC}^{\dagger(\beta\alpha)}(\omega) \right] \right. \\
&\quad + \sum_{\gamma, \gamma'} [F_{\gamma\gamma'}(\omega, \omega) + F_{\alpha\beta}(\omega, \omega)] \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\beta\gamma)}(\omega) \mathbf{T}_{CC}^{(\beta\gamma')}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma')}(\omega) \right] \\
&\quad + i \sum_{\gamma} \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\beta\gamma)}(\omega) \left(F_{\gamma\beta}(\omega, \omega) \mathbf{T}_{CC}^{\dagger(\alpha\beta)}(\omega) - F_{\gamma\alpha}(\omega, \omega) \mathbf{T}_{CC}^{(\beta\alpha)}(\omega) \right) \right. \\
&\quad \left. + \mathbf{T}_{CC}^{(\beta\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \left(F_{\gamma\alpha}(\omega, \omega) \mathbf{T}_{CC}^{\dagger(\beta\alpha)}(\omega) - F_{\gamma\beta}(\omega, \omega) \mathbf{T}_{CC}^{(\alpha\beta)}(\omega) \right) \right] \Big\} \quad (3.4.32)
\end{aligned}$$

To better understand the content of the expression (3.4.32), we consider the special case where $\alpha = \beta$. In this case, use of Eq. (3.4.31) enables us to replace the single summation with a double sum, and we can use the identity:

$$F_{\alpha\gamma}(\omega, \omega) = \frac{1}{2} \left[F_{\alpha\alpha}(\omega, \omega) + F_{\gamma\gamma}(\omega, \omega) + 2(f_{\alpha}(\omega - \mu) - f_{\gamma}(\omega - \mu))^2 \right] \quad (3.4.33)$$

to give

$$\lim_{\Omega \rightarrow 0} P_{\alpha\alpha}(\Omega) = P_{\alpha\alpha}^{(thermal)}(\Omega) + P_{\alpha\alpha}^{(shot)}(\Omega) \quad (3.4.34)$$

where we identify both the *generalized thermal noise*, which vanishes when the temperature $T = 0$, and the *generalized shot noise*, which vanishes when $V_{\gamma} = 0$ for all γ :

$$\lim_{\Omega \rightarrow 0} P_{\alpha\alpha}^{(thermal)}(\Omega) = 2q^2 \int \frac{d\omega}{2\pi} \sum_{\gamma \neq \alpha} [F_{\alpha\alpha}(\omega, \omega) + F_{\gamma\gamma}(\omega, \omega)] \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \right] \quad (3.4.35)$$

$$\begin{aligned}
\lim_{\Omega \rightarrow \infty} P_{\alpha\alpha}^{(shot)}(\Omega) &= 2q^2 \int \frac{d\omega}{2\pi} \left\{ 2 \sum_{\gamma \neq \alpha} (f_{\alpha}(\omega - \mu) - f_{\gamma}(\omega - \mu))^2 \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \left(1 - \sum_{\gamma'} \mathbf{T}_{CC}^{(\alpha\gamma')}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma')}(\omega) \right) \right] \right. \\
&\quad \left. + \sum_{\gamma, \gamma'} (f_{\gamma}(\omega - \mu) - f_{\gamma'}(\omega - \mu))^2 \text{Tr}_C \left[\mathbf{T}_{CC}^{(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma)}(\omega) \mathbf{T}_{CC}^{(\alpha\gamma')}(\omega) \mathbf{T}_{CC}^{\dagger(\alpha\gamma')}(\omega) \right] \right\} \quad (3.4.36)
\end{aligned}$$

If we now specialize this discussion to the case of a two-lead junction, i.e. a junction in which α may be one of two indices L, R, we recover the following well-known results for the thermal and shot noise, respectively:

$$\lim_{\Omega \rightarrow 0} P_{LL}^{(thermal)}(\Omega) = 4q^2 \int \frac{d\omega}{2\pi} ((1 - f_L(\omega - \mu)) f_L(\omega - \mu) + (1 - f_R(\omega - \mu)) f_R(\omega - \mu)) \text{Tr}_C \left[\mathbf{T}_{CC}^{(LR)}(\omega) \mathbf{T}_{CC}^{\dagger(LR)}(\omega) \right] \quad (3.4.37)$$

$$\lim_{\Omega \rightarrow 0} P_{LL}^{(shot)}(\Omega) = 4q^2 \int \frac{d\omega}{2\pi} (f_L(\omega - \mu) - f_R(\omega - \mu))^2 \text{Tr}_C \left[\mathbf{T}_{CC}^{(LR)}(\omega) \mathbf{T}_{CC}^{\dagger(LR)}(\omega) \left(1 - \mathbf{T}_{CC}^{(LR)}(\omega) \mathbf{T}_{CC}^{\dagger(LR)}(\omega) \right) \right] \quad (3.4.38)$$

Identifying the transmission probability $T_{LR}(\omega)$ as in Eq. (2.8.16), we see that Eq. (3.4.36) reproduces (1.4.20) exactly.

Chapter 4

Implementation of the Current and Current Noise

4.1 Introduction

This Chapter is intended for those readers who are more interested in how to practically apply our formalism than in how it was derived from NEGF. It constitutes an extension of the work published in Refs. [2, 4], where formulas were presented for the time-dependent current through an arbitrarily large molecule with all frequency integrals removed. The formulas (2.5.89), (2.6.11) and (3.3.5) for the Green's functions, current and current correlations are compact and useful for the derivation of theoretical results. When one wishes to demonstrate their equivalence to published work within a particular model, it will therefore always be more convenient to start with these expressions. In the published work of Ref. [1], numerical integration was used to compute the frequency integrals in the current formula (2.6.10) at different times for a single level system. We now seek to systematically extend this work to a numerical method that facilitates time-dependent transport calculations of the current and current noise in more complex molecules. We are interested in the development of a method that can be used for the calculation of time-dependent transport quantities in extended molecular structures, which could be for instance molecular wires [285, 136], organic molecules [286], or GNR systems [172].

In this chapter, we show how all formulas needed to characterize the partition-free TD transport can be made fast-to-implement. This speed-up is based upon the analytical removal of all frequency integrals via Padé and Matsubara expansions of the Fermi functions appearing in the integrands. We include a brief description of the algorithm we used to expand the Fermi function in terms of Padé parameters, and in Section 4.2 we re-express the lesser and greater Green's functions in terms of these parameters and some special functions. We then derive explicit formulas for the current and for each and every term in the formula for the two-time correlation function in Sections 4.3 and 4.4, respectively. These formulas are completely independent of the particular Hamiltonian chosen, and so they can be used to study finite size effects in the transport properties of many different molecular structures.

4.2 Implementation of the lesser and greater Green's functions

We have previously derived a compact expression for the greater and lesser Green's functions, Eq. (2.5.89). Whereas this formula proved useful analytically manipulating the quantum noise, the computer prefers that we expand it

into a rather more explicit form. In everything that follows, we take $\tilde{\mathbf{h}}_{eff} = \mathbf{h}_{eff}$, i.e. we do not consider static modifications to the central region Hamiltonian, because we are primarily concerned with the effects of explicit time-dependent driving on the transport. By making an expansion in the left/right eigenbasis defined in Eq. (2.5.19), we can re-express the Green's functions in terms of scalar integrals:

$$\begin{aligned} \mathbf{G}^{\gtrless}(t_1, t_2) = & \mp \frac{i}{2\pi} \int d\omega f(\mp(\omega - \mu)) \sum_{\gamma, k, j} \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \Gamma_{\gamma} |\varphi_k^L\rangle \langle \varphi_k^R|}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} e^{-i\varphi_C(t_1, t_2)} e^{-i\bar{\varepsilon}_j(t_1 - t_0)} e^{i\bar{\varepsilon}_k^*(t_2 - t_0)} \\ & \times \left(\frac{1}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} - i \left(\int_{t_0}^{t_1} d\tau \frac{e^{-i(\omega - \bar{\varepsilon}_j)(\tau - t_0)} e^{i(\varphi_C - \psi_{\gamma})(\tau, t_0)}}{\omega - \bar{\varepsilon}_k^*} - \int_{t_0}^{t_2} d\tau \frac{e^{i(\omega - \bar{\varepsilon}_k^*)(\tau - t_0)} e^{-i(\varphi_C - \psi_{\gamma})(\tau, t_0)}}{\omega - \bar{\varepsilon}_j} \right) \right. \\ & \left. + \int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{-i\omega(\tau - \bar{\tau})} e^{i\bar{\varepsilon}_j(\tau - t_0)} e^{-i\bar{\varepsilon}_k^*(\bar{\tau} - t_0)} e^{i(\varphi_C - \psi_{\alpha})(\tau, \bar{\tau})} \right) \end{aligned} \quad (4.2.1)$$

Here, and for the remainder of this thesis, the ‘ CC ’ notation will be dropped on all Green's functions as every Green's function we encounter from now will be defined on the molecular region. The Fermi function can be re-expressed with a series expansion whose terms possess a simple pole structure [287, 288, 289]:

$$f(x) = \frac{1}{e^{\beta x} + 1} = \frac{1}{2} - \lim_{N_p \rightarrow \infty} \sum_{l=1}^{N_p} \eta_l \left(\frac{1}{\beta x + i\zeta_l} + \frac{1}{\beta x - i\zeta_l} \right) \quad (4.2.2)$$

When the parameter values are $\eta_l = 1$ and $\zeta_l = \pi(2l - 1)$, this is referred to as the Matsubara expansion:

$$f(x) = \frac{1}{2} - \sum_{l=1}^{\infty} \left[\frac{1}{\beta x + i\pi(2l - 1)} + \frac{1}{\beta x - i\pi(2l - 1)} \right] \quad (4.2.3)$$

However, one can improve the convergence of this series for finite N_p by expressing the Fermi function as a finite continued fraction, and then poles of the Fermi function can be found as the solution to the eigenproblem for a tridiagonal matrix, in the so-called Padé approximation [210, 288, 289]. The algorithm for computing the parameters η_l and ζ_l for fixed N_p is described in detail in Appendix A.3, where we also include the actual parameter values for $N_p = 20$. Unlike the Matsubara expansion, in which the poles are spaced at fixed intervals of $\frac{2\pi}{\beta}$ along the imaginary axis, the poles $i\zeta_l/\beta$ in the Padé expansion are spaced unevenly along the imaginary axis. The prefactors η_l are all real and positive-valued, and may take values other than 1. In practice, the expansion $f_N(x)$ truncated at some finite value of N_p is used, with N_p chosen such that for values of $L \gg \varepsilon$, where ε denotes the typical energy scale of the problem, the deviation $\delta f_N(L) \equiv |f(x) - f_N(x)|_{\beta x=L} < 10^{-p}$, where p can be chosen to give arbitrary accuracy [288, 289, 215]. The rate of convergence of the Padé expansion to the Fermi function at all energies increases as the temperature is increased, as discussed in Appendix A.3. However, for numerical implementations the Padé expansion converges much more rapidly for increasing N_p , and has been used to speed up several time-dependent transport schemes [211, 214, 83].

Upon substituting the expansion (4.2.2) into Eq. (4.2.1), all the frequency integrals occurring there can all be removed, using the identities (A.2.6), (A.2.13) and (A.2.22) in Appendix A, which replace frequency integrals with special functions such as the *digamma function*, defined as the logarithmic derivative of the gamma function:

$$\Psi(z) \equiv \frac{d \ln \Gamma(z)}{dz} \quad (4.2.4)$$

In addition, we will make use of the function

$$\bar{\Phi}(\tau, \beta, z) \equiv \exp\left(-\frac{\pi\tau}{\beta}\right) \Phi\left(e^{-\frac{2\pi\tau}{\beta}}, 1, \frac{1}{2} + \frac{\beta z}{2i\pi}\right) \quad (4.2.5)$$

where Φ is the so-called *Hurwitz-Lerch Transcendent* [290]:

$$\Phi(z, s, a) \equiv \sum_{n=0}^{\infty} \frac{z^n}{(n+a)^s} \quad (4.2.6)$$

After substituting the aforementioned integral identities into the appropriate parts of Eq. (4.2.1), one obtains

$$\begin{aligned} \mathbf{G}^{\geq}(t_1, t_2) = & \frac{1}{2\pi} \sum_{\gamma, k, j} \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \mathbf{\Gamma}_{\gamma} |\varphi_k^L\rangle \langle \varphi_k^R|}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} e^{-i\varphi_C(t_1, t_2)} e^{-i\bar{\varepsilon}_j(t_1 - t_0)} e^{i\bar{\varepsilon}_k^*(t_2 - t_0)} \\ & \times \left\{ \frac{i}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi\left(\frac{1}{2} + \frac{\beta}{2i\pi}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}(\bar{\varepsilon}_j - \mu)\right) \right] \right. \\ & \pm \frac{\pi}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \mp i\pi \int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) \\ & - \left(\int_{t_0}^{t_1} d\tau e^{i(\bar{\varepsilon}_j - \mu)(\tau - t_0)} e^{i(\varphi_C - \psi_{\gamma})(\tau, t_0)} \bar{\Phi}(\tau - t_0, \beta, \bar{\varepsilon}_k^* - \mu) - c.c.j \leftrightarrow k, t_1 \leftrightarrow t_2 \right) \\ & \left. - \frac{\pi}{\beta} \int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \mu)(\tau - t_0)} e^{-i(\bar{\varepsilon}_k^* - \mu)(\bar{\tau} - t_0)} e^{i(\varphi_C - \psi_{\gamma})(\tau, \bar{\tau})} \operatorname{cosech}\left(\frac{\pi}{\beta}(\tau - \bar{\tau})\right) \Big|_{\tau \neq \bar{\tau}} \right\} \quad (4.2.7) \end{aligned}$$

where $c.c.j \leftrightarrow k, t_1 \leftrightarrow t_2$ denotes the complex conjugation of the preceding term with both the j and k indices and the times t_1 and t_2 exchanged, and $\operatorname{cosech}\left(\frac{\pi}{\beta}(\tau - \bar{\tau})\right) \Big|_{\tau \neq \bar{\tau}}$ is defined in Eq. (A.2.21). In this expression, we see two double integral terms, where the integrand contains either a Dirac delta or a step function. These may be removed by paying close attention to the relative ordering of t_1 and t_2 in the two-time plane:

$$\begin{aligned} i\pi \int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) = & i\pi \left[\theta(t_1 - t_2) \left(\int_{t_0}^{t_2} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) + \int_{t_2}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) \right) \right. \\ & \left. + \theta(t_2 - t_1) \left(\int_{t_0}^{t_1} d\tau \int_{t_0}^{t_1} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) + \int_{t_1}^{t_2} d\tau \int_{t_0}^{t_1} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) \right) \right] \quad (4.2.8) \end{aligned}$$

Evidently, the second integral on each line of Eq. (4.2.8) vanishes so that one is left with:

$$i\pi \int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(\tau - t_0)} \delta(\tau - \bar{\tau}) = \frac{\pi}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\theta(t_1 - t_2) \left[1 - e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t_2 - t_0)} \right] + \theta(t_2 - t_1) \left[1 - e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t_1 - t_0)} \right] \right] \quad (4.2.9)$$

If we now turn to the double integral on the last line of Eq. (4.2.7), we must contend with integrals of the form:

$$\int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} \theta(\tau - \bar{\tau}) f(\tau, \bar{\tau}) \quad (4.2.10)$$

$$\int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} \theta(\bar{\tau} - \tau) g(\tau, \bar{\tau}) \quad (4.2.11)$$

Once more, we split the integral ranges into (i) a double integral with both upper bounds set to $\min[t_1, t_2]$, and (ii) a double integral where the variable integrated over the largest range goes from $\min[t_1, t_2]$ up to $\max[t_1, t_2]$. This leads to the following identities, in which all step functions have been removed from the integrands:

$$\int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} \theta(\tau - \bar{\tau}) f(\tau, \bar{\tau}) = \theta(t_1 - t_2) \left[\int_{t_0}^{t_2} d\tau \int_{t_0}^{\tau} d\bar{\tau} f(\tau, \bar{\tau}) + \int_{t_2}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} f(\tau, \bar{\tau}) \right] + \theta(t_2 - t_1) \int_{t_0}^{t_1} d\tau \int_{t_0}^{\tau} d\bar{\tau} f(\tau, \bar{\tau}) \quad (4.2.12)$$

$$\int_{t_0}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} \theta(\bar{\tau} - \tau) g(\tau, \bar{\tau}) = \theta(t_1 - t_2) \int_{t_0}^{t_2} d\bar{\tau} \int_{t_0}^{\bar{\tau}} d\tau g(\tau, \bar{\tau}) + \theta(t_2 - t_1) \left[\int_{t_0}^{t_1} d\bar{\tau} \int_{t_0}^{\bar{\tau}} d\tau g(\tau, \bar{\tau}) + \int_{t_1}^{t_2} d\bar{\tau} \int_{t_0}^{t_1} d\tau g(\tau, \bar{\tau}) \right] \quad (4.2.13)$$

This means that, following some algebra, we can finally write:

$$\begin{aligned} \mathbf{G}^{\geq}(t_1, t_2) &= \frac{1}{2\pi} \sum_{\gamma, k, j} \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \mathbf{\Gamma}_{\gamma} |\varphi_k^L\rangle \langle \varphi_k^R|}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} e^{-i\varphi_C(t_1, t_2)} e^{-i\bar{\varepsilon}_j(t_1 - t_0)} e^{i\bar{\varepsilon}_k^*(t_2 - t_0)} \\ &\quad \times \left\{ \frac{i}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi\left(\frac{1}{2} + \frac{\beta}{2i\pi}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}(\bar{\varepsilon}_j - \mu)\right) \right] \right. \\ &\quad \pm \frac{\pi}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\theta(t_1 - t_2) e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t_2 - t_0)} + \theta(t_2 - t_1) e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t_1 - t_0)} \right] \\ &\quad \left. - \left(\int_{t_0}^{t_1} d\tau e^{i(\bar{\varepsilon}_j - \mu)(\tau - t_0)} e^{i(\varphi_C - \psi_{\gamma})(\tau, t_0)} \bar{\Phi}(\tau - t_0, \beta, \bar{\varepsilon}_k^* - \mu) - c.c. j \leftrightarrow k, t_1 \leftrightarrow t_2 \right) \right. \\ &\quad \left. - \frac{2\pi}{\beta} [\theta(t_1 - t_2) I_{\gamma}(t_2, \beta, \mu, \bar{\varepsilon}_j, \bar{\varepsilon}_k^*) + \theta(t_2 - t_1) I_{\gamma}(t_1, \beta, \mu, \bar{\varepsilon}_j, \bar{\varepsilon}_k^*)] \right\} \\ &\quad - \frac{2\pi}{\beta} \sum_l \eta_l \left[\theta(t_1 - t_2) \int_{t_2}^{t_1} d\tau \int_{t_0}^{t_2} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \mu + i\frac{\zeta_l}{\beta})(\tau - t_0)} e^{-i(\bar{\varepsilon}_k^* - \mu + i\frac{\zeta_l}{\beta})(\bar{\tau} - t_0)} e^{i(\varphi_C - \psi_{\gamma})(\tau, \bar{\tau})} - c.c. j \leftrightarrow k, t_1 \leftrightarrow t_2 \right] \end{aligned} \quad (4.2.14)$$

The following function was introduced here for compactness:

$$I_{\gamma}(t, \beta, \mu, \bar{\varepsilon}_j, \bar{\varepsilon}_k^*) = \frac{1}{2} \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\bar{\tau} e^{i(\bar{\varepsilon}_j - \mu)(\tau - t_0)} e^{-i(\bar{\varepsilon}_k^* - \mu)(\bar{\tau} - t_0)} e^{i(\varphi_C - \psi_{\gamma})(\tau, \bar{\tau})} \operatorname{cosech}\left(\frac{\pi}{\beta}(\tau - \bar{\tau})\right) \Big|_{\tau \neq \bar{\tau}} \quad (4.2.15)$$

Eqs. (4.2.7) and (4.2.14) also give us a very useful relationship between the lesser and greater Green's functions:

$$\mathbf{G}^>(t_1, t_2) - \mathbf{G}^<(t_1, t_2) = -ie^{-i\varphi_C(t_1, t_2)} \sum_j \left[\frac{|\varphi_j^R\rangle\langle\varphi_j^L|}{\langle\varphi_j^L|\varphi_j^R\rangle} e^{-i\bar{\varepsilon}_j(t_1-t_2)} \theta(t_1-t_2) + \frac{|\varphi_j^L\rangle\langle\varphi_j^R|}{\langle\varphi_j^R|\varphi_j^L\rangle} e^{i\bar{\varepsilon}_j^*(t_2-t_1)} \theta(t_2-t_1) \right] \quad (4.2.16)$$

where we have used the identity:

$$\sum_\gamma \langle\varphi_j^L|\mathbf{\Gamma}_\gamma|\varphi_k^L\rangle = i\langle\varphi_j^L|(\mathbf{h}^{eff} - (\mathbf{h}^{eff})^\dagger)|\varphi_k^L\rangle = i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)\langle\varphi_j^L|\varphi_k^L\rangle \quad (4.2.17)$$

along with the idempotency relation (2.5.20) to remove one of the summations. In practice, when we calculate the lesser and greater Green's functions numerically, we therefore only need to evaluate (4.2.7) for one of these functions, before obtaining the other from Eq. (4.2.16). Looking at Eqs. (2.5.22) and (2.5.24) in Chapter 2, we see that (4.2.16) is just an expression of the general relation:

$$\mathbf{G}^>(t_1, t_2) - \mathbf{G}^<(t_1, t_2) = \mathbf{G}^r(t_1, t_2) - \mathbf{G}^a(t_1, t_2) \quad (4.2.18)$$

which also follows from Eqs. (1.5.64) and (1.5.65) in Chapter 1. At equal times, Eq. (4.2.18) reduces to

$$\mathbf{G}^>(t_1, t_2) - \mathbf{G}^<(t_1, t_2) = -i\mathbf{I} \quad (4.2.19)$$

where $\mathbf{I}$ is the $N_s \times N_s$ matrix defined on the CC region for a molecule with N_s sites. We now define the time dependent hole number of the central region:

$$N_h(t) \equiv 2i\text{Tr}_C[\mathbf{G}^>(t, t)] \quad (4.2.20)$$

Using the identity (4.2.19), we find that this is related to the electron number $N_C(t)$ (defined in Eq. (2.7.2)) via the physically intuitive relation:

$$N_h(t) = 2N_s - N_C(t) \quad (4.2.21)$$

Finally, there is a source of computational speed-up in the following property, which follows straightforwardly from Eq. (2.5.89):

$$\mathbf{G}^{\geq}(t_1, t_2)^\dagger = -\mathbf{G}^{\geq}(t_2, t_1) \quad (4.2.22)$$

This approximately halves the number of Green's function calculations one has to perform in the two-time plane. We note in passing that, if one follows the steps in the formal integration of the lesser GF $\mathbf{G}^<(t_1, t_2)$ in [1], one uses a well-known [128] transformation of Matsubara summations into frequency integrals when evaluating a set of convolution integrals taken along the vertical branch of the Konstantinov-Perel' contour. However, these steps can be omitted altogether, and a direct route can be taken to an expression for $I_\alpha(t)$ in terms of Φ which retains the Matsubara summation at all stages. The particle number only depends upon a single time argument and is obtained as

$$N_C(t) = -2i\text{Tr}_C[\mathbf{G}^<(t, t)] \quad (4.2.23)$$

$$= \frac{1}{\pi} \sum_{\gamma, j, k} \frac{\langle\varphi_k^R|\varphi_j^R\rangle\langle\varphi_j^L|\mathbf{\Gamma}_\gamma|\varphi_k^L\rangle}{\langle\varphi_j^L|\varphi_j^R\rangle\langle\varphi_k^R|\varphi_k^L\rangle} \left[\frac{i\pi}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} + \frac{e^{i(\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi\left(\frac{1}{2} + \frac{\beta}{2i\pi}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}(\bar{\varepsilon}_j - \mu)\right) \right] \right]$$

$$\begin{aligned}
& +ie^{i(\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)(t-t_0)} \left(\int_{t_0}^t d\tau e^{i(\bar{\varepsilon}_j - \mu)(\tau-t_0)} e^{i(\varphi_C - \psi_\gamma)(\tau, t_0)} \bar{\Phi}(\tau - t_0, \beta, \bar{\varepsilon}_k^* - \mu) - c.c.j \leftrightarrow k \right) \\
& + \frac{2\pi i}{\beta} e^{i(\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)(t-t_0)} I_\gamma(t, \beta, \mu, \bar{\varepsilon}_j, \bar{\varepsilon}_k^*) \Big] \quad (4.2.24)
\end{aligned}$$

4.3 Implementation of the current

The compact expression (2.6.11) for the current can be re-written in terms of the lesser Greens function, which we have treated in the previous Section:

$$I_\alpha(t) = \frac{1}{\pi} \int d\omega f(\omega - \mu) \text{Tr}_C \left[2\text{Re} \left[i\mathbf{\Gamma}_\alpha e^{i\omega(t-t_0)} e^{i\psi_\alpha(t, t_0)} \mathbf{S}_\alpha(t, t_0; \omega) \right] \right] + 2i\text{Tr}_C [\mathbf{\Gamma}_\alpha \mathbf{G}^<(t, t)] \quad (4.3.1)$$

Eq. (4.3.1) is now represented in the left/right eigenbasis:

$$\begin{aligned}
I_\alpha(t) &= \frac{1}{\pi} \sum_j 2\text{Re} \left[i \frac{\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \int d\omega f(\omega - \mu) e^{i(\omega - \bar{\varepsilon}_j)(t-t_0)} e^{i\psi_\alpha(t, t_0)} \right. \\
&\quad \times \left. \left[\frac{1}{\omega - \bar{\varepsilon}_j} - i \int_{t_0}^t d\tau e^{-i(\omega - \bar{\varepsilon}_j)(\tau-t_0)} e^{-i\psi_\alpha(\tau, t_0)} \right] \right] + 2i\text{Tr}_C [\mathbf{\Gamma}_\alpha \mathbf{G}^<(t, t)] \quad (4.3.2)
\end{aligned}$$

The frequency integrals in this expression are removed using the identity (A.2.19), and also the complex conjugation of the identity (A.2.13),

$$\int d\omega \frac{f(\mp(\omega - \mu))}{\omega - \bar{\varepsilon}_j} e^{i\omega(t-t_0)} = \pm e^{i\mu(t-t_0)} \bar{\Phi}(t - t_0, \beta, \bar{\varepsilon}_j - \mu) \quad (4.3.3)$$

To give:

$$\begin{aligned}
I_\alpha(t) &= \frac{1}{\pi} \sum_j 2\text{Re} \left[\frac{\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \left(-ie^{i\psi_\alpha(t, t_0)} e^{-i(\bar{\varepsilon}_j - \mu)(t-t_0)} \bar{\Phi}(t - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) \right. \right. \\
&\quad \left. \left. + \int_{t_0}^t d\tau e^{-i(\bar{\varepsilon}_j - \mu)(t-\tau)} e^{i\psi_\alpha(t, \tau)} \left[\pi\delta(t - \tau) - \frac{i\pi}{\beta} \text{cosech} \left(\frac{\pi}{\beta} (t - \tau) \right) \right]_{t \neq \tau} \right) \right] + 2i\text{Tr}_C [\mathbf{\Gamma}_\alpha \mathbf{G}^<(t, t)] \quad (4.3.4)
\end{aligned}$$

In the second line of Eq. (4.3.4) we encounter the integral ¹:

¹The upper bound of the integral is contained in the delta function, but the symmetry of the delta in this case guarantees that the integral has a unique value:

$$\begin{aligned}
\int_{t-t_0}^0 d\tau \delta(\tau) &= \frac{1}{2} \left[\int_{t-t_0}^0 d\tau \delta(\tau) + \int_{t-t_0}^0 d\tau \delta(-\tau) \right] = \frac{1}{2} \left[\int_{t-t_0}^0 d\tau \delta(\tau) + \int_0^{t_0-t} d\tau \delta(\tau) \right] \\
&= \frac{1}{2} \int_{t-t_0}^{t_0-t} d\tau \delta(\tau) = \frac{1}{2}
\end{aligned}$$

$$\int_{t_0}^t d\tau \delta(t - \tau) f(\tau) = f(t) \int_{t-t_0}^0 d\tau \delta(\tau) = \frac{f(t)}{2} \quad (4.3.5)$$

This leads to the fully-expanded formula for the current in lead α :

$$\begin{aligned} I_\alpha(t) = & \frac{1}{\pi} \sum_j \left\{ \text{Re} \left[2 \frac{\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \left(-ie^{i\psi_\alpha(t, t_0)} e^{-i(\bar{\varepsilon}_j - \mu)(t - t_0)} \bar{\Phi}(t - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) \right. \right. \right. \\ & \left. \left. \left. + \frac{\pi}{2} - \frac{i\pi}{\beta} \int_{t_0}^t d\tau e^{-i(\bar{\varepsilon}_j - \mu)(t - \tau)} e^{i\psi_\alpha(t, \tau)} \right) \right] \right. \\ & - \sum_{\gamma, k} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t - t_0)} \left[\frac{\Psi\left(\frac{1}{2} + \frac{\beta}{2i\pi}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}(\bar{\varepsilon}_j - \mu)\right)}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} + \frac{i\pi e^{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t - t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \right. \\ & \left. \left. + \int_{t_0}^t d\bar{t} \left[-ie^{-i(\bar{\varepsilon}_k^* - \mu)(\bar{t} - t_0)} e^{i\psi_\beta(\bar{t}, t_0)} \bar{\Phi}(\bar{t} - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) + c.c_{j \leftrightarrow k} \right] + \frac{2i\pi}{\beta} I(t, \beta, \mu, \bar{\varepsilon}_j, \bar{\varepsilon}_k^*) \right] \right\} \quad (4.3.6) \end{aligned}$$

There is a final cancellation of terms due to the identity:

$$\frac{2}{\pi} \text{Re} \sum_j \frac{\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \frac{\pi}{2} = \sum_{j, k} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} = -i \sum_{\gamma, j, k} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)} \quad (4.3.7)$$

where the second equality is implied by the Eq. (4.2.17). From this the constant terms in the single and double summations cancel, to finally give a formula that is a ‘single shot’ function of time:

$$\begin{aligned} I_\alpha(t) = & \frac{1}{\pi} \sum_j \left\{ \text{Re} \left[2 \frac{\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \left(-ie^{i\psi_\alpha(t, t_0)} e^{-i(\bar{\varepsilon}_j - \mu)(t - t_0)} \bar{\Phi}(t - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) \right. \right. \right. \\ & \left. \left. \left. - \frac{i\pi}{\beta} \int_{t_0}^t d\tau e^{-i(\bar{\varepsilon}_j - \mu)(t - \tau)} e^{i\psi_\alpha(t, \tau)} \text{cosech}\left(\frac{\pi}{\beta}(t - \tau)\right) \Big|_{t \neq \tau} \right) \right] \right. \\ & - \sum_{\gamma, k} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t - t_0)} \left[\frac{\Psi\left(\frac{1}{2} + \frac{\beta}{2i\pi}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}(\bar{\varepsilon}_j - \mu)\right)}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \right. \\ & \left. \left. + \int_{t_0}^t d\bar{t} \left[-ie^{-i(\bar{\varepsilon}_k^* - \mu)(\bar{t} - t_0)} e^{i\psi_\beta(\bar{t}, t_0)} \bar{\Phi}(\bar{t} - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) + c.c_{j \leftrightarrow k} \right] + \frac{2i\pi}{\beta} I_\gamma(t, \beta, \mu, \bar{\varepsilon}_j, \bar{\varepsilon}_k^*) \right] \right\} \quad (4.3.8) \end{aligned}$$

The general result (4.3.8) will form the basis for all subsequent numerical work involving the calculation of the current response to an arbitrary time-dependent bias. In practice, the time integrals may be performed numerically or removed analytically given the assumption of a particular functional form for $V_\alpha(t)$. Several of the decaying modes in the current can be directly identified by inspection of (4.3.8), although the exact nature of its long-time behaviour depends on the bias chosen. In particular, if we separate out the real and imaginary parts of the complex eigenvalues, $\bar{\varepsilon}_j = \lambda_j - i\gamma_j$, we see that modes appearing in the single summation decay as $e^{-\gamma_j(t - t_0)}$, whereas the prefactor governing the decay of modes in the double sum is $e^{-(\gamma_j + \gamma_k)(t - t_0)}$. This defines a timescale

of $\tau_d \equiv \text{Max}\{1/\gamma_j\}$ as the time taken for transient behaviour to decay following the switch-on.

For completeness, it is useful to also give the expansion of the LB formula (2.8.14) in terms of special functions and the left/right eigenbasis. The Padé expansion of this is given by

$$I_\alpha^{LB} = \frac{2i}{\beta} \sum_\gamma (V_\alpha - V_\gamma) \sum_{j,k} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \sum_{l=1}^{\infty} \eta_l \left[\frac{1}{\left(\bar{\varepsilon}_j - V_\alpha - \mu - i \frac{\zeta_l}{\beta} \right) \left(\bar{\varepsilon}_j - V_\gamma - \mu - i \frac{\zeta_l}{\beta} \right)} + c.c.j \leftrightarrow k \right] \quad (4.3.9)$$

To prove the formula in Eq. (4.3.9), one can either substitute Eq. (4.2.2) into (2.8.14) and remove all frequency integrals, or alternatively one can take the long-time limit of Eq. (4.3.8) with a static bias and use the identity (4.3.7). One can finally insert Matsubara parameters into the expansion (4.3.9) to get a rather compact form of the steady-state current:

$$I_\alpha^{LB} = \frac{1}{\pi} \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\alpha) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\alpha) \right) - c.c.j \leftrightarrow k \right] \quad (4.3.10)$$

This formula enables calculation of the LB current without resorting to frequency integration.

4.4 Implementation of the noise

In the general expression (3.3.5) for the quantum noise, we have, in addition to the lesser and greater Green's functions, lesser and greater self-energy components and the $\mathbf{\Lambda}^\pm$ matrices defined in Eqs. (3.3.12) and (3.3.13). The lesser and greater self energies are easy to evaluate using the identity A.2.19, and can be written as follows:

$$\Sigma_\alpha^\gtrless(t_1, t_2) = \mp i \frac{\mathbf{\Gamma}_\alpha}{2} \delta(t_1 - t_2) - \mathbf{\Gamma}_\alpha e^{-i\psi_\alpha(t_1, t_2)} e^{-i\mu(t_1 - t_2)} \text{cosech} \left(\frac{\pi}{\beta} (t_1 - t_2) \right) \Big|_{t_1 \neq t_2} \quad (4.4.1)$$

In addition a similar, and similarly useful relation to (4.2.22) exists for the self-energy components:

$$\Sigma_\alpha^\gtrless(t_1, t_2)^\dagger = -\Sigma_\alpha^\gtrless(t_2, t_1) \quad (4.4.2)$$

The first term in Eq. 4.4.1 is singular at the time $t_1 = t_2$. As the self energies only enter into the general expression (3.3.5) with a premultiplying factor of $\delta_{\alpha\beta}$, this singularity causes the autocorrelation $C_{\alpha\alpha}(t + \tau, t)$ to diverge at $\tau = 0$. This is an artefact of the WBLA, and does not exist in numerical approaches that take the electronic structure of the leads into account with a finite bandwidth [209, 274]. These approaches include a numerical scheme for moving beyond the WBLA, and are in this sense more general than the formalism presented in this thesis. However our scheme can be used for rapid calculations on extended molecules with a far larger spectrum than a quantum dot, and in such molecules the WBLA is an increasingly accurate approximation [138, 139]. Moreover, within the WBLA formalism developed here, it will be possible to overcome the problem of divergence in the autocorrelation for systems driven at a frequency Ω by integrating out all time variables in $C_{\alpha\alpha}(t + \tau, t)$, i.e. one may replace it with $\frac{\Omega}{2\pi} \int_0^{\frac{2\pi}{\Omega}} dt \int_{-\infty}^{\infty} d\tau C_{\alpha\alpha}(t + \tau, t)$. Indeed, it is this time-averaged noise which has been the target physical quantity in the majority of studies on AC-driven shot noise [291, 200, 252, 257, 292]. We defer this to a future work and will instead focus on calculations of the time-dependent average cross-correlation $C^{(\times)}(t + \tau, t)$ in the numerical sections of this thesis.

To this end, we consider the expansion into the left/right eigenbasis of the $\Lambda^\pm$ matrices defined in Chapter 3, with $\varphi_C = 0$ due to the gauge invariance proven in that Chapter:

$$\begin{aligned} \Lambda_\beta^+(t_2, t_1) &= ie^{-i\psi_\beta(t_2, t_0)} \sum_j \frac{\Gamma_\beta |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \int \frac{d\omega}{2\pi} f(\omega - \mu) e^{-i\omega(t_2 - t_0)} \\ &\quad \times \left[\frac{1}{\omega - \bar{\varepsilon}_j^*} + i \int_{t_0}^{t_1} d\tau e^{i(\omega - \bar{\varepsilon}_j^*)(\tau - t_0)} e^{i\psi_\beta(\tau, t_0)} \right] e^{i\bar{\varepsilon}_j^*(t_1 - t_0)} \end{aligned} \quad (4.4.3)$$

$$\begin{aligned} \Lambda_\alpha^-(t_1, t_2) &= -ie^{-i\psi_\alpha(t_1, t_0)} \sum_j \frac{\Gamma_\alpha |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \int \frac{d\omega}{2\pi} f(-(\omega - \mu)) e^{-i\omega(t_1 - t_0)} \\ &\quad \times \left[\frac{1}{\omega - \bar{\varepsilon}_j^*} + i \int_{t_0}^{t_2} d\tau e^{i(\omega - \bar{\varepsilon}_j^*)(\tau - t_0)} e^{i\psi_\alpha(\tau, t_0)} \right] e^{i\bar{\varepsilon}_j^*(t_2 - t_0)} \end{aligned} \quad (4.4.4)$$

Using the identities (A.2.13) and (A.2.19), we re-express Eq. (4.4.3) in terms of the Hurwitz-Lerch Transcendent discussed in Appendix (A):

$$\begin{aligned} \Lambda_\beta^+(t_2, t_1) &= \frac{i}{2\pi} e^{-i\psi_\beta(t_2, t_0)} \sum_j \frac{\Gamma_\beta |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \left[-\frac{\pi}{\beta} \int_{t_0}^{t_1} d\tau e^{i\bar{\varepsilon}_j^*(t_1 - \tau)} e^{-i\mu(t_2 - \tau)} e^{i\psi_\beta(\tau, t_0)} \operatorname{cosech} \left(\frac{\pi}{\beta} (t_2 - \tau) \right) \right]_{t_2 \neq \tau} \\ &\quad + i\pi \int_{t_0}^{t_1} d\tau e^{-i\bar{\varepsilon}_j^*(\tau - t_0)} e^{i\psi_\beta(\tau, t_0)} \delta(t_2 - \tau) - e^{i\bar{\varepsilon}_j^*(t_1 - t_0)} e^{-i\mu(t_2 - t_0)} \bar{\Phi}(t_2 - t_0, \beta, \bar{\varepsilon}_j^* - \mu) \end{aligned} \quad (4.4.5)$$

We now use an identity, which follows from (4.3.5) at $t_1 = t_2$

$$\int_{t_0}^{t_1} d\tau f(\tau) \delta(t_2 - \tau) = \begin{cases} \frac{f(t_2)}{2}, & t_1 = t_2 \\ 0, & t_1 < t_2 \\ f(t_2), & t_1 > t_2 \end{cases} \quad (4.4.6)$$

to obtain the following formula for Λ^+ :

$$\begin{aligned} \Lambda_\beta^+(t_2, t_1) &= \sum_j \frac{\Gamma_\beta |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \left[-\frac{i}{2\beta} \int_{t_0}^{t_1} d\tau e^{i\bar{\varepsilon}_j^*(t_1 - \tau)} e^{-i\mu(t_2 - \tau)} e^{-i\psi_\beta(t_2, \tau)} \operatorname{cosech} \left(\frac{\pi}{\beta} (t_2 - \tau) \right) \right]_{t_2 \neq \tau} \\ &\quad - \theta(t_1 - t_2) \frac{e^{i\bar{\varepsilon}_j^*(t_1 - t_2)}}{2} - \frac{i}{2\pi} e^{i\bar{\varepsilon}_j^*(t_1 - t_0)} e^{-i\psi_\beta(t_2, t_0)} e^{-i\mu(t_2 - t_0)} \bar{\Phi}(t_2 - t_0, \beta, \bar{\varepsilon}_j^* - \mu) \end{aligned} \quad (4.4.7)$$

This may be used directly in numerical implementations of the noise. Note that the $t_1 = t_2$ value of the identity (4.4.6) is taken into account by defining the Heaviside step function using the half-maximum convention introduced in Eq. (1.5.62). To evaluate the frequency integrals in (4.4.4), we again use the identities (A.2.13), (A.2.19) and (4.4.6) which puts it into a useful form:

$$\begin{aligned}
\Lambda_{\alpha}^{-}(t_1, t_2) = & \sum_j \frac{\Gamma_{\alpha} |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \left[-\frac{i}{2\beta} \int_{t_0}^{t_2} d\tau e^{i\bar{\varepsilon}_j^*(t_2-\tau)} e^{-i\mu(t_1-\tau)} e^{-i\psi_{\alpha}(t_1, \tau)} \operatorname{cosech} \left(\frac{\pi}{\beta} (t_1 - \tau) \right) \right]_{t_1 \neq \tau} \\
& + \theta(t_2 - t_1) \frac{e^{i\bar{\varepsilon}_j^*(t_2-t_1)}}{2} - \frac{i}{2\pi} e^{i\bar{\varepsilon}_j^*(t_2-t_0)} e^{-i\psi_{\alpha}(t_1, t_0)} e^{-i\mu(t_1-t_0)} \bar{\Phi}(t_1 - t_0, \beta, \bar{\varepsilon}_j^* - \mu) \Bigg] \quad (4.4.8)
\end{aligned}$$

We then obtain the additional lambda matrices in Eqs. (3.3.7) and (3.3.9) via complex conjugation and exchange of the time and lead indices. The results are included here for completeness:

$$\begin{aligned}
(\Lambda_{\alpha}^{+})^{\dagger}(t_1, t_2) = & \sum_j \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \Gamma_{\alpha}}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[\frac{i}{2\beta} \int_{t_0}^{t_2} d\tau e^{-i\bar{\varepsilon}_j(t_2-\tau)} e^{i\mu(t_1-\tau)} e^{i\psi_{\alpha}(t_1, \tau)} \operatorname{cosech} \left(\frac{\pi}{\beta} (t_1 - \tau) \right) \right]_{t_1 \neq \tau} \\
& - \theta(t_2 - t_1) \frac{e^{-i\bar{\varepsilon}_j(t_2-t_1)}}{2} + \frac{i}{2\pi} e^{-i\bar{\varepsilon}_j(t_2-t_0)} e^{i\psi_{\alpha}(t_1, t_0)} e^{i\mu(t_1-t_0)} \bar{\Phi}(t_1 - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) \Bigg] \quad (4.4.9)
\end{aligned}$$

$$\begin{aligned}
(\Lambda_{\beta}^{-})^{\dagger}(t_2, t_1) = & \sum_j \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \Gamma_{\beta}}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[\frac{i}{2\beta} \int_{t_0}^{t_1} d\tau e^{-i\bar{\varepsilon}_j(t_1-\tau)} e^{i\mu(t_2-\tau)} e^{i\psi_{\beta}(t_2, \tau)} \operatorname{cosech} \left(\frac{\pi}{\beta} (t_2 - \tau) \right) \right]_{t_2 \neq \tau} \\
& + \theta(t_1 - t_2) \frac{e^{-i\bar{\varepsilon}_j(t_1-t_2)}}{2} + \frac{i}{2\pi} e^{-i\bar{\varepsilon}_j(t_1-t_0)} e^{i\psi_{\beta}(t_2, t_0)} e^{i\mu(t_2-t_0)} \bar{\Phi}(t_2 - t_0, \beta, -(\bar{\varepsilon}_j - \mu)) \Bigg] \quad (4.4.10)
\end{aligned}$$

With these formulas, we have reduced every term in the two-time correlation function into a summation over single or double time integrals.

Chapter 5

Quantum Transport in Response to a Time-Dependent Bias

5.1 Introduction

In this Chapter the methodology developed in Chapters 2-4 will be used to study the time-dependent response of the current and current noise to a particular kind of bias, namely a bias containing a constant shift added to a periodic term. The current and noise response to a periodic time-dependent bias has been the subject of much experimental and theoretical investigation, as detailed in the overview of Chapter 1. In Section 5.2, we apply the formalism developed in Chapter 2 to a single level quantum dot system with a single periodically-varying term added to the bias. Calculations (previously published in Ref. [1]) of the current Eq. (2.6.10) are carried out on this system, and the frequency integrals in the current formula are performed numerically due to its low dimensionality. Signatures of photon-assisted tunneling (PAT) are seen in the time-dependent current characteristics, and we observe a ‘ringing’ oscillatory signal that derives from intrinsic energy scales of the system.

In Section 5.3 we introduce the concept of a pump current as the time-integrated net current through the nano-junction with a zero DC bias and lead-dependent AC bias. It turns out that, even when a periodic bias is applied that integrates to zero over a full time period, sufficient conditions can be derived for the pump current to have a finite value. We refer to this result as the *quantum pump symmetry theorem*. In Section 5.4, we first choose a double-harmonic periodic bias that satisfies the conditions of the quantum pump symmetry theorem for a finite pump current and derive explicit formulas for the current, lesser and greater Green’s functions for an arbitrarily large molecular system, using the general equations of Chapter 4. These equations are benchmarked against the numerical calculations of Section 5.2 and to test their physical content we go on to apply them to the cases of transport through quantum dot and linear molecular wire structures in Section 5.4.3. In particular, we study the evolution in time of the $I - V$ characteristics for dots and for molecular wires lying both perpendicular and parallel to the plane of the leads. These calculations numerically demonstrate that the transient oscillations in the current are strongly dependent upon the initial preparation of the system and they relax to step-like $I - V$ curves in the long-time limit. The same formalism is then used to illustrate novel finite-size effects in driven transport through extended molecules, including some results published in Ref. [2], which are to be found in Section 5.4.4.

In Section 5.5, we derive an explicit formula for the steady-state pump current in extended molecules for the biharmonic bias, and investigate the effects on the pump current of the frequency, Fermi level shift and dynamical time reversal symmetry-breaking in a quantum dot. Using the generic formula for the pump current in Eq. (5.5.2), we then show that it is equivalent to the well-known [85, 199] result in Eq. (1.4.27) of Chapter 1.

Finally, in Section 5.7, we turn our attention to calculations of the partition-free time dependent cross-correlations in response to either a DC or an AC driving bias. In Section 5.7.1 we perform calculations of the cross-lead current correlations in a molecular wire as a function of both the relative time τ and observation time t , and identify particular values of τ and t at which these correlations are maximized. By investigating the dependence of these resonant times on the length of the wire and the inter-site hopping strength, we conclude that they provide a signature of the traversal time for electrons crossing the system in both the steady state and transient cross-lead correlations. Finally, in Section 5.7.2 we compute cross-correlations in the N_s -site perpendicular molecular wire. By analyzing the cross-correlations in the time and frequency domains, we find that the resonant times t_{res} and τ_{max} that were identified in Section 5.7.1 in, respectively, the transient and steady-state cross correlations are *independent* of the applied bias. They instead depend upon the internal coupling λ and system size N_s in the same way as in the DC bias case. These timescales are therefore identified with the transit time for electronic information to cross the molecular junction.

5.2 A Single Level Toy Model

Before we use the formalism developed in Chapter 4 to study larger systems we investigate the physics contained in the formula (2.6.10) using a numerical study of the two-lead quantum dot junction described at the end of Section 2.8.2. This example and the discussion of results is contained in Ref. [1]. In addition to the assumptions used there, we assume that the two leads are symmetric, i.e. the coupling to each lead is identical: $\Gamma_L = \Gamma_R = \frac{1}{2}\Gamma$. We choose our zero of energy to be equal to the chemical potential by setting $\mu = 0$. Thus the intrinsic frequency scales of the system are given by the difference $|\varepsilon_0 - \mu|$ and by Γ . The temperature is set to a value which is an order of magnitude smaller than any other characteristic energy of the problem: $k_B T = 0.1$.

We consider a bias in the left lead that is switched on instantaneously at $t_0 = 0$ and thereafter sinusoidally varying in time with frequency Ω_L about a fixed value V_L , and a bias in the right lead that is set to zero:

$$V_L(t) = V_L + A_L \cos(\Omega_L t), \quad V_R(t) = 0, \quad t \geq t_0 = 0 \quad (5.2.1)$$

Either bias is zero at $t < 0$. This particular choice of the bias introduces two new energy scales into the problem: firstly, there is an intrinsic energy difference of $|\mu + V_L - \varepsilon_0|$ between the fixed point of the left lead Fermi level and the dot energy. In addition, there is a new energy scale set by the driving frequency Ω_L . When $A_L \neq 0$, this driving frequency causes the Fermi level of the left lead to vary on a timescale that is slower than the inverse plasmon frequency ω_p of the leads, so that at each time step there is a new energy gap which must be traversed for electron hopping between the quantum dot and the lead L to occur.

To evaluate the current in the left lead we use the generating function expansion for the Bessel functions in Eq. (1.4.29), so that the time integrals can be calculated analytically (cf. [154]). This puts the K_L time integral (2.5.68) into the form

$$K_L(t, 0; \omega) = i \sum_{r=-\infty}^{\infty} J_r \left(\frac{A_L}{\Omega_L} \right) G^r(\omega + V_L + r\Omega_L) \left[e^{-i(\omega + V_L + r\Omega_L - h^{eff})t} - 1 \right] \quad (5.2.2)$$

where $h^{eff} = h - i\Gamma/2$, while the K_R integral is simply

$$K_R(t, 0; \omega) = i G^r(\omega) \left[e^{-i(\omega - h^{eff})t} - 1 \right] \quad (5.2.3)$$

These are substituted into (2.6.10) to yield a frequency integral for the time-dependent current. One can separate

the resulting formula into three terms, two of which decay due to factors of $e^{-\Gamma(t-t_0)/2}$ and $e^{-\Gamma(t-t_0)}$, given as follows:

$$\begin{aligned}
I_L^{(1)}(t) = & e^{-\frac{\Gamma}{2}(t-t_0)} 4 \int \frac{d\omega}{2\pi} f(\omega - \mu) \Gamma_L \left[\text{Im} \left[e^{i(\omega+V_L-\varepsilon_0)(t-t_0)} e^{i\frac{A_L}{\Omega_L} \sin(\Omega_L t)} \right. \right. \\
& \times \left(\sum_r J_r \left(\frac{A_L}{\Omega_L} \right) G^r(\omega + V_L + r\Omega_L) e^{-ir\Omega_L t_0} - G^r(\omega) e^{-i\frac{A_L}{\Omega_L} \sin(\Omega_L t_0)} \right) \left. \right] \\
& + \text{Re} \left[\Gamma_L \sum_r J_r \left(\frac{A_L}{\Omega_L} \right) G^a(\omega + V_L + r\Omega_L) e^{i(\omega+V_L-\varepsilon_0)(t-t_0)} e^{ir\Omega_L t} \right. \\
& \times \left. \left(\sum_s J_s \left(\frac{A_L}{\Omega_L} \right) G^r(\omega + V_L + s\Omega_L) e^{-is\Omega_L t_0} - G^r(\omega) e^{i\frac{A_L}{\Omega_L} \sin(\Omega_L t_0)} \right) \right] \quad (5.2.4)
\end{aligned}$$

$$\begin{aligned}
I^{(2)}(t) = & e^{-\Gamma(t-t_0)} 2 \int \frac{d\omega}{2\pi} f(\omega - \mu) \Gamma_L^2 \left[2\text{Re} \left[\sum_r J_r \left(\frac{A_L}{\Omega_L} \right) e^{i\frac{A_L}{\Omega_L} \sin(\Omega_L t_0)} e^{-ir\Omega_L t_0} G^r(\omega + V_L + r\Omega_L) G^a(\omega) \right] \right. \\
& \left. - \sum_{r,s} J_r \left(\frac{A_L}{\Omega_L} \right) J_s \left(\frac{A_L}{\Omega_L} \right) G^r(\omega + V_L + r\Omega_L) G^a(\omega + V_L + s\Omega_L) e^{i\Omega_L(s-r)t_0} - G^r(\omega) G^a(\omega) \right] \quad (5.2.5)
\end{aligned}$$

The long-time behaviour of the current is therefore given by the remaining term in the current formula:

$$\begin{aligned}
\lim_{t_0 \rightarrow -\infty} I_L(t) = & \frac{2}{\pi} \int d\omega f(\omega - \mu) \Gamma_L \text{Im} \left[\sum_r J_r \left(\frac{A_L}{\Omega_L} \right) e^{-i\frac{A_L}{\Omega_L} (\sin(\Omega_L t) - \sin(\Omega_L t_0))} e^{ir\Omega_L t} G^a(\omega + V_L + r\Omega_L) \right. \\
& \left. - \sum_{r,s} J_r \left(\frac{A_L}{\Omega_L} \right) J_s \left(\frac{A_L}{\Omega_L} \right) e^{i(s-r)\Omega_L t} G^r(\omega + V_L + r\Omega_L) \Gamma_L G^a(\omega + V_L + s\Omega_L) - G^r(\omega) \Gamma_R G^a(\omega) \right] \quad (5.2.6)
\end{aligned}$$

which may then be calculated numerically. In the following we shall plot the resulting current in the left lead, $I_L(t)$, for various combinations of the parameters of the problem, using *Mathematica* to perform the frequency integrals. These plots will also exhibit the suitably normalized time dependent bias (dotted line) as well as the prediction of the current calculated using the steady-state (SS) expression for the current at the instantaneous value of the bias (red line):

$$I_L^{(LB)} = \frac{\Gamma^2}{4\pi} \int d\omega \frac{[f(\omega - V - \mu) - f(\omega - \mu)]}{(\omega - \varepsilon_0)^2 + (\Gamma/2)^2} \quad (5.2.7)$$

The exact TD current response calculated using our new formula will be shown by a black line. Comparison of the exact current with the one calculated using the SS expression is intended to illustrate the additional effects that can be captured with an exact TD approach.

We illustrate the set-up schematically in Fig. 5.2.1(a) for the parameterisation $\varepsilon_0 = 1$, $\mu = 0$, $V_L = 5$ and $A_L = 4$. In this particular case, the effect of the bias is to cause the Fermi level of the left lead to move down and ‘touch’ the dot energy, before being removed far away from ε_0 . The corresponding time-dependence of the current is displayed in Fig. 5.2.1(b) for $\Gamma = 1$ and $\Omega_L = 1$. It has several features in common with all calculated currents we shall discuss below.

To understand the steady-state current, we can take the zero temperature limit of the formula (2.8.14) for the two lead case we are considering. This gives the following expression for the current:

$$\lim_{t_0 \rightarrow -\infty, T \rightarrow 0} I_L(t) = \frac{\Gamma}{2\pi} \left[\arctan \left[\frac{\mu + V_L - \varepsilon_0}{\Gamma/2} \right] - \arctan \left[\frac{\mu - \varepsilon_0}{\Gamma/2} \right] \right] \quad (5.2.8)$$

This has a roughly linear or ohmic behaviour when the chemical potential is within $\frac{1}{2}\Gamma$ of ε_0 and saturates otherwise, as seen in the red curve in Fig. 5.2.1(b). The curve follows the bias for low bias, but is cut-off at higher bias.

Our results on the time-dependent current were obtained by numerically carrying out the frequency integrals in Eqs. (5.2.4), (5.2.5) and (5.2.6) using *Mathematica*. They all show a rapidly varying transient that relaxes to a periodic steady-state solution on a timescale of $2/\Gamma$, a fact which can be predicted from the terms multiplied by exponential factors $e^{-\Gamma t}$ and $e^{-\Gamma t/2}$ in the analytic formulas (5.2.4) and (5.2.5). All plots therefore exhibit at least two effects: the transient reaction to the switch-on event and the time-varying current due to the persistent bias oscillations. This much can be seen from the graph in Fig. 5.2.1 (b), where for times greater than $2/\Gamma$, the current response is periodic with a period of $\tau_L = 2\pi/\Omega_L$. In addition to these two features, we observe a ‘ringing’ oscillation of the current (first observed in Ref. [154]) occurring within each period, leading to asymmetry of the current about those voltage peaks located at multiples of 2π . This ‘ringing’ signal is evidence of an internal frequency of the system at which resonances in the current signal occur on a shorter timescale than τ_L . It consists of a series of peaks which are damped consecutively before tending to flatten, and which then agree for a short time with the steady-state formula. We also observe that, although the steady-state current is always in phase with the voltage, the minimum of the exact current is delayed with respect to the voltage.

Let us first consider the effect on this system of varying the dot energy level. This is done in steps of unit energy, and the resulting plots for the current as a function of time are shown in Fig. 5.2.2 (a)-(d). It is clear from these plots that the frequency of the ‘ringing’ oscillations of the TD current is determined by the position of the dot relative to the two Fermi levels. In particular, it seems that the frequency of these oscillations is roughly equal to the energy gap $|\mu + V_L - \varepsilon_0|$, as each unit increase in ε_0 tends to flatten or remove a peak from the ‘ringing’ transient. The dependence of this effect on the left gap alone can be checked by moving V_L and ε_0 by the same amount; indeed our calculations demonstrate that this leaves the number of ‘ringing’ peaks unchanged. When the gap $|\mu + V_L - \varepsilon_0|$ is equal to zero (Fig. 5.2.2 (d)), the ‘ringing’ ceases to be significant, although an asymmetric peak after the minimum of the bias is still present, as discussed above. This is not surprising, because when $\varepsilon_0 = V_L$ the time-dependent shift in the Fermi level of the left lead is symmetric about ε_0 . In the time domain, we interpret the ‘ringing’ current signal as an outcome of competing intrinsic timescales: the timescale of tunnelling from the left lead onto the dot is smaller than the typical lifetime of an electron in the dot state, given by $\tau_{el} \sim 2/\Gamma$. It is apparent from the Figs. 5.2.2 (a)-(d) that the possibility for a negative current is also determined by the position of the dot energy relative to the left Fermi level, and that the minima of the current becomes increasingly negative as ε_0 is brought closer to V_L . A schematic illustration of the energetics involved is shown in Fig. 5.2.3: the external electromagnetic field excites electrons in the left lead with photons of energy $n\Omega_L$, where n is some integer. Additional pathways for electrons to tunnel onto the dot appear with the creation of energy side bands at $V_L + n\Omega_L$, in accordance with the discussion of photon-assisted tunneling in Section 1.4.2.2. The dominant transport channel is provided by the $n = 0$ band, as in this energy state is weighted most strongly in the transmission function, with the Bessel function $J_0\left(\frac{A_L}{\Omega_L}\right)$. This dominant channel corresponds to the intrinsic resonant energy gap of $|\mu + V_L - \varepsilon_0|$, and the relative weight of the side bands is indicated by the length of the horizontal lines beside each side band in Fig. 5.2.3.

In Figs. 5.2.4 (a-d), we plot (in units of the fundamental frequency Ω_L) the Fourier transform of the current signals in Figs. 5.2.2 (a-d):

$$\mathcal{F}[I_L(t); \omega] \equiv \int_{-\infty}^{\infty} dt e^{i\omega\tau} I_L(t) \quad (5.2.9)$$

We see that as ε_0 approaches V_L in Figs. 5.2.4 (a-c), the resonant peak at the fundamental frequency $\omega = \Omega_L$

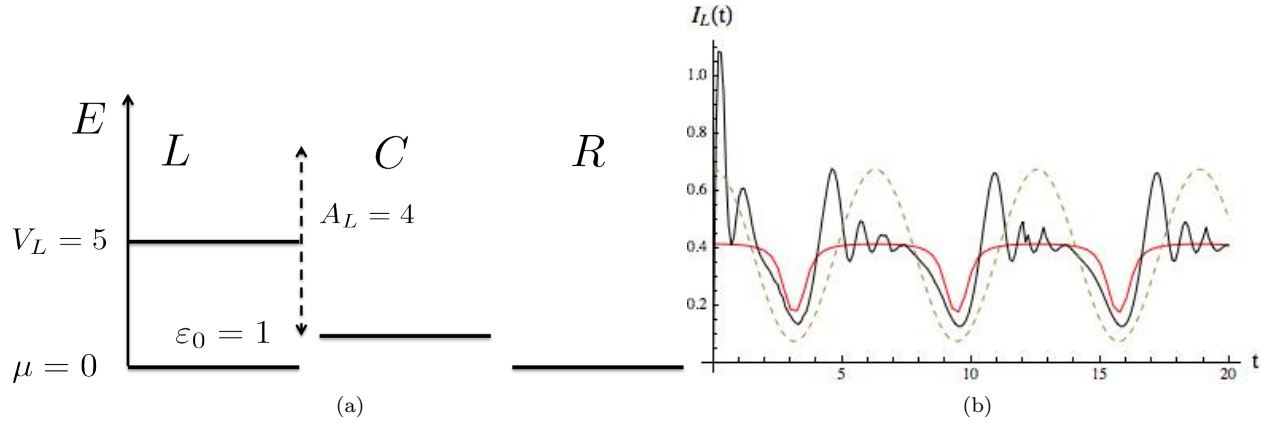


Figure 5.2.1: The basic system we are considering, with parameters $\Gamma = 1$, $\varepsilon_0 = 1$, $\mu = 0$, $V_L = 5$, $A_L = 4$, $\Omega_L = 1$. This system is illustrated schematically in (a), and the time-dependent current in the left lead is shown in (b), computed from the steady state LB formula (red line) and using our TD-bias TD-LB method (black line). The AC driving voltage is shown with the dashed line.

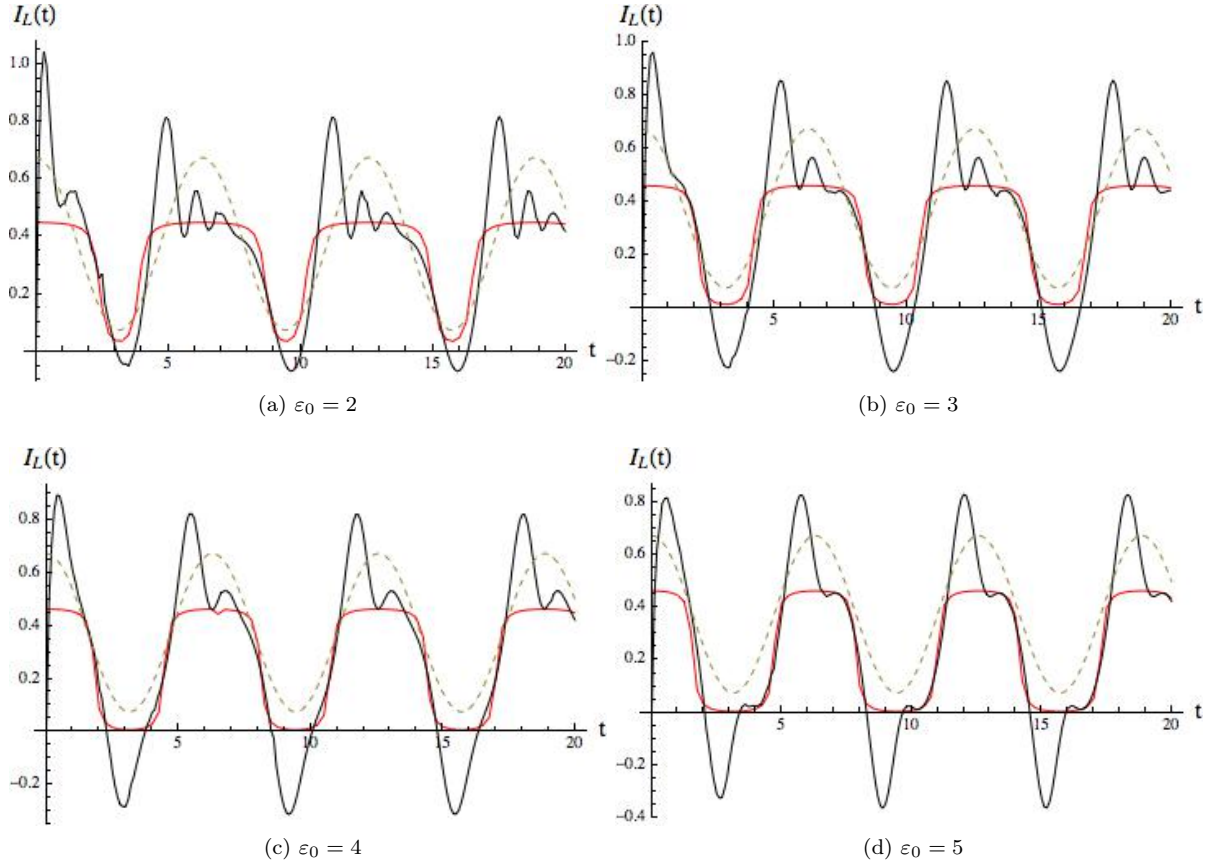


Figure 5.2.2: The effect of varying the dot energy. As ε_0 is moved closer to V_L , the intrinsic frequency of the 'ringing' oscillations is increased.

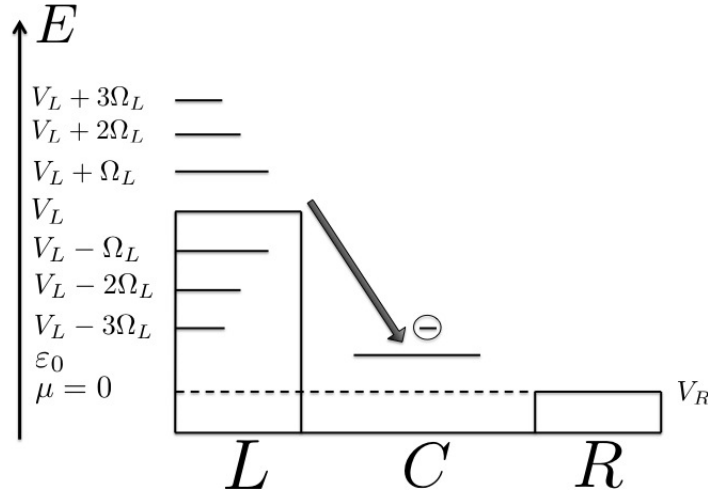


Figure 5.2.3: Energy diagram of the photon-assisted resonant tunneling seen in the single-level system.

increases sharply, because the gap between the average value of the left lead Fermi level and ϵ_0 approaches 0. Interestingly, at $V_L = \epsilon_0$ (shown in Fig. 5.2.4 (d)), all resonances $n\Omega_L$ at even values of n vanish. This is because the current in Fig. 5.2.2 (d) is symmetric about a fixed point of $I_{mid} \sim 0.225$, as the movement of the left Fermi level is symmetric around ϵ_0 . More formally, in this case we can write the periodic current at long times as

$$\lim_{t_0 \rightarrow -\infty} I_L(t) = I_{mid} + I'_L(t) \quad (5.2.10)$$

where $I'_L(t)$ satisfies the antisymmetry property

$$I'_L(t) = -I'_L(t + \pi) \quad (5.2.11)$$

If we then represent this in terms of its Fourier series, $I'_L(t) = \sum_{n=-\infty}^{\infty} c_n e^{-in\Omega_L t}$, it is easy to show that the relation (5.2.11) implies that only the odd n harmonics survive. It should be noted here that additional oscillation frequencies in the current can be observed in transport schemes that go beyond the WBLA; in particular, for narrow-band electrodes transitions from the band edge to ϵ_0 may occur [293]. The WBLA effectively pushes the bottom of the band to minus infinity so that the time scale associated with these transitions is negligible.

Next, we consider the effects on the current response of varying the driving frequency. One would intuitively expect that, as the driving frequency of the bias is lowered, the agreement between our TD formula and the LB formula for the SS current becomes better as the bias varies more slowly, suggesting that the LB formula derived for the case of a static bias would become appropriate. In Fig. 5.2.5, all parameters, except for the bias frequency, are the same as in Fig. 5.2.1 (b). In Fig. 5.2.5 (a) the driving frequency of the bias was scaled down to $\Omega_L = 0.1$. One can see that in this adiabatic limit there is excellent agreement with the steady-state formula, with the exception of a quickly oscillating transient following t_0 , and a very quickly suppressed single ‘ringing’ peak. In Fig. 5.2.5 (b), the driving frequency is scaled up to $\Omega_L = 10$, with the effect that the current response deviates significantly from that given by the LB formula. Interestingly, in this high frequency case it takes around 4 to 5 bias cycles for the current to stabilise into steady oscillations. In addition, a phase-shift of the current response with respect to the steady-state value is clearly visible. During the transient regime, the amplitude of the exact current disagrees with the steady state current at all times. The amplitude of the exact current at the bias peaks is much greater than the amplitude of the current in the long-time regime.

In Fig. 5.2.6 we consider the effect of varying the level width Γ , where all other parameters are fixed at the same

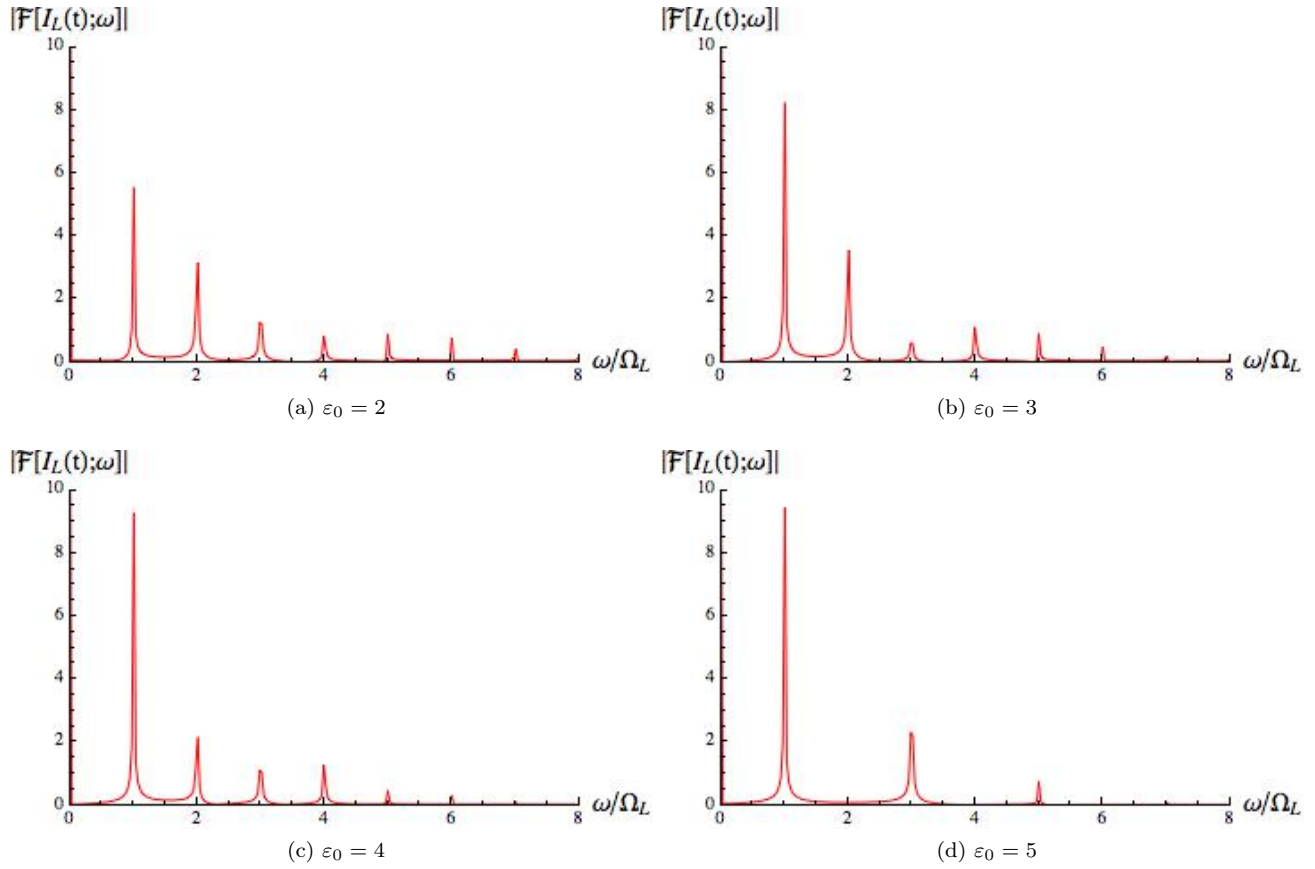


Figure 5.2.4: The Fourier spectra of $I_L(t)$ for each value of ε_0 considered in the time domain in Fig. 5.2.2, in units of the fundamental driving frequency Ω_L .

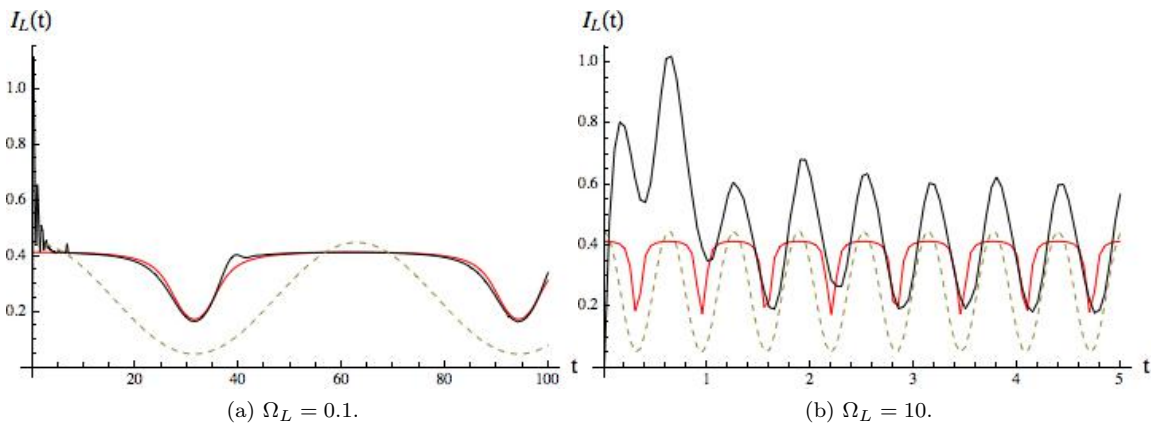


Figure 5.2.5: The effect of varying the driving frequency, with all other parameters as in Fig. 5.2.1(b). In (a), we see that our formula gives a good agreement with the steady-state LB formula, as this is tending towards the adiabatic limit. In (b), the high driving frequency causes the current to be phase-delayed, and also to strongly disagree with the LB formula in amplitude.

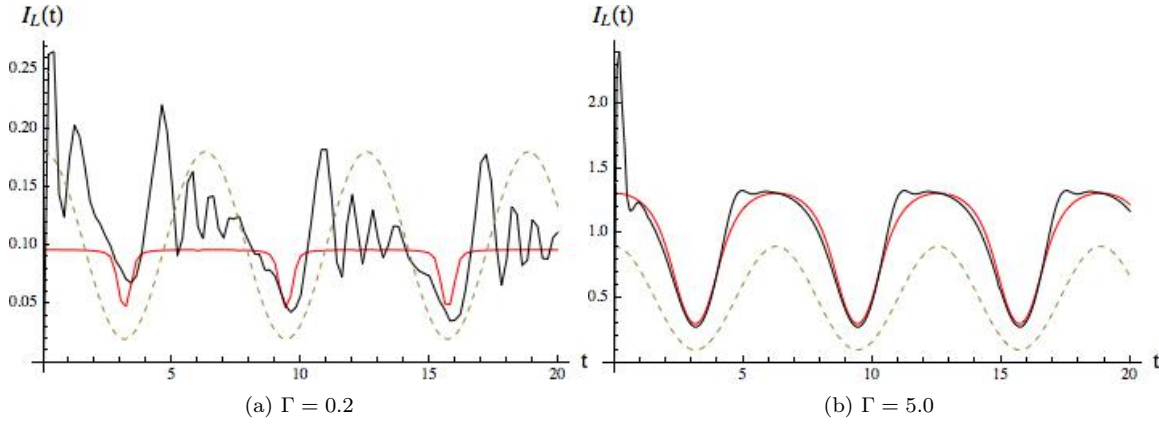


Figure 5.2.6: We exhibit the effects of varying the level width, where all other parameters as in Fig. 5.2.1(b). We find that Γ tends to suppress any non-adiabatic features as it increases in magnitude.

values as in Fig. 5.2.1(b). As discussed above, this quantity fixes the timescale over which the transient current decays. We display the effects of setting $\Gamma = 0.2$ in panel (a). We see that this has the effect of prolonging the transient and of accentuating the ‘ringing’ peaks in the TD current, without adding any new peaks to this part of the signal. In Fig. 5.2.6(b) the level width $\Gamma = 5.0$; we see that for $t > 2.5 = \tau_{el}$, the TD formula is periodic, but it is also interesting to note that the ‘ringing’ oscillations are greatly suppressed, in a manner which is qualitatively similar to the suppression observed above for an adiabatic driving frequency, Fig. 5.2.5(a). Interpreting Γ as the frequency with which electrons tunnel on and off the dot, we see that in this case it is greater than any other typical energy gap in the problem, so that the time scale with which electrons tunnel onto the dot is greater than that with which they escape.

We also investigate the effect of decreasing the amplitude A_L of the bias oscillations about the fixed point V_L , and the result for $A_L = 2$ is shown in Fig. 5.2.7. The main effects observed in Fig. 5.2.1 (b) are present, but as the left Fermi level never comes all the way down to ‘touch’ ε_0 , there is relatively little ‘ringing’ in the TD current in addition to the SS behaviour. In the temperature regime we are considering, Eq. (5.2.8) is in close agreement with the SS formula at all values of the time-dependent bias inserted into V_L . Large variations of the bias bring it closer to ε_0 , where the arctan function varies most rapidly. For an oscillation amplitude that simply moves the bias by a small amount around a value of V_L which is much larger than ε_0 , the SS current will move up and down an asymptote of the arctan function and remain almost static, becoming completely static as $A_L \rightarrow 0$. Finally, we can see in Fig. 5.2.8 that increasing the system temperature so that $k_B T = 1.0$ has the effect of suppressing the ‘ringing’ peaks on the current signal. Increasing the temperature thus has a qualitatively similar effect to an increase in Γ . In Chapter 6 the effect of temperature change on the time-dependent dynamics will be discussed further, in the context of a stochastic driving bias.

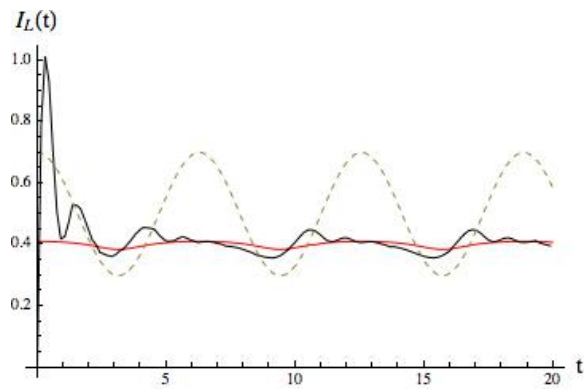


Figure 5.2.7: Effect on the current response of reducing the bias amplitude from $A_L = 4$ (as in Fig. 5.2.1 (b)) to $A_L = 2$.

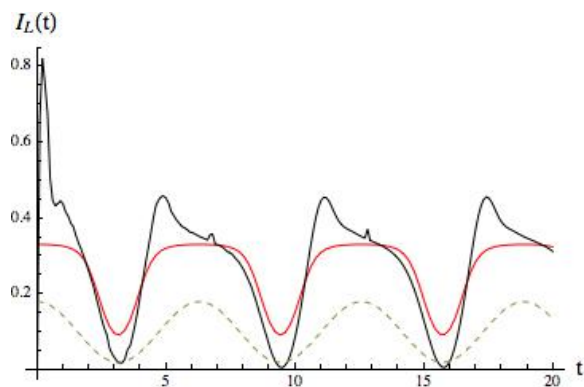


Figure 5.2.8: The high temperature behaviour of the current is investigated. Here we plot the TD current for $k_B T = 1.0$, and all other parameters are as in Fig. 5.2.1 (b).

5.3 The Quantum Pump

The idea of defining the direction of time by reference to the loss of order in asymmetric nonequilibrium processes is an old one [294]. Conversely, it is sometimes possible to induce a nonequilibrium process that breaks the spatial symmetry of current flow by introducing a term in the Hamiltonian that breaks time-reversal (TR) symmetry. Choosing $\Omega_\alpha = \Omega_D = \Omega_\beta$ to be the fundamental driving frequency of the periodic signal in the leads, we now define the pump current (also referred to as the DC component of the current in the literature [101, 92]) at time τ after the switch-on time:

$$I_{\alpha\beta}^{(pump)}(\tau) \equiv \frac{\Omega_D}{2\pi} \int_{\tau}^{\tau + \frac{2\pi}{\Omega_D}} dt (I_\alpha(t) - I_\beta(t)) \quad (5.3.1)$$

There may be conditions under which a finite pumping current exists in the transient regime following the switch-on, but not in the steady-state limit, when transient modes in the current have decayed to zero. We would like to define general conditions under which this is *not* true, i.e. we wish to investigate *stable* quantum pumps generated by dynamical driving fields satisfying the following condition:

$$\lim_{t_0 \rightarrow -\infty} I_{\alpha\beta}^{(pump)}(\tau) \neq 0 \quad (5.3.2)$$

We work in the long time limit, because in this limit the charge pumped per cycle should have settled into a steady-state value. In this limit, it was shown in Chapter 2 that the long time current can be expressed as

$$\begin{aligned} \lim_{t_0 \rightarrow -\infty} I_\alpha(t) = \lim_{t_0 \rightarrow -\infty} \frac{1}{\pi} \int d\omega f(\omega - \mu) \text{Tr}_C \left\{ 2\text{Re} \Gamma_\alpha e^{i(\omega - \mathbf{h}^{eff})(t-t_0)} e^{i\psi_\alpha(t, t_0)} \mathbf{K}_\alpha(t, t_0; \omega) \right. \\ \left. - e^{-i\mathbf{h}^{eff}(t-t_0)} \Gamma_\alpha \sum_\gamma \mathbf{K}_\gamma(t, t_0; \omega) \Gamma_\gamma \mathbf{K}_\gamma^\dagger(t, t_0; \omega) e^{i(\mathbf{h}^{eff})^\dagger(t-t_0)} \right\} \end{aligned} \quad (5.3.3)$$

where we defined the $\mathbf{K}_\alpha$ matrices in Eq. (2.5.68). In addition, we drop the tilde on the effective hamiltonian and assume any time dependence of the central region to lie in ψ_α , i.e. any time-dependence in C will be incorporated as a lead-independent term in the bias $V_\alpha(t)$. We impose that the bias driving the system is periodic with a basic driving frequency of Ω_D ,

$$V_\alpha(t) = V_\alpha \left(t + \frac{2\pi}{\Omega_D} \right) \quad (5.3.4)$$

We can then show that the phase factor of the bias is periodic, and can therefore be represented as a Fourier Series with undetermined coefficients:

$$e^{-i\psi_\alpha(t, -\infty)} = \exp \left(-i \int_{-\infty}^t d\tau V_\alpha(\tau) \right) = \exp \left(-i \int_{-\infty}^{t - \frac{2\pi}{\Omega_D}} d\tau V_\alpha(\tau) \right) \quad (5.3.5)$$

$$= \sum_n c_n^\alpha e^{-in\Omega_D t} \quad (5.3.6)$$

Here, we introduce the Fourier coefficient:

$$c_n^\alpha = \frac{\Omega_D}{2\pi} \int_0^{\frac{2\pi}{\Omega_D}} dt e^{-i\psi_\alpha(t, -\infty)} e^{in\Omega_D t} \quad (5.3.7)$$

If, in addition, the bias is TR-symmetric, $V_\alpha(t) = V_\alpha(-t)$, then the phase factor satisfies another useful property in the long-time regime:

$$\begin{aligned} e^{-i\psi_\alpha(t, -\infty)} &= \exp\left(-i \int_{-\infty}^t d\tau V_\alpha(-\tau)\right) = \exp\left(i \int_{-\infty}^{-t} d\tau V_\alpha(\tau)\right) \exp\left(i \int_{-\infty}^{\infty} d\tau V_\alpha(\tau)\right) \\ &= \left[e^{-i\psi_\alpha(-t, -\infty)}\right]^* \end{aligned} \quad (5.3.8)$$

Thus, from the identity (5.3.6) we conclude that the Fourier coefficients must satisfy the property

$$c_n^\alpha = c_n^{\alpha*} \in \mathbb{R} \quad (5.3.9)$$

Thus, any bias which breaks TR symmetry leads to a phase with complex Fourier coefficients $c_n^\alpha = |c_n^\alpha| e^{i\phi_\alpha^{(n)}}$. The bias itself can always be represented as a sum of N periodic terms with frequencies that are integer multiples of Ω_D ,

$$V_\alpha(t) = \sum_{n=1}^N V_\alpha^{(n)}(t) = \sum_{n=1}^N V_\alpha^{(n)}\left(t + \frac{2\pi}{p_n \Omega_D}\right) \quad (5.3.10)$$

where p_n is an integer depending on the position n in the series. For example the Fourier Series of $V_\alpha(t)$ has the form of Eq. (5.3.10) with $N \rightarrow \infty$ and with the p_n ranging from minus to plus infinity. The trivial case of $N = 1$ and $p_1 = 1$ returns us to the basic periodic form (5.3.4), but it should be noted that whereas the full signal $V_\alpha(t)$ has a time period of $\frac{2\pi}{\Omega_D}$, it does not have the periodicity $\frac{2\pi}{p_n \Omega_D}$ of its constituent terms. This allows us to study not just the periodicity of the driving field, but also the decomposition of the driving field into harmonics of the fundamental driving frequency and the effect of the interplay of these harmonics on the pump current. With the representation of Eq. (5.3.10), the exponential phase factor is a product of periodic functions:

$$\begin{aligned} e^{-i\psi_\alpha(t, -\infty)} &= \exp\left(-i \int_{-\infty}^t d\tau V_\alpha(\tau)\right) = \prod_{n=1}^N \exp\left(-i \int_{-\infty}^t d\tau V_\alpha^{(n)}(\tau)\right) \\ &= \prod_{n=1}^N \exp\left(-i \int_{-\infty}^{t - \frac{2\pi}{p_n \Omega_D}} d\tau V_\alpha^{(n)}(\tau)\right) \end{aligned} \quad (5.3.11)$$

Each term in this product can therefore be expressed as a Fourier Series, as in Eq. (5.3.4):

$$e^{-i\psi_\alpha(t, -\infty)} = \sum_{m_1 \dots m_N} c_{m_1}^\alpha \dots c_{m_N}^\alpha e^{-i\Omega_D(p_1 m_1 + p_2 m_2 + \dots + p_N m_N)t} \quad (5.3.12)$$

Where the $c_{m_i}^\alpha$ are undetermined lead-dependent Fourier coefficients whose value depends upon the particular form of $V_\alpha^{(i)}(t)$. When we substitute Eq. (5.3.12) into Eq. (5.3.3) and evaluate the time integrals, one obtains:

$$\begin{aligned}
\lim_{t_0 \rightarrow -\infty} (I_\alpha(t) - I_\beta(t)) &= \frac{1}{\pi} \int d\omega f(\omega - \mu) \sum_{\substack{m_1, \dots, m_N \\ l_1, \dots, l_N}} \text{Tr}_C \left[2\text{Re} \left[i \left(\Gamma_\alpha c_{m_1}^\alpha c_{l_1}^{\alpha*} \dots c_{m_N}^\alpha c_{l_N}^{\alpha*} - \Gamma_\beta c_{m_1}^\beta c_{l_1}^{\beta*} \dots c_{m_N}^\beta c_{l_N}^{\beta*} \right) \right. \right. \\
&\quad \times e^{-i\Omega_D(p_1(m_1-l_1)+\dots+p_N(m_N-l_N))t} \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \left. \right] \\
&\quad - (\Gamma_\alpha - \Gamma_\beta) c_{m_1}^\gamma c_{l_1}^{\gamma*} \dots c_{m_N}^\gamma c_{l_N}^{\gamma*} e^{-i\Omega_D(p_1(m_1-l_1)+\dots+p_N(m_N-l_N))t} \\
&\quad \times \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \Gamma_\gamma \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N)) \left. \right] \quad (5.3.13)
\end{aligned}$$

Note that the expression (5.3.13) is periodic with time period $2\pi/\Omega_D$, and therefore the long-time pump current can be evaluated over the integration range $[0, 2\pi/\Omega_D]$:

$$\begin{aligned}
I_{\alpha\beta}^{(pump)} &\equiv \lim_{t_0 \rightarrow -\infty} I_{\alpha\beta}^{(pump)}(\tau) = \frac{\Omega_D}{2\pi} \int_0^{\frac{2\pi}{\Omega_D}} dt \lim_{t_0 \rightarrow -\infty} (I_\alpha(t) - I_\beta(t)) \\
&= \frac{1}{\pi} \int d\omega f(\omega - \mu) \sum_{\substack{m_1, \dots, m_N \\ l_1, \dots, l_N}} \delta_{m_i l_i}(N) \text{Tr}_C \left[2\text{Re} \left[i \left(\Gamma_\alpha c_{m_1}^\alpha c_{l_1}^{\alpha*} \dots c_{m_N}^\alpha c_{l_N}^{\alpha*} - \Gamma_\beta c_{m_1}^\beta c_{l_1}^{\beta*} \dots c_{m_N}^\beta c_{l_N}^{\beta*} \right) \right. \right. \\
&\quad \times \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \left. \right] \\
&\quad - (\Gamma_\alpha - \Gamma_\beta) \sum_\gamma c_{m_1}^\gamma c_{l_1}^{\gamma*} \dots c_{m_N}^\gamma c_{l_N}^{\gamma*} \\
&\quad \times \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \Gamma_\gamma \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N)) \left. \right] \quad (5.3.14)
\end{aligned}$$

Here we make the definition:

$$\delta_{m_i l_i}(N) \equiv \begin{cases} 1, & p_1(m_1 - l_1) + \dots + p_N(m_N - l_N) = 0 \\ 0, & \text{else} \end{cases} \quad (5.3.15)$$

For instance, when $N = 2$, this can be written:

$$\delta_{m_i l_i}(N) = \delta_{p_1 m_1, p_1 l_1} \delta_{p_2 m_2, p_2 l_2} + \delta_{p_1 m_1, p_2 l_2} \delta_{p_2 m_2, p_1 l_1} + \delta_{p_1 m_1, -p_2 m_2} \delta_{p_1 l_1, -p_2 l_2} \quad (5.3.16)$$

To simplify Eq. (5.3.14), we use the identity:

$$\mathbf{G}^r(\omega + A) - \mathbf{G}^a(\omega + B) = \mathbf{G}^r(\omega + A)(B - A - i\Gamma)\mathbf{G}^a(\omega + B) \quad (5.3.17)$$

thereby obtaining:

$$\begin{aligned}
I_{\alpha\beta}^{(pump)} = & \frac{1}{\pi} \int d\omega f(\omega - \mu) \sum_{\substack{m_1, \dots, m_N \\ l_1, \dots, l_N}} \delta_{m_i l_i}(N) \text{Tr}_C \left[\left(\Gamma_\alpha c_{m_1}^\alpha c_{l_1}^{\alpha*} \dots c_{m_N}^\alpha c_{l_N}^{\alpha*} - \Gamma_\beta c_{m_1}^\beta c_{l_1}^{\beta*} \dots c_{m_N}^\beta c_{l_N}^{\beta*} \right) \right. \\
& \times [\mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) (\mathbf{\Gamma} - i(p_1(m_1 - l_1) + \dots + p_N(m_N - l_N))) \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N))] \\
& \left. - (\Gamma_\alpha - \Gamma_\beta) \sum_\gamma c_{m_1}^\gamma c_{l_1}^{\gamma*} \dots c_{m_N}^\gamma c_{l_N}^{\gamma*} \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \Gamma_\gamma \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N)) \right] \quad (5.3.18)
\end{aligned}$$

Due to the presence of the generalized Kronecker function $\delta_{m_i l_i}(N)$, the second term on the second line of Eq. (5.3.18) vanishes, and after some cancellations we arrive at the following:

$$\begin{aligned}
I_{\alpha\beta}^{(pump)} = & \frac{1}{\pi} \int d\omega f(\omega - \mu) \sum_{\substack{m_1, \dots, m_N \\ l_1, \dots, l_N}} \delta_{m_i l_i}(N) \text{Tr}_C \left[\left(c_{m_1}^\alpha c_{l_1}^{\alpha*} \dots c_{m_N}^\alpha c_{l_N}^{\alpha*} - c_{m_1}^\beta c_{l_1}^{\beta*} \dots c_{m_N}^\beta c_{l_N}^{\beta*} \right) \right. \\
& \times [\Gamma_\alpha \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \Gamma_\beta \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N)) \\
& + \Gamma_\beta \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \Gamma_\alpha \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N))] \\
& \left. - (\Gamma_\alpha - \Gamma_\beta) \sum_{\gamma \neq \alpha, \beta} c_{m_1}^\gamma c_{l_1}^{\gamma*} \dots c_{m_N}^\gamma c_{l_N}^{\gamma*} \mathbf{G}^r(\omega + \Omega_D(p_1 m_1 + \dots + p_N m_N)) \Gamma_\gamma \mathbf{G}^a(\omega + \Omega_D(p_1 l_1 + \dots + p_N l_N)) \right] \quad (5.3.19)
\end{aligned}$$

We can immediately derive from equation (5.3.19) some general rules for different numbers of harmonics. To focus on the effect of TR symmetry-breaking, we assume that for all terms except the j -th, the coefficients in each lead are TR symmetric. The j -th harmonic in lead β is assumed TR symmetric, and therefore real (by relation (5.3.9)), whereas the j -th harmonic in lead α is assumed to break the TR symmetry, so it must be complex. We also assume that the coefficients of the j -th harmonic have the same magnitude in each lead (i.e. that the *only* difference between harmonics in leads α and β is the broken TR symmetry of the latter), so that they are related by a multiplicative phase factor only

$$c_{m_j}^\alpha = c_{m_j}^\beta e^{i\phi_{m_j}^\alpha} \quad (5.3.20)$$

Finally we are in a position to prove some general results for different choices of N :

(i) $N = 1$

In the single harmonic case, coefficients of the different leads are related by a multiplicative phase factor, and so we obtain:

$$\sum_{m_1, l_1} \left(c_{m_1}^\alpha c_{l_1}^{\alpha*} - c_{m_1}^\beta c_{l_1}^{\beta*} \right) \delta_{m_i l_i}(1) = \sum_{m_1} \left(|c_{m_1}^\alpha|^2 - |c_{m_1}^\beta|^2 \right) = 0 \quad (5.3.21)$$

This is exactly the case when the bias (5.4.1) is used with lead-independent V_α and A_α but a phase ϕ_α that does depend upon lead α . A pump current between leads α and β cannot be guaranteed in this case unless there are

more than two electrodes (if there are just two, then the final term in Eq. (5.3.19) is zero), and $\Gamma_\alpha \neq \Gamma_\beta$. For almost all systems of interest, therefore, $N = 1$ implies that $I_{\alpha\beta}^{(pump)} = 0$.

(ii) $N \neq 1$

If for all n_i , $c_{n_i}^\alpha = c_{n_i}^\beta$ then there would trivially be a zero pump current. However, the assumption (5.3.20) means that one can write:

$$\left(c_{m_1}^\alpha c_{l_1}^{\alpha*} \dots c_{m_N}^\alpha c_{l_N}^{\alpha*} - c_{m_1}^\beta c_{l_1}^{\beta*} \dots c_{m_N}^\beta c_{l_N}^{\beta*} \right) = \left(c_{m_1}^\alpha c_{l_1}^{\alpha*} \dots c_{m_{j-1}}^\alpha c_{l_{j-1}}^{\alpha*} c_{m_{j+1}}^\alpha c_{l_{j+1}}^{\alpha*} \dots c_{m_N}^\alpha c_{l_N}^{\alpha*} \right) c_{m_j}^\alpha c_{l_j}^{\alpha*} \left(e^{i(\phi_{m_j}^\alpha - \phi_{l_j}^\alpha)} - 1 \right) \quad (5.3.22)$$

The generalized Kronecker $\delta_{m_i l_i}(N)$ does retain a term in which $m_j = l_j$, in which case the pump current vanishes, but it also returns a term which equals 1 when, for example, $p_j m_j = p_N l_N$ and $p_j l_j = p_N m_N$, as illustrated in the expansion (5.3.16) for $N = 2$. This term will be finite, giving a non-zero pump current in general. We have therefore proven a general result, which we refer to as the *quantum pump symmetry theorem*:

If (i) $V_\alpha(t)$ and/or $V_\beta(t)$ is given by a sum of more than one harmonic with frequencies that are all integer multiples of Ω_D , (ii) in at least one of the leads, TR symmetry is broken in at least one of the harmonics, and (iii) the voltages satisfy $V_\alpha(t) \neq V_\beta(t)$, then there is a non-zero net pump current running between the α and β leads.

Out of conditions (i)-(iii), condition (iii) of this theorem is the only *necessary* condition for a pump current to exist, as there can be no pump current if the bias in each lead is identical. The additional satisfaction of conditions (i) and (ii) together with (iii) constitutes a *sufficient*, but *unnecessary* condition for the existence of a non-zero pump current, i.e. the stronger statement that the existence of a non-zero pump current requires (i) and (ii) to hold in addition to (iii) is not true. A pump current could exist, for instance, if TR symmetry was broken in one of the leads without the additional assumption that the relation (5.3.20) holds, which would be true if, e.g. the amplitude of the driving signal was different in each lead. This quantum pump symmetry theorem however gives experimentalists a means of generating a net current per driving cycle with zero net bias per cycle and with no difference in the amplitude of driving signals across the terminals of a nanodevice. It should also be noted that in the so-called quantum ratchet effect, spatial asymmetry of the junction in addition to a periodic driving is used to generate a pumped current [93], but according to the quantum pump symmetry theorem proven here, the system may be completely spatially symmetric, so that $\Gamma_\alpha = \Gamma_\beta$, and still there will be a reliable rectified current if the purely dynamical conditions (i)-(iii) of this theorem are satisfied. Calculations of the pump current through such a spatially symmetric system will be presented in Section 5.5.

5.4 Calculations of the Time-Dependent Current

5.4.1 Basic Formulas and Benchmarking

The quantum pump symmetry theorem tells us that, all else being equal between the biases in different leads, broken TR symmetry alone is not enough to generate a pump current. In addition to broken TR symmetry, harmonics with higher fundamental frequencies than the basic driving frequency should be present in the driving field. We have in Section 5.2 already implemented the current in lead L of an $L - C - R$ junction for a sinusoidal bias of the form:

$$V_\alpha(t) = V_\alpha + A_\alpha \cos(\Omega_\alpha(t - t_0) + \phi_\alpha) \quad (5.4.1)$$

where the phase shift ϕ_α was set to zero in those calculations. Note here that the origin of the cosine is taken to be the switch-on time t_0 , because we wish to study the short-time transient in the current response. The quantum

pump symmetry theorem was proven for pumping at long times, so when one is in this regime one can pick some finite time ‘origin’ $t_0 = 0$ to eliminate all remaining dependence on the parameter t_0 in formulas for the current. Given that one is in this regime, setting $\phi_\alpha = 0$ in Eq. (5.4.1) for all leads α means that the system Hamiltonian in Eqs. (2.2.6)-(2.2.8) is invariant under the TR transformation:

$$t \rightarrow -t \quad (5.4.2)$$

More generally, TR symmetry is broken unless ϕ_α takes the same value ϕ for all α , in which case one could just shift the zero of time so that the TR symmetry condition in Eq. (5.4.2) is replaced by invariance under the transformation

$$t \rightarrow -\frac{2\phi}{\Omega_D} - t \quad (5.4.3)$$

So TR symmetry of the system Hamiltonian is broken whenever the phase shift ϕ_α is *not* the same in every lead. However, even in this case the driving field is not sufficient to get a pump current as it does not satisfy condition (i) of the quantum pump symmetry theorem proven in Section 5.3, requiring higher frequency harmonics in addition to the fundamental driving frequency. Even though with the choice of bias in Eq. (5.4.1) the local Hamiltonian of a single bare lead cannot break TR symmetry, the global Hamiltonian corresponding to the leads, $\sum_{k\alpha\sigma} (\varepsilon_{k\alpha} + V_\alpha(t)) \hat{d}_{k\alpha\sigma}^\dagger \hat{d}_{k\alpha\sigma}$ can have broken TR symmetry due to the relative phase shift between the different $V_\alpha(t)$. To satisfy all three conditions of the quantum pump theorem, one can introduce a second harmonic in the bias with a time period that is some multiple of $2\pi/\Omega_D$:

$$V_\alpha(t) = V_\alpha + A_\alpha^{(1)} \cos(p_1 \Omega_\alpha (t - t_0) + \phi_\alpha) + A_\alpha^{(2)} \cos(p_2 \Omega_\alpha (t - t_0)) \quad (5.4.4)$$

Here p_1, p_2 are any integers. Plots of this bias with a second harmonic oscillating with twice the frequency of the first ($p_1 = 1, p_2 = 2$) are displayed for various values of the phase and different amplitudes of the second harmonic are shown in Fig. 5.4.1. Clearly the second higher frequency harmonic breaks the sinusoidal character of the bias when the amplitudes $A_\alpha^{(1)}$ and $A_\alpha^{(2)}$ are comparable. We note that in Ref. [269], measurements of the shot noise were carried out for an AC excitation with the lead independent bias $V(t) = V_{ac1} \cos(\Omega_D t) + V_{ac2} \cos(2\Omega_D t + \phi)$ added to a net (lead-dependent) DC bias V_{dc} . This can be accounted for by choosing $p_1 = 2$ in the first harmonic of Eq. (5.4.4), and $p_2 = 1$ in the second.

According to the identity (1.4.29), this choice of bias leads to the following representation of the exponential phase factor appearing in Eq. (2.6.10):

$$\begin{aligned} e^{i\psi_\alpha(t_1, t_2)} &= e^{iV_\alpha(t_1 - t_2)} \sum_{r, r', s, s'} J_r \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_{r'} \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_s \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) J_{s'} \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) \\ &\quad \times e^{i(r - r')\phi_\alpha} e^{i\Omega_\alpha(p_1 r + p_2 s)(t_1 - t_0)} e^{-i\Omega_\alpha(p_1 r' + p_2 s')(t_2 - t_0)} \end{aligned} \quad (5.4.5)$$

We substitute Eq. (5.4.5) into Eq. (4.2.14) to give an extremely lengthy formula for the lesser and greater Green’s functions, which is given by Eq. (B.1.1) of Appendix B.1. Whereas this expression is tedious to derive and very long, it does enable fast calculation of the lesser Green’s function, from which the particle number may be quickly extracted. The formula for the current in lead α can be similarly derived from Eq. (4.3.8), giving the expression in Eq. (B.1.2) of Appendix B.1. This expression consists of a term that arises from single photon processes in lead α , and a second term which contains interference effects due to photo-excited electrons moving across the

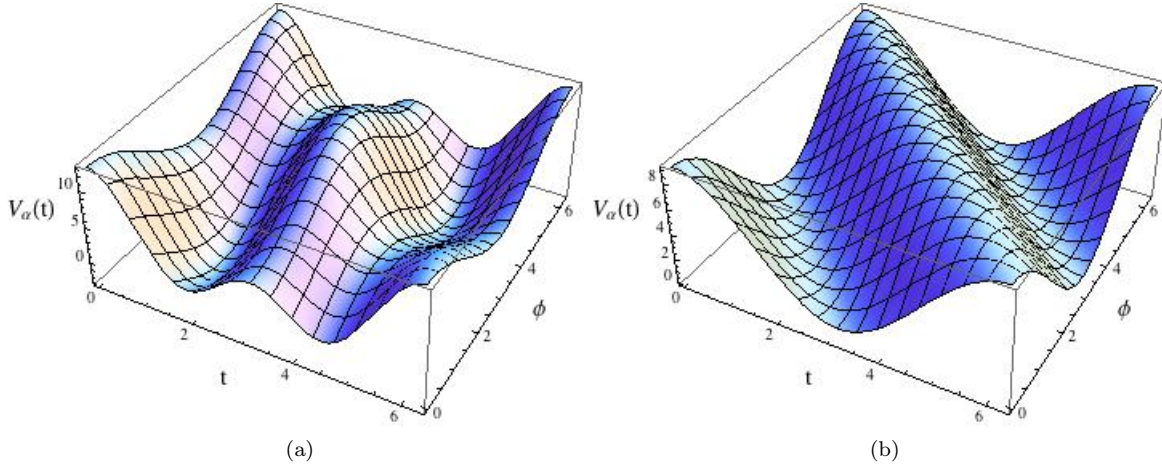


Figure 5.4.1: $V_\alpha(t)$ for values of ϕ_α between 0 and 2π , where $\Omega_D = 1$ sets the energy scale, (a) $V_\alpha = 5$, $A_\alpha^1 = A_\alpha^2 = 4$, and (b) $V_\alpha = 5$, $A_\alpha^1 = 4$, $A_\alpha^2 = 0.1$. We take $p_1 = 1$ and $p_2 = 2$.

nanojunction.

To check the validity of Eq. (B.1.2), we apply it to the case of a driven single-level system considered in Section 5.2. A C^{++} code has been written implementing this formula using the Padé expansion of the special functions Φ and Ψ discussed in Appendix A.3, and we now apply this code to the single level symmetrically-coupled system with parameters $\Gamma_L = \Gamma/2 = \Gamma_R = 1/2$, $\varepsilon_0 = 1$, $\mu = 0$, $V_L = 5$, $V_R = 0$, $A_L^{(1)} = 4$, $A_R^{(1)} = 0$, $A_L^{(2)} = 0 = A_R^{(2)}$, $\Omega_L = 1$, $p_1 = 1$. In Fig. 5.4.2, the calculation of $I_L(t)$ from the code is plotted against the results from numerically integrating the frequency integrals within the *Mathematica* package. Encouragingly, we find that the code actually *improves* upon the calculations done with *Mathematica*, since it does not lead to the sporadic numerical anomalies of the latter, which were removed by hand in the published work [1]. It is also a much faster calculation due to the replacement of any quadrature routines with embedded Bessel function summations.

5.4.2 Model of a Molecular Wire

Much has been made in this thesis and elsewhere of the importance of using a partition-free formalism rather than the partitioned approach to a bias switch-on process which has dominated transport calculations. This is mainly due to the fact that steady-state transport is usually the focus of numerical studies. However, the possibility of utilising fast-switching behaviour in molecular devices to carry out logical operations means that one may need to take into account the short-time behaviour of the junction to reliably design electronic switches and sensors at the nanoscale. The simplest extension of the quantum dot model studied previously is to the system composed of a molecular wire - essentially a chain of N_s quantum dot sites coupled to a thermal reservoir at either end [295, 213], shown in Fig. 5.4.3 (a) for the 5-site case. This model was introduced by Mujica *et al.* in [296, 297] and has provided a useful tool in the development of the field, particularly with regards to the investigation of the dependence of the conductance on the length of the molecule [298], amongst other finite-size effects, most recently the dynamical finite-size effects published in Ref. [2], which will be discussed in Section 5.4.4. It has also been applied to molecular junctions consisting of an STM-molecule-substrate geometry, which is asymmetric in the coupling strengths of the leads at either end of the wire [299, 300]. To see whether the different switch-on procedures give significantly different outcomes we shall apply our formalism to the transport properties of the molecular wire. We assume that each site corresponds to a single energy level, which may have a maximum occupation of 2 due to spin degeneracy. The Hamiltonian describing this molecular wire is assumed to have on-site energies equal to the constant value $[\mathbf{h}_{CC}]_{k,k} \equiv E$ and hopping elements all given by $[\mathbf{h}_{CC}]_{k,k+1} = [\mathbf{h}_{CC}]_{k+1,k} \equiv \lambda$. All quantities will be given in

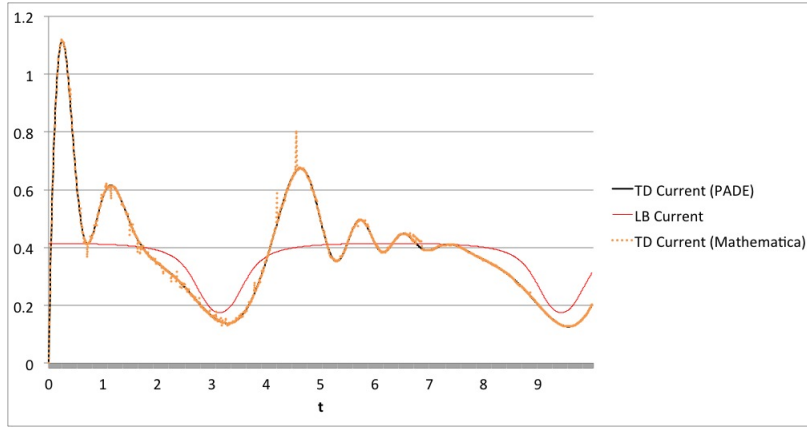


Figure 5.4.2: The TD current $I_L(t)$ from the Padé scheme (black line) and from the LB formula (red line) is plotted against the current obtained from numerical integration in *Mathematica* (orange dotted line), for the choice of parameters $\Gamma = 1$, $\varepsilon_0 = 1$, $\mu = 0$, $V_L = 5$, $A_L^{(1)} = 4$, $\Omega_L = 1$. Sudden unphysical spikes in the latter are not present in the former, justifying their original removal. Conversely, the high degree of agreement between the two schemes where the latter varies smoothly provides evidence for the correctness of the Padé scheme, suggesting that it can also be used to model a general molecular region possessing multiple energy levels.

arbitrary units, and we choose the chemical potential $\mu = 0$ as the zero of energy. Next, we model the orientation of the wire between the leads via our choice of elements in the level-width matrix, Eq. (2.4.14).

In Fig. 5.4.3 (a), we illustrate the configuration in which only the end sites of the wire are coupled to their neighboring lead. We refer to this as the *perpendicular* configuration. In this model, the Hamiltonian (2.2.1) is used, with spin degrees of freedom σ neglected, specialized to the two-lead case, in which only the lead-molecule couplings at the junction interfaces are included. In short, site 1 is coupled to the left lead eigenstates, and site N_s coupled to the right lead, with no other lead-molecular couplings included, giving for the equilibrium Hamiltonian:

$$\hat{H}_{TB} = \sum_{k\alpha \in (L,R)} \varepsilon_{k\alpha} \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha} + \sum_{m \in C}^{N_s} \varepsilon_m \hat{d}_m^\dagger \hat{d}_m + \hat{V}_C + \left[\sum_{i \in L} T_{i,1} \hat{d}_i^\dagger \hat{d}_1 + \sum_{j \in R} T_{N_s,j} \hat{d}_{N_s}^\dagger \hat{d}_j + h.c \right] \quad (5.4.6)$$

Here, $\hat{V}_C$ denotes an internal coupling for the molecular region. For times $t > t_0$, the lead energies undergo the modification $\varepsilon_{k\alpha} \rightarrow \varepsilon_{k\alpha} + V_\alpha(t)$. Taking into account the form of (5.4.6), we can thus put (2.4.14) into the form:

$$\Gamma_{mn} = 2\pi \left[\delta_{mn} \delta_{n1} \sum_{i \in L} |T_{i,1}| \delta(\varepsilon_L^F - \varepsilon_{iL}) + \delta_{mn} \delta_{nN_s} \sum_{j \in R} |T_{N_s,j}| \delta(\varepsilon_R^F - \varepsilon_{jR}) \right] \quad (5.4.7)$$

Evidently (5.4.7) implies that in the molecular basis only the Γ_{11} and $\Gamma_{N_s N_s}$ elements are non-zero, i.e. this tight-binding Hamiltonian leads to an extremely sparse level-width matrix for long chains. Finally, we assume that only a nearest-neighbor coupling is present in the molecular chain:

$$\hat{V}_M = \sum_{n=1}^{N_s} V_{n,n+1} \hat{d}_n^\dagger \hat{d}_{n+1} + h.c \quad (5.4.8)$$

These assumptions generate the following effective Hamiltonian matrix for the molecular wire:

$$\mathbf{h}_{CC}^{eff} = \begin{pmatrix} \varepsilon_1 - i\pi \sum_{i \in L} |T_{i,1}| \delta(\varepsilon_L^F - \varepsilon_{iL}) & V_{12} & 0 & \cdots & 0 \\ V_{21} & \varepsilon_2 & V_{23} & \cdots & 0 \\ 0 & V_{32} & \varepsilon_3 & V_{34} & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \varepsilon_{N_d} - i\pi \sum_{j \in R} |T_{N_s,j}| \delta(\varepsilon_R^F - \varepsilon_{jR}) \end{pmatrix} \quad (5.4.9)$$

Hence, when we model the 5-site molecular chain in the perpendicular configuration illustrated in Fig. (5.4.3) (a), the only non-zero elements of the level width are $\Gamma_{L,11}$ and $\Gamma_{R,55}$.

In Fig. 5.4.3 (b), all sites in the wire are coupled to both the left and right leads, and internally coupled to their neighbors, in what we will refer to as the *parallel* configuration. This situation requires a modification of the molecular wire model introduced above. We make the physical assumption that lead states which are close to a molecular wire site are the most strongly coupled to that site, so we effectively partition the leads $L(R)$ into N_s different lead sections, $L_1(R_1), \dots, L_{N_s}(R_{N_s})$ which couple only to the respective sites $1, \dots, N_s$. This leads to a modified tight-binding Hamiltonian of the form:

$$\hat{H}_{TB} = \sum_{k\alpha \in (L,R)} \varepsilon_{k\alpha} \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha} + \sum_{m \in C} \varepsilon_m \hat{d}_m^\dagger \hat{d}_m + \hat{V}_C + \sum_{j=1}^{N_s} \left[\sum_{i \in L_j} T_{i,j} \hat{d}_j^\dagger \hat{d}_i + \sum_{i \in R_j} T_{i,j} \hat{d}_j^\dagger \hat{d}_i + h.c \right] \quad (5.4.10)$$

This equates to a level width (2.4.14) with the following structure:

$$\mathbf{\Gamma}_{mn} = 2\pi \delta_{mn} \sum_{j=1}^{N_d} \delta_{nj} \left[\sum_{i \in L_j} |T_{i,j}| \delta(\varepsilon_L^F - \varepsilon_{iL_j}) + \sum_{i \in R_j} |T_{i,j}| \delta(\varepsilon_R^F - \varepsilon_{iR_j}) \right] \quad (5.4.11)$$

Using the same Hamiltonian for the molecular wire as in Eq. (5.4.8), these assumptions generate the following effective Hamiltonian matrix for the molecular wire:

$$\mathbf{h}_{CC}^{eff} = \begin{pmatrix} \varepsilon_1 - i\pi \sum_{\alpha_1} \sum_{i \in \alpha_1} |T_{i,1}| \delta(\varepsilon_\alpha^F - \varepsilon_{i\alpha_1}) & V_{12} & \cdots & 0 \\ V_{21} & \varepsilon_2 - i\pi \sum_{\alpha_2} \sum_{i \in \alpha_2} |T_{i,2}| \delta(\varepsilon_\alpha^F - \varepsilon_{i\alpha_2}) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon_{N_d} - i\pi \sum_{\alpha_{N_d}} \sum_{i \in \alpha_{N_d}} |T_{i,N_s}| \delta(\varepsilon_\alpha^F - \varepsilon_{i\alpha_{N_d}}) \end{pmatrix} \quad (5.4.12)$$

where the α_i is summed over L_i and R_i . We see that both the left and right level width matrices $\mathbf{\Gamma}_L, \mathbf{\Gamma}_R$ are diagonal in this model. This is intended to capture the physics of electrons tunneling onto molecular chain sites from local lead sites which are all close to the Fermi level in energy. Intramolecular electron hopping may occur, but no hopping from an α_j lead region onto a site $\neq j$. For simplicity, we will assume that sites are symmetrically coupled to the left and right leads. This means that in the perpendicular configuration, $\Gamma_{L,11} = \Gamma = \Gamma_{R,N_s N_s}$, whereas in the parallel configuration, all the $\Gamma_{\alpha,nn}$ are equal to the same fixed value, with $\Gamma_{\alpha,n \neq m} = 0$. It should be remarked here that if the leads are truly without structure, one would expect $\Gamma_{\alpha,n \neq m} \neq 0$, and the off-diagonal elements of the $\mathbf{\Gamma}_\alpha$ to be just as large as its diagonal elements. However, this neglects the local nature of the wire's bond to the electrodes, and does not distinguish between a molecule composed of five sites that are separated in space to form a wire-like structure from a molecule located at a single position which can be in five different energy states. It is common in practice to only include the strongest overlap integral between a molecular site and

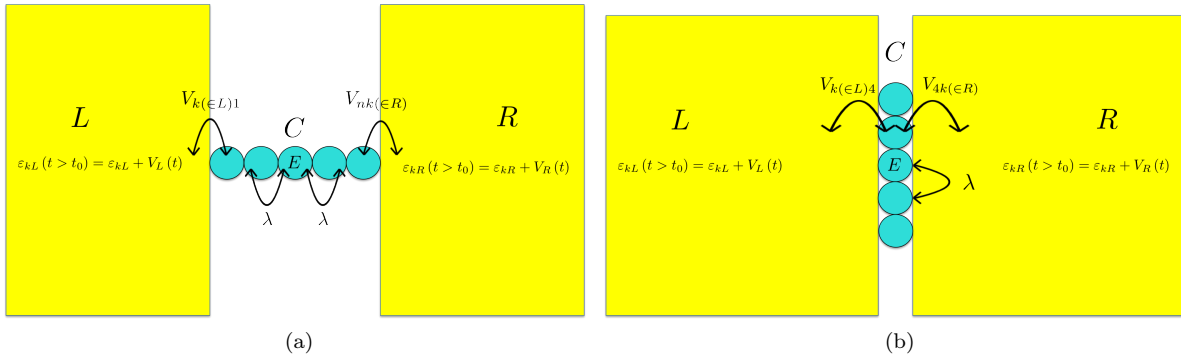


Figure 5.4.3: Schematic of a typical two-lead molecular junction consisting of the left (L) and right (R) leads bridged by a molecular system C , which in this case is chosen to be a molecular wire composed of $N_s = 5$ atomic sites with nearest neighbour hopping. In (a), we illustrate a configuration where the molecular wire lies perpendicular to the plane of the leads with end-site coupling. In (b), we show this molecular wire rotated by 90° such that each site is coupled to both leads as strongly as every other.

a single electrode atom at the lead-electrode interface, and thus obtain a diagonal level width of the kind we are using [285, 140, 190]. This enables one to encode subtle changes of molecular geometry into the structure of the level width matrices. For example in Ref. [301] a T-shaped junction was modelled using a wire in the parallel configuration but with only one end site coupled to states in the lead, i.e. with only $\Gamma_{\alpha,11} \neq 0$, and all other entries in the level width equal to zero.

5.4.3 Current Calculations for a Static Bias

To fix physical ideas, we first present calculations of the current through a quantum dot of energy $\varepsilon_0 = 1$, keeping the right lead bias fixed at $V_R = 0$ and varying $V \equiv V_L - V_R$ by computing the symmetrized current, defined as

$$I_{LR}(t) \equiv \frac{I_L(t) - I_R(t)}{2} \quad (5.4.13)$$

at all times following the switch-on of the bias at $t_0 = 0$. Fig. 5.4.4 demonstrates the relaxation of $I_{LR}(t)$ to a steady-state steplike $I - V$ characteristic at long times, i.e. it relaxes to the kind of $I - V$ characteristic previously seen in Fig. 1.4.2 of Chapter 1. In the transient, one observes rapid oscillations that occur on a short timescale after the beginning of the experiment, before dying out. This is due to the preparation-dependent terms in Eqs. (2.8.1) and (2.8.2), which contain decaying modes of the form $e^{-i(\bar{\varepsilon}_j - \mu - V_\alpha)(t - t_0)}$ and hence oscillate on a timescale set by $1/|\text{Re}(\bar{\varepsilon}_j) - \mu - V_\alpha|$.

In Fig. 5.4.5, we present a similar calculation for the case of the perpendicular molecular wire configuration of Fig. 5.4.3 (a), in the partition-free approach. In this example the magnitude of oscillations in the transient are much larger than the steady-state value of the current, which is suppressed due to the fact that the overlap integral prefactors (for example $\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle$) are smaller on average when Γ_α is sparse. The initial transient contains more peaks than were seen in the quantum dot case, and the duration of the transient is extended relative to the system studied in Fig. 5.4.4, as electron transfer between leads is mediated by a sequence of hopping events between quasi-stable states on the molecular wire.

In Fig. 5.4.6 the relaxation behaviour of the current through a molecular wire in the parallel configuration is computed. We see that the transient lifetime is much shorter than for the perpendicular case, with transient oscillations that are close in amplitude to the amplitude of the steady state $I - V$ value. This is because the level width matrices are densely filled compared with the level width matrices used in the perpendicular configuration.

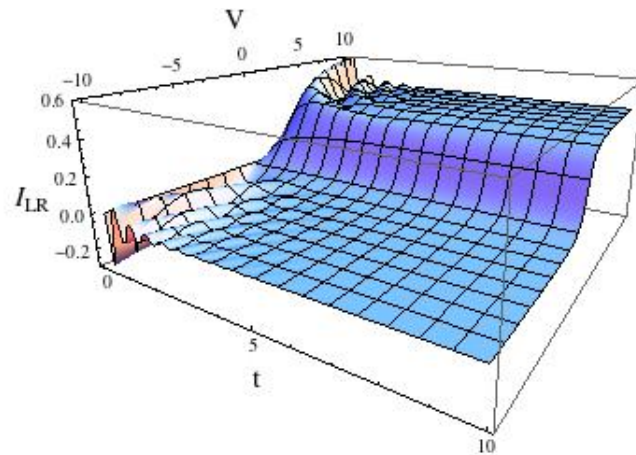


Figure 5.4.4: Calculation of the symmetrized current through a quantum dot, with parameter values $\varepsilon_0 = 1$, $\Gamma_L = 0.5 = \Gamma_R$.

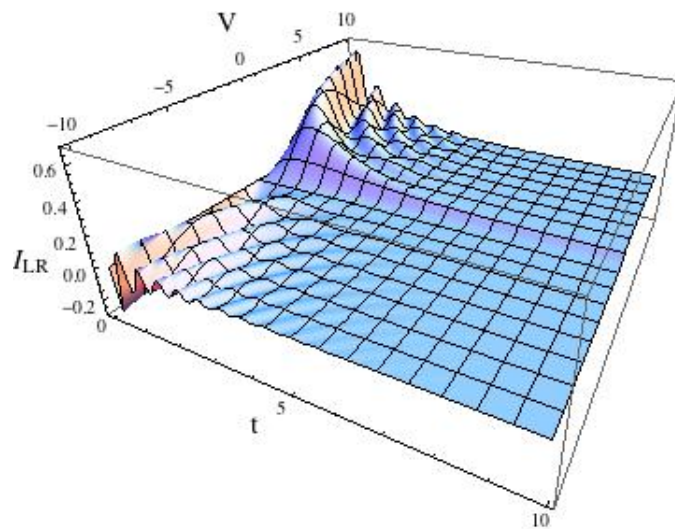


Figure 5.4.5: Calculation of the symmetrized current through a molecular wire in the perpendicular configuration, with parameter values $E = 1$, $\Gamma_{L,11} = 0.5 = \Gamma_{R,55}$, $\lambda = 0.1$.

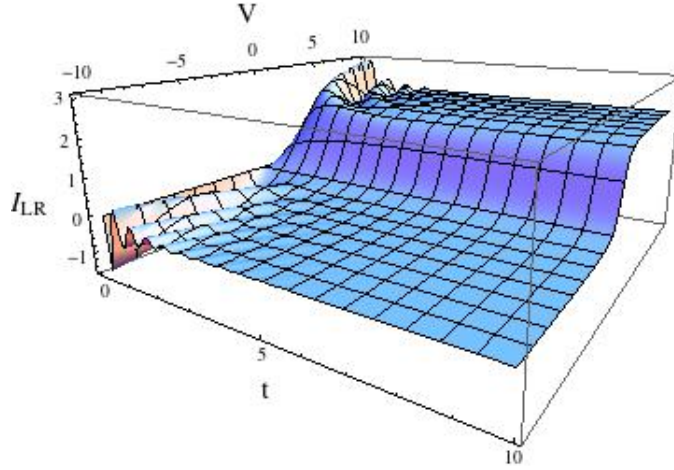


Figure 5.4.6: Calculation of the symmetrized current through a molecular wire in the parallel configuration, with parameter values $E = 1$, $\Gamma_{\alpha,nn} = 0.5$, $\lambda = 0.1$.

Physically, the parallel configuration shown in Fig. 5.4.3 (b) is equivalent to a row of quantum dots symmetrically coupled to leads on either side, so the current relaxation is not slowed down by the time taken for an electron to move from a lead onto the LUMO state of the molecule, hop to the HOMO state and move onto the next lead, although intradot hopping is possible due to the presence of the coupling term λ . This equivalence to a row of 5 coupled quantum dots is reflected in the similarity with the single level $I - t - V$ characteristics in Fig. 5.4.4. Indeed, the current in Fig. 5.4.6 appears to be identical to that in Fig. 5.4.4, but scaled up by a factor of ~ 5 .

In all three systems studied in this Section, we have therefore found a real difference in the amplitude and frequency of transient oscillations following the bias switch-on depending specifically on whether that switch-on takes place within a finite- or zero-dimensional system. Molecular wires in the perpendicular configuration with a weak end-site coupling show a particularly well-defined switching between different values of the current following the initial time t_0 . This fact could be used in the experimental characterisation and identification of molecular structures.

5.4.4 AC-Driven Transport in the Molecular Wire

To begin to understand the physics of finite time-dependent systems we apply the bias (5.4.1) to the leads L and R in the system shown in the perpendicular molecular wire configuration of Fig. 5.4.3(a). The amplitudes A_α and constant bias shifts V_α are taken to be identical for each lead, as is the driving frequency of the bias, Ω_α . The physical symmetry of this transport problem is then broken by a relative phase-shift of $\phi_R = -\pi/2$ of $V_R(t)$ with respect to $V_L(t)$, whose phase is fixed at $\phi_L = 0$. The tridiagonal central region Hamiltonian has all diagonal terms fixed at $E = 1$, and all off-diagonal terms $\lambda = 0.1$. Other parameters in the model are $V_L = 5 = V_R$, $A_L^{(1)} = 4 = A_R^{(1)}$, $\Gamma_{11} = \Gamma = \Gamma_{55} = 0.5$, $p_1 = 1$, and the inverse temperature $\beta = 10$. We evaluate Eq. (B.1.2) using the Padé parameters, and for this temperature we find good convergence with a Padé expansion order of $N_p \sim 20$. The resulting current in each lead is plotted in Fig. 5.4.7 (a) (thick lines), along with the suitably rescaled bias applied to the leads (dotted lines). In addition, we plot the steady-state value of the current at each time, using the LB formula. This serves as a comparison between the best predictions of the steady-state formalism and our fully time-dependent method, from which it is instantly apparent that the TD current amplitude is an order of magnitude greater than that of the LB current. There is a much sharper peak in the transient current in lead L than in R , because the bias applied in L has the value $V_L + A_L$ at the switch-on time $t_0 = 0$, whereas the corresponding bias in lead R has the value V_R . In the long-time regime, the current signal in each lead has the same form but the signal in R is phase-shifted by $-\pi/2$ with respect to the signal in L . Additionally, ‘ringing’ oscillations

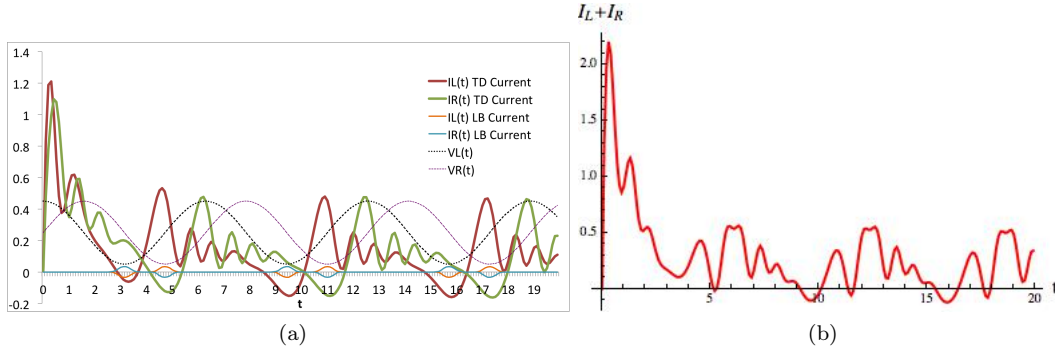


Figure 5.4.7: (a) Current and bias through each lead of a molecular wire junction in which the symmetry is broken due to biases phase-shifted by $\pi/2$, i.e. $\phi_L = 0, \phi_R = -\pi/2$. The number of molecular sites is 5, and other parameters chosen are $k_B T = 0.1$, $V_L = 5.0 = V_R$, $A_L = 4.0 = A_R$, $\Omega_L = 1.0 = \Omega_R$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = h_{kk} = 1.0$, $\lambda = h_{kk+1} = h_{k+1k} = 0.1$. (b) The sum of currents $I_L(t) + I_R(t)$ for this system.

in the current occurring at higher frequencies than the driving frequency Ω_α can be seen, as also observed in [154] and [1]. We identify the physical source of these frequencies in the energy gap $|V_\alpha + \mu - E|$ between onsite energies and the constant bias shift in the leads.

One can also see from Fig. 5.4.7 (a) that, whereas the LB formalism preserves the condition of charge conservation, $I_L(t) + I_R(t) = 0$, at all times, this condition is not satisfied by the two TD currents, and we plot $I_L(t) + I_R(t)$ in Fig. 5.4.7 (b) for clarity. We understand this phenomenon as follows: electrons propagate in the lead at the finite Fermi velocity v_α^F , so that the effects of a bias applied locally will take a finite time to propagate to other parts of the junction [128]. If a constant bias is switched on in each lead, then following a time delay equal to the transmission time of this signal across the junction, the rate of flow of electrons from C to L (I_L) must equal the rate of electron transport from R to C ($-I_R$), as in this case the number of electrons in the molecular region $N_C(t) = -2i\text{Tr}[\mathbf{G}^<(t, t)]$ is constant in time. If the bias is time-dependent, then the Hamiltonian is no longer symmetric under time translations and, in general, $N_C(t)$ also varies with time. Therefore local charge conservation does not apply in this case, a fact that is reflected in the current characteristics of Figs. 5.4.7 (a) and (b).

It is a point of concern with Fig. 5.4.7 (b) that it appears to indicate an unbroken net flow of charge into the molecule, because after the usual transient ‘ringing’ regime is over, the average value of $I_L(t) + I_R(t)$ *per cycle* appears to be positive (i.e. the area under the graph during the time period 2π is greater than zero). This is a property which, if sustained indefinitely, means that there will always be a charge increase in the central region of the junction - clearly an unphysical situation. To investigate what is occurring here, we compute in Fig. 5.4.8 the transport properties over a much longer time range of the same 5-site model as was considered in Fig. 5.4.7. The long time plots of both the sum of the currents (blue curve) and the particle number N_C (black) are displayed in Fig. 5.4.8, for this system, where to compute N_C we have expanded (2.7.2) into the left/right eigenbasis in a similar fashion to (4.3.8). Certain qualitative features of the plots stand out, in particular a periodic ‘sloshing’ of the charge in the molecular region as the number of particles increases there, before levelling off at a value below the maximum charge of 10. Simultaneously with this dynamic filling of the molecular levels, the average value of $I_L(t) + I_R(t)$ drops until the integral under this curve evaluates to zero over a full cycle. Thus in addition to the fast decay of the initial transient, there is a secondary underlying decay which occurs over a much longer time scale. Note that this decay over two time scales is not possible with a single-level model, so that it is fundamentally a finite-size effect.

In Fig. 5.4.8 we also compare the results obtained for the sparse tight-binding level-width matrix of the perpendicular configuration with the same plots for level-widths that are relatively non-sparse, in the parallel configuration of

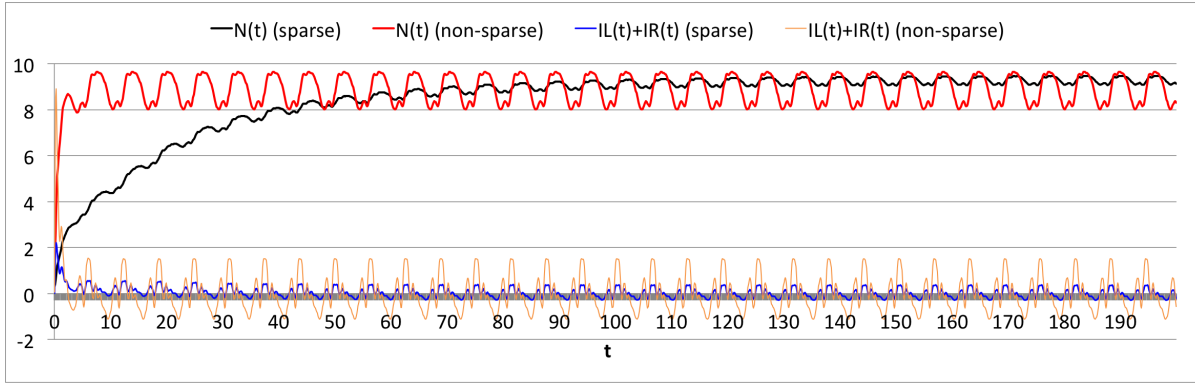


Figure 5.4.8: The electron number (black line) and sum of currents (blue line) for the sparse tight-binding hamiltonian is compared with the electron number (red line) and sum of currents (orange line) for a hamiltonian in which each lead is coupled with the same strength to every site in the chain.

Fig. 5.4.3 (b). Specifically, we take $[\mathbf{\Gamma}_L]_{ij} = \delta_{ij}0.5 = [\mathbf{\Gamma}_R]_{ij}$, giving a level-width with a constant term along the main diagonal. As discussed in Chapter 4, the timescale for decay of all transient modes in formula (4.3.8) is $\tau \equiv \text{Max}\{1/\gamma_j\}$, where the γ_j are defined as imaginary parts of the complex eigenvalues, $\bar{\epsilon}_j = \lambda_j - i\gamma_j$. For the perpendicular tight-binding level-width $\tau = 61.9$, whereas in the parallel case we have a decay time of $\tau = 2$. This order-of-magnitude difference is well illustrated by the extremely fast relaxation of the parallel configuration number density (red curve) to a steady oscillation below $N_C = 10$. This implies that the integral of $I_L(t) + I_R(t)$ over one cycle is zero, implying no long-term change in the sum of currents, as shown by the orange curve in Fig. 5.4.8. Additionally, we note that despite the qualitatively similar ‘sloshing’ between two values of the electron number in the molecule after $t \sim \tau$ has elapsed, there is a difference in the amplitude of the oscillating signal for the perpendicular and parallel cases. This is simply due to the fact that the overlap integral prefactors (for example $\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle$) are smaller on average when $\mathbf{\Gamma}_\alpha$ is sparse.

5.5 Quantum Pump Calculations

We are now in a position to make a numerical study of the pump current for the specific case of the biharmonic bias in Eq. (5.4.4). In the long time limit, all transient modes in Eq. (B.1.2) vanish and one is left with the following time-dependent behaviour:

$$\begin{aligned}
 I_\alpha(t) = & \frac{1}{\pi} \sum_j \sum_{r,r',s,s'} \left\{ 2\text{Re} \left[\frac{\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} i J_r \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_{r'} \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_s \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) J_{s'} \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) \right. \right. \\
 & \times e^{-i(r-r')\phi_\alpha} e^{-i\Omega_\alpha(p_1(r-r')+p_2(s-s'))(t-t_0)} \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\epsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right) \Big] \\
 & - \sum_{\gamma,k} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} J_r \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \right) J_{r'} \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \right) J_s \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_\gamma} \right) J_{s'} \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_\gamma} \right) \\
 & \times \left[\frac{e^{-i(r-r')\phi_\gamma} e^{-i\Omega_\gamma(p_1(r-r')+p_2(s-s'))(t-t_0)}}{\bar{\epsilon}_j - \bar{\epsilon}_k^* - \Omega_\gamma(p_1(r-r') + p_2(s-s'))} \right]
 \end{aligned}$$

$$\times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma (p_1 r' + p_2 s')) \right) \right] \right] \} \quad (5.5.1)$$

In this expression we can replace $t_0 = 0$, in accordance with the discussion under Eq. (5.4.1). Now we assume that the fundamental driving frequency is lead-independent, $\Omega_\gamma = \Omega_D$, for all γ . This allows us to derive a formula for the time-independent, steady-state pump current using the definition in Eq. (5.3.1):

$$\begin{aligned} I_{\alpha\beta}^{(pump)} &= \frac{1}{\pi} \sum_{\gamma} \sum_{j,k} \sum_{r,r',s,s'} \delta_{ss'}^{rr'}(p_i) \\ &\times \left[\frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \left[e^{-i(r-r')\phi_\alpha} J_r \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_D} \right) \right. \right. \\ &\times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\alpha - \Omega_D (p_1 r' + p_2 s')) \right) \right] \\ &\quad \left. - e^{-i(r-r')\phi_\gamma} J_r \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_D} \right) \right. \\ &\times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_D (p_1 r' + p_2 s')) \right) \right] \right] \\ &\quad \left. - \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\beta | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \left[e^{-i(r-r')\phi_\beta} J_r \left(\frac{A_\beta^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A_\beta^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A_\beta^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A_\beta^{(2)}}{p_2 \Omega_D} \right) \right. \right. \\ &\times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\beta - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\beta - \Omega_D (p_1 r' + p_2 s')) \right) \right] \\ &\quad \left. - e^{-i(r-r')\phi_\gamma} J_r \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_D} \right) \right. \\ &\times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_D (p_1 r' + p_2 s')) \right) \right] \right] \right] \right] \quad (5.5.2) \end{aligned}$$

In this expression, we have used the modified Kronecker function

$$\delta_{ss'}^{rr'}(p_i) \equiv \begin{cases} 1, & p_1 (r - r') + p_2 (s - s') = 0 \\ 0, & \text{else} \end{cases} \quad (5.5.3)$$

to make the replacement $\bar{\varepsilon}_j - \bar{\varepsilon}_k^* - \Omega_D (p_1 (r - r') + p_2 (s - s')) \leftrightarrow \bar{\varepsilon}_j - \bar{\varepsilon}_k^*$. Now we choose our system so that it is a two-terminal junction with left and right leads L and R . Following some algebra, cancellations occur in the larger expression (5.5.2) and one is left with a formula that is very simple to implement:

$$I_{LR}^{(pump)} = \frac{1}{\pi} \sum_{j,k} \sum_{r,r',s,s'} \delta_{ss'}^{rr'}(p_i) \left[\frac{\langle \varphi_k^R | \mathbf{\Gamma}_L | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_R | \varphi_k^L \rangle + \langle \varphi_k^R | \mathbf{\Gamma}_R | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_L | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \right]$$

$$\begin{aligned}
& \times \left[e^{-i(r-r')\phi_L} J_r \left(\frac{A_L^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A_L^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A_L^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A_L^{(2)}}{p_2 \Omega_D} \right) \right. \\
& \times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_L - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_L - \Omega_D (p_1 r' + p_2 s')) \right) \right] \\
& \left. - e^{-i(r-r')\phi_R} J_r \left(\frac{A_R^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A_R^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A_R^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A_R^{(2)}}{p_2 \Omega_D} \right) \right. \\
& \times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_R - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_R - \Omega_D (p_1 r' + p_2 s')) \right) \right] \Big] \quad (5.5.4)
\end{aligned}$$

The expression (5.5.4) may be straightforwardly implemented in C^{++} and is the basis of all calculations on the quantum pump which follow. To understand the role of the TR symmetry-breaking phase in Eq. (5.5.4), we assume all other dynamical parameters are lead-independent, i.e. $V_L = V = V_R$, $A_L^{(1)} = A^{(1)} = A_R^{(1)}$, $A_L^{(2)} = A^{(2)} = A_R^{(2)}$, with $\phi_L \neq \phi_R$:

$$\begin{aligned}
I_{LR}^{(pump)} &= \frac{1}{\pi} \sum_{j,k} \sum_{r,r',s,s'} \delta_{ss'}^{rr'}(p_i) J_r \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) \\
& \times \left[\frac{\langle \varphi_k^R | \mathbf{\Gamma}_L | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_R | \varphi_k^L \rangle + \langle \varphi_k^R | \mathbf{\Gamma}_R | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_L | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \right] \left[e^{-i(r-r')\phi_L} - e^{-i(r-r')\phi_R} \right] \\
& \times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V - \Omega_D (p_1 r' + p_2 s')) \right) \right] \quad (5.5.5)
\end{aligned}$$

Note the similarity of this formula to the generic case in Eq. (5.3.19), and in particular note how the phase difference $[e^{-i(r-r')\phi_L} - e^{-i(r-r')\phi_R}]$ has an identical structure to Eq. (5.3.22). The presence of the function $\delta_{ss'}^{rr'}(p_i)$ guarantees that there is no pump current without a second harmonic in any lead (i.e. when $A_\gamma^{(2)} = 0$ for all γ), as in this case the summations over s, s' vanish and $r = r'$ ¹. This means the condition (i) of the quantum pump symmetry theorem is satisfied. We also see from Eq. (5.5.5) that the pump current is caused by a difference in the symmetry-breaking phase, i.e. as long as condition (ii) of the quantum pump symmetry theorem is satisfied, and $\phi_L \neq \phi_R$ (which guarantees condition (iii) of that theorem). As observed in Ref. [302], this is to be expected from the fact that the effective bias placed across this system is given by:

$$V_{LR}(t) \equiv V_L(t) - V_R(t) = 2A^{(1)} \sin \left(\frac{\Delta\phi_{LR}}{2} \right) \sin \left(p_1 \Omega_D (t - t_0) + \frac{\phi_L + \phi_R}{2} \right) \quad (5.5.7)$$

We therefore expect that a pump current will exist when the phase difference $\Delta\phi_{LR} \equiv \phi_L - \phi_R \neq 0$, in which case condition (ii) of the quantum pump symmetry theorem is satisfied. The lead-independent harmonic $A^{(2)} \cos(p_2 \Omega_D (t - t_0))$ may in this case be interpreted as a spatially homogeneous shift of all the molecular levels, by the gauge invariance illustrated in Fig. (2.6.1). The system then formally resembles the oscillating scatterer with external periodic fields studied by Moskalets and Büttiker in Ref. [302].

¹This follows from the series expansion for the Bessel functions of the first kind

$$J_n(x) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m! \Gamma(m+n+1)} \left(\frac{x}{2} \right)^{2m+n} \quad (5.5.6)$$

which implies $J_n(0) = 0$ for all $n \neq 0$, and $J_0(0) = 1$.

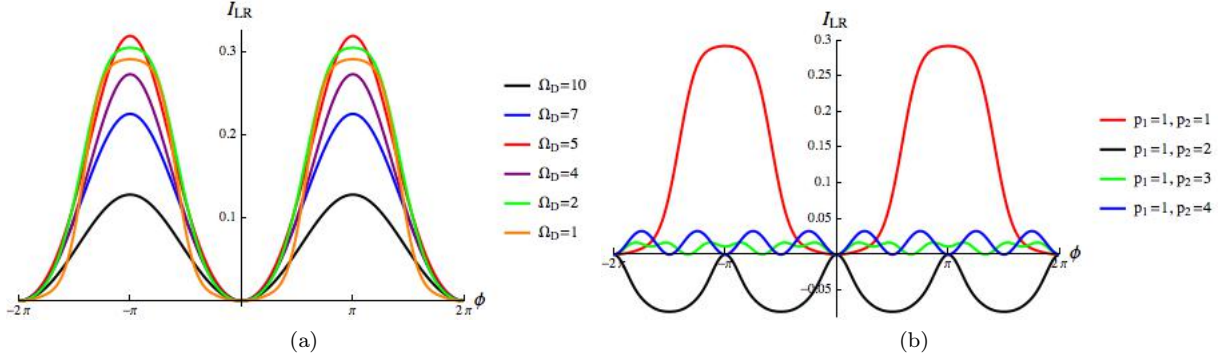


Figure 5.5.1: Phase-dependence of the pump current, in (a) for $p_1 = 1 = p_2$ and different Ω_D and (b) for $\Omega_D = 1$, $p_1 = 1$ and various values of the second harmonic frequency scaling parameter p_2 . Other parameters chosen in this calculation are $V_L = 5 = V_R$, $A_L^{(1)} = 4 = A_R^{(1)}$, $A_L^{(2)} = 4 = A_R^{(2)}$.

In Fig. 5.5.1 (a), we plot the pumped current $I_{LR}^{(pump)}$ as a function of $\Delta\phi_{LR}$ for a single-level system with $\varepsilon_0 = 1$, $\Gamma_L = \Gamma/2 = \Gamma_R = 0.5$ and $k_B T = 0.1$. Fig. 5.5.1 (a) exhibits $I_{LR}^{(pump)}$ as a function of $\Delta\phi_{LR}$, fixing $\phi_R = 0$ and with lead independent parameters $V = 5$, $A^{(1)}$, $A^{(2)}$, $p_1 = 1 = p_2$ for a variety of values of the driving frequency Ω_D . First note that from the identity

$$e^{-i(r-r')\phi_L} - e^{-i(r-r')\phi_R} = -2i \sin\left((r-r') \frac{\Delta\phi_{LR}}{2}\right) e^{-i(r-r')\left(\frac{\phi_L + \phi_R}{2}\right)} \quad (5.5.8)$$

it is evident that the pump current in this system must be zero when $\Delta\phi_{LR} = 0, \pm 2n\pi$ for integer n , and that it possesses maximal values when $\Delta\phi_{LR} = \pm n\pi$. As the formula for $I_{LR}^{(pump)}$ must be unchanged under the exchange of indices $r \leftrightarrow r'$, the expression (5.5.8) also implies that the pump current is unchanged upon reversal of sign $\Delta\phi_{LR} \leftrightarrow -\Delta\phi_{LR}$. Both these facts are reflected in the pump current characteristics of Fig. 5.5.1 (a).

It is important to remark at this point that in the majority of literature on double parametric quantum pumping depending on a phase difference δ between two oscillating parameters, the adiabatic pumped current is proportional to $\sin(\delta)$ and is therefore asymmetric about its zero points, which occur at multiples of $\pm\pi$ [303, 304, 100, 305, 101, 93, 109, 306]. This dependence arises from the nature of the interference between scattering amplitudes in transmission functions via structures of the form $\left| \sum_j c_j e^{i\varphi_j} \right|^2$, where φ_j is the phase shift associated with a scatterer at the j -th site of the molecule [305]. By contrast, in our formalism, the interference between photo-excited electron wavefunctions leaving the leads is additive. Pumping due to external ac fields therefore has a qualitatively different signature as a function of the phase difference between fields, when compared with the phase-dependence of standard parametric pumping.

In Fig. 5.5.1 (b), we fix $\Omega_D = 1$ and instead vary the frequency scaling parameter p_2 , keeping $p_1 = 1$ in all calculations, i.e. the second harmonic in Eq. (5.4.4) drives the system with a frequency that is a multiple of the frequency of the first harmonic. This causes additional nodes to form at $\pm n2\pi/p_2$ in the phase-dependent pump current. At first when one inspects Eqs. (5.5.5), (5.5.7) and (5.5.8) it is not clear why, as the phase-dependence of these formulas appears to be independent of p_2 . However, the phase dependence is coupled to p_2 through the presence of the generalized Kronecker $\delta_{ss'}^{rr'}(p_i)$ in Eq. (5.5.5). The definition of this object, Eq. (5.5.3) implies that we can make the replacement $r - r' \rightarrow -p_2(s - s')$ everywhere in Eq. (5.5.5), and therefore in the phase-difference-dependent factor Eq. (5.5.8), so that the nodes of Eq. (5.5.8) appear when $p_2(s' - s) \frac{\Delta\phi_{LR}}{2} = \pm n\pi$, which is exactly what we see in Fig. 5.5.1 (b).

In Fig. 5.5.2 (a), calculations of the Ω_D -dependence of the pump current are presented for the same system at

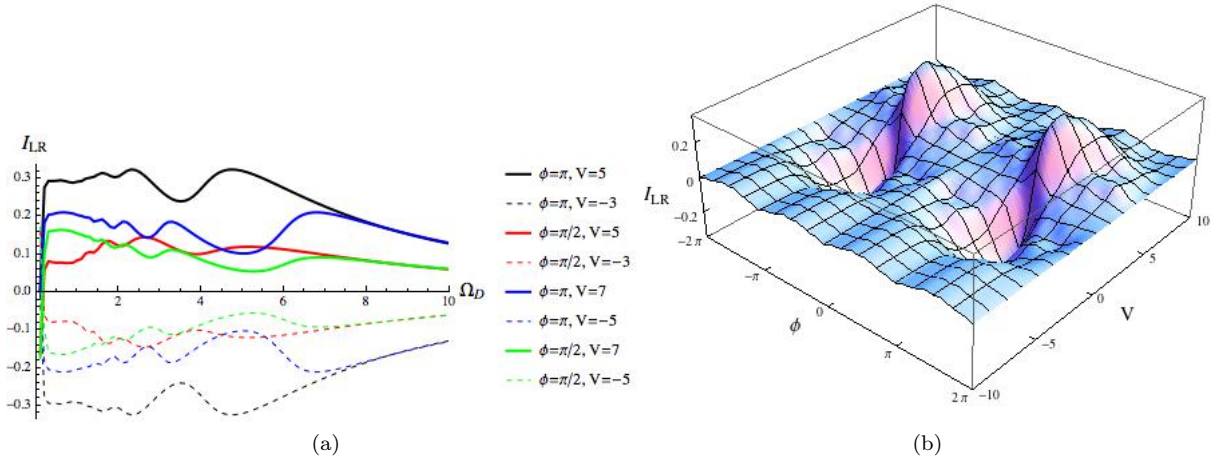


Figure 5.5.2: (a) For different values of V and $\Delta\phi_{LR}$, the Ω_D dependence of the pump current is plotted for values of $V > \varepsilon_0 = 1$ (thick lines), and values of $V < \varepsilon_0 = 1$ (dashed lines) that give the reflection of the pump current about $I_{LR}^{(pump)} = 0$. (b) The contour plot of $I_{LR}^{(pump)}$ as a function of V and $\Delta\phi_{LR}$. The parameters chosen are $V_L = 5 = V_R$, $A^{(1)} = 4$, $A^{(2)} = 4$.

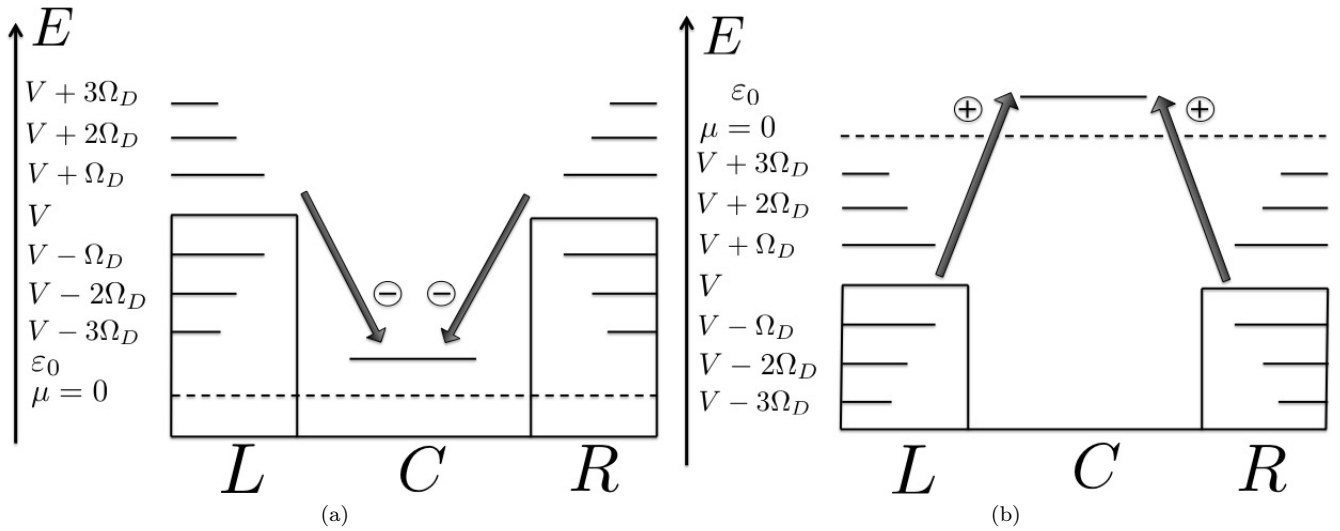


Figure 5.5.3: Schematic illustration of the processes involved in generating a pump current for the cases (a) $V > \varepsilon_0$ and (b) $V < \varepsilon_0$.

$\Delta\phi_{LR} = \pi$ and $\Delta\phi_{LR} = \pi/2$, for different values of the constant bias shift V . It must be emphasized that V is not a net bias across the device region; rather, V is just a constant shift in all energy levels of both leads, so the net bias averaged over a full driving period is fixed at zero. The thick lines show the pump current at values of $V > \varepsilon_0 = 1$, and each thick line has an associated dashed line of the same colour calculated for $V < \varepsilon_0$, but the same absolute value of the gap $|V + \mu - \varepsilon_0|$. We see that, following an initial oscillation as a function of Ω_D , there exist ‘resonances’ in the rectified current at $\Omega_D \sim |\mu + V - \varepsilon_0|/n$ (n is some integer) and therefore that the pump current for a gap of $|\mu + V - \varepsilon_0| = 6$ (blue line) exhibits more peaks than the pump current for a gap of $|\mu + V - \varepsilon_0| = 4$ (black line). These resonances occur when the frequency of the illuminating signal matches with the fundamental energy gap separating the lead Fermi energies from the dot level. We also see that the sign of the pump current changes at $V = \varepsilon_0$, and that, whereas the magnitude of the pump current is a unique function of the energy gap $|\mu + V - \varepsilon_0|$, the sign of this current flips when V crosses the dot energy level. This is further evidenced in Fig. 5.5.2 (b), where a 3D plot of the pump current versus both the phase difference $\Delta\phi_{LR}$ and the constant Fermi level shift V is displayed.

To interpret this sign change physically, we display a schematic representation of the energetics involved in Fig. 5.5.3. The $V > \varepsilon_0$ case is shown in Fig. 5.5.3 (a). Due to the driving in the leads, the electrons there are excited and a bias window is opened between the right lead and the various photon-assisted sidebands. This enables electrons to tunnel from the lead onto the dot from the sidebands, with a fundamental energy gap of $|\mu + V - \varepsilon_0|$ for the 0-th harmonic mode. In Fig. 5.5.3 (b) the $V < \varepsilon_0$ process is illustrated, which is simply an inversion of the system about ε_0 in energy space. In this case, positively-charged holes tunnel from the leads onto the dot by traversing the energy gap of $|\varepsilon_0 + \mu - V|$ for the 0-th mode, and for every electron tunneling event with energy gap $|\mu + V + n\Omega_D - \varepsilon_0|$ in Fig. 5.5.3 (a), there is a corresponding hole tunneling event with energy gap $|\varepsilon_0 + \mu - V - n\Omega_D|$ in Fig. 5.5.3 (b), with equal weighting in the PAT transmission. In both cases, the interference of the propagating waves arriving from the leads with a time delay caused by the relative phase shift leads to a net directed current across the junction. Since in the $V < \varepsilon_0$ case, motion of electrons across the junction is effectively replaced by motion of holes (which have the opposite charge to electrons in the units we have used, i.e. $q_h = 1$), there must be a reversal in the sign of the pump current. To further support this interpretation of Fig. 5.5.2 (b) we plot in Fig. 5.5.4 the time-dependent particle and hole numbers of the dot (given by $N_C(t)$ and $N_h(t)$ defined in Eqs. (2.7.2) and (4.2.20) of this thesis). In Fig. 5.5.4 (a) we show the $V = 5$ transient, and in Fig. 5.5.4 (b) the transient for the reflection about $\varepsilon_0 = 1$, $V = -3$, is shown. Remarkably, after the transient ringing has elapsed, we find that $N_C(t; V = 5) = N_h(t + \phi; V = -3)$ and $N_C(t; V = -3) = N_h(t + \phi; V = 5)$, i.e. that switching the Fermi level around ε_0 , causes the population of electrons on the dot to be replaced with an identical but phase-shifted signal for the population of holes, and vice versa. Integrated over a full oscillation period of 2π , the population of holes on the dot is therefore identical to the population of electrons on the dot with the lead Fermi level $\mu + V$ reflected in ε_0 .

5.6 Recovery of Known Results

In the original theory of PAT [196], and in the driven systems studied using the time-averaged noise in Refs. [258, 263, 292], the net bias chosen to drive the system contained a static component that was nonzero on average, and a time-dependent part $V_\alpha(t) = V(t)$ that was independent of the lead index α . This case can also be accounted for in the formalism presented here, if we now let all AC parameters in the bias become lead independent, but keep a finite DC component across the leads, i.e. we take $V_L \neq V_R$, $A_L^{(1)} = A^{(1)} = A_R^{(1)}$, $A_L^{(2)} = A^{(2)} = A_R^{(2)}$, $\phi_L = \phi_R$ in Eq. (5.5.4), and note that the presence of $\delta_{ss'}^{rr'}(p_i)$ implies that $p_1 r + p_2 s = p_1 r' + p_2 s'$ in this formula, to get:

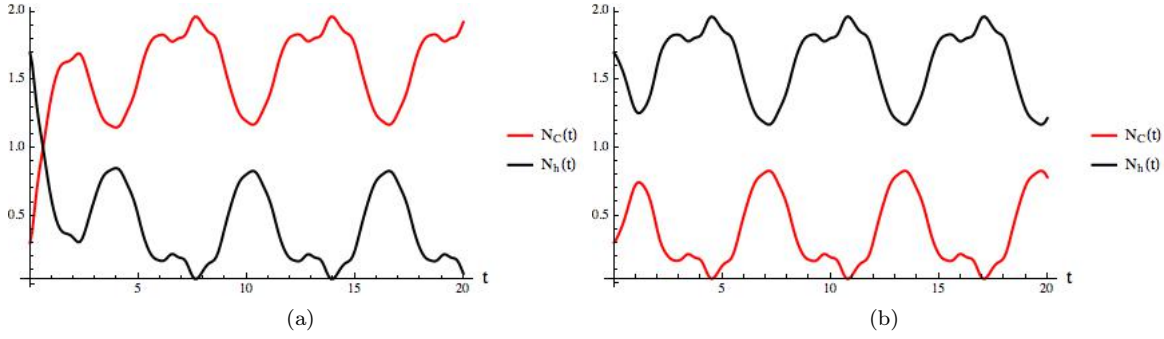


Figure 5.5.4: Comparison of the electron (red line) and hole (black line) numbers for the same quantum pump system in Fig. 5.5.2, with $\Delta\phi_{LR} = \pi$. These plots correspond to the constant Fermi level shifts of (a) $V = 5$ and (b) $V = -3$.

$$\begin{aligned}
I_{LR}^{(pump)} = & \frac{1}{\pi} \sum_{j,k} \sum_{r,r',s,s'} \delta_{ss'}^{rr'}(p_i) \left[\frac{\langle \varphi_k^R | \mathbf{\Gamma}_L | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_R | \varphi_k^L \rangle + \langle \varphi_k^R | \mathbf{\Gamma}_R | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_L | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\epsilon}_j - \bar{\epsilon}_k^*)} \right] \\
& \times \left[e^{-ip_1(r-r')\phi} J_r \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) \right. \\
& \times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\epsilon}_j - \mu - V_L - \Omega_D (p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\epsilon}_k^* - \mu - V_L - \Omega_D (p_1 r' + p_2 s')) \right) \right. \\
& \left. \left. - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\epsilon}_j - \mu - V_R - \Omega_D (p_1 r + p_2 s)) \right) + \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\epsilon}_k^* - \mu - V_R - \Omega_D (p_1 r' + p_2 s')) \right) \right] \right] \quad (5.6.1)
\end{aligned}$$

Using the simple pole expansion of the Fermi function in Eq. (4.2.2), this may be rewritten as

$$\begin{aligned}
I_{LR}^{(pump)} = & \frac{1}{\pi} \sum_{j,k} \sum_{r,r',s,s'} \delta_{ss'}^{rr'}(p_i) e^{-ip_1(r-r')\phi} J_r \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) \\
& \times \int d\omega [f_L(\omega - \mu - \Omega_D (p_1 r + p_2 s)) - f_R(\omega - \mu - \Omega_D (p_1 r + p_2 s))] [T_{RL}(\omega) + T_{LR}(\omega)] \quad (5.6.2)
\end{aligned}$$

where $T_{RL}(\omega)$ is given by Eq. (2.8.16). Note that, in the long-time limit, the Fourier transform of Eq. (5.4.5) has coefficients given by

$$c_n^\alpha = e^{-iV_\alpha t} \sum_{r,s} \delta_{n,p_1 r + p_2 s} J_r \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) e^{-ip_1 r \phi} \quad (5.6.3)$$

so that

$$|c_n^\alpha|^2 = \sum_{r,r',s,s'} \delta_{n,p_1 r + p_2 s} \delta_{n,p_1 r' + p_2 s'} J_r \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_{r'} \left(\frac{A^{(1)}}{p_1 \Omega_D} \right) J_s \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) J_{s'} \left(\frac{A^{(2)}}{p_2 \Omega_D} \right) e^{-ip_1(r-r')\phi} \quad (5.6.4)$$

Thus, using the identity

$$\sum_n \sum_{r,r',s,s'} \delta_{n,p_1 r + p_2 s} \delta_{n,p_1 r' + p_2 s'} f_n = \sum_{r,r',s,s'} \delta_{ss'}^{rr'}(p_i) f_{p_1 r + p_2 s} \quad (5.6.5)$$

for some arbitrary function f_n , we see that Eq. (5.6.2) is identical to the steady-state LB formula but with the Fermi distribution function in the leads replaced by a nonequilibrium distribution function:

$$f_\alpha(\omega - \mu) \rightarrow \sum_n |c_n^\alpha|^2 f_\alpha(\omega - \mu - n\Omega_D) \quad (5.6.6)$$

This replacement is found throughout the literature on time-averaged current, for example in the Floquet tight-binding approach used in Ref. [307]. Eq. (5.6.6) is exactly equivalent to replacing the transmission function in the LB formula with an effective transmission composed of a weighted sum of transmissions with maxima shifted by multiples of Ω_D , i.e. it leads to a time-averaged current formula which is exactly equivalent to the published result in Eq. (1.4.27).

5.7 Time-Dependent Quantum Noise

Calculations of current fluctuations in the time domain exist in the literature, but to date they have been restricted to the fluctuation response to a static bias switch-on [209, 187, 274], or to fluctuations in driven systems averaged over a time period [272, 71]. Although the noise on the current in a quantum dot with AC driving in the leads has been calculated for a wide parameter range in Refs. [257] and [125] (in the latter paper, the noise response to magnetic fields was also considered), there have been no calculations to date on the real time current fluctuations for extended (beyond a single site) molecules driven by an AC field. This gap in the literature will now be addressed. The methodology described in Chapter 4 for the calculation of $\mathbf{G}^\geq(t_1, t_2)$ and the $\mathbf{\Lambda}^\pm$ matrices entering into the two time current correlation function is particularly suited to the study of systems whose driving bias has a known analytic form. In this case the single and double time integrals occurring in these formulae may be removed by hand, and numerical time integrals are replaced by a ‘one-shot’ calculation of noise as a function of time. The onerous task of removing all the time integrals involved in the two-time correlation function for the biharmonic bias (5.4.4) has been relegated to Appendix B.1.

5.7.1 DC-Driven Noise in the Molecular Wire

In Fig 5.7.1 (a), we plot the cross-correlation $C^{(\times)}(t, t)$ through an $N_s = 5$ -site molecular wire in the perpendicular configuration for different values of the static bias $V = V_L = -V_R$, with $\Gamma_{L,11} = \Gamma = \Gamma_{R,55} = 0.5$, on-site energy $E = 1$ and the hopping parameter is set to $\lambda = 0.1$. We see that the time-dependent response contains a resonance in the cross-correlation signal beginning at a resonance time of about $t_{res} \simeq 20$, before the signal decays towards zero. This resonance is extremely small (shown in the insets to Fig. 5.7.1 (a)) when $V < E$, as in this case the on-site energy of the chain lies outside the bias window $[-V, V]$. The magnitude of the resonance sharply increases when E crosses into the bias window at $V = 1$, before saturating at a maximum value at around $V = 2$, which can be seen from the fact that the $V = 5$ (green) curve sits almost exactly on top of the $V = 2$ (blue) one. In Fig. 5.7.1 (b), we plot the absolute value of the Fourier transform of the signal in Fig. 5.7.1 (a) with respect to the *measurement time*, i.e. we compute $|\mathcal{F}[C^{(\times)}(t, t); \omega]|$, where the frequency is given in units of the on-site energy E . We find that the position of the resonance in frequency space is independent of the value of V , and corresponds to the ‘kick’ that the *diagonal* ($\tau = 0$) cross-correlation receives at $t_{res} \simeq 20$, via the relation $\omega_{res} = 2\pi/t_{res}$.

In Fig 5.7.2 we exhibit the contour plot of $\text{Re}[C^{(\times)}(t + \tau, t)]$ for the $V = 5$ case, and for different numbers of atomic sites $N_s = 3, 4, 5, 6$. Notice that this plot is symmetric in the $\tau = 0$ main diagonal, in accordance with the analytic result of Eq. (3.4.10). Unlike the single-site case considered in Ref. [274], the magnitude of the cross-correlation is *not* in general maximized along the $\tau = 0$ diagonal. Instead, we see a very strong ‘ripple’ spreading out from the diagonal for all values of N_s with a maximum magnitude at a value of $\tau_{max} = t_1 - t_2$ satisfying

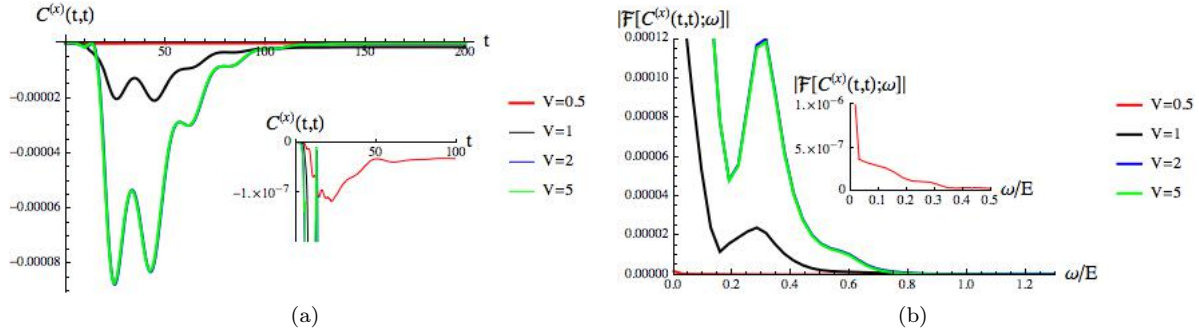


Figure 5.7.1: (a) Plot of $C^{(\times)}(t, t)$ for the switch-on of a constant bias $V = V_L = -V_R$, for a wire of length $N_s = 5$ for the perpendicular configuration shown in Fig. 5.4.3 (a). (b) The Fourier transform of the diagonal cross-correlation with respect to the measurement time, $|F[C^{(\times)}(t, t); \omega]|$. We make the parameter choice $E = 1$, $\Gamma = 1$, $\lambda = 0.1$.

the relation $\max |\text{Re}[C^{(\times)}(t + \tau, t)]| = \text{Re}[C^{(\times)}(t \pm \tau_{max}, t)]$. It appears from the plots 5.7.2 (a)-(d) that τ_{max} increases linearly with increasing N_s . In the $N_s = 5$ case $\tau_{max} \simeq 20$, i.e. it is roughly equal to the resonance time t_{res} in $C^{(\times)}(t, t)$, so we expect that the two time scales τ_{max} and t_{res} may be physically related.

The fact that τ_{max} increases with N_s implies that its position is due to the finite size of the molecular wire and its intrinsic properties. To understand this heuristically, one may consider the Schrödinger equation for a wire of N_s sites with a spacing of size 1 (i.e. of length $N_s - 1$), energy E and inter-site coupling λ . This leads to a dispersion $\varepsilon(k) = E + 2\lambda \cos(k)$, and therefore the traversal time for an electron of unit mass to pass through the wire is approximated by (note that $\hbar = 1$):

$$\tau_{traversal} \approx \frac{N_s - 1}{\partial_k \varepsilon(k)} = \frac{N_s - 1}{2\lambda \sin(k)} \quad (5.7.1)$$

Whereas this expression neglects the presence of the leads and cannot be taken as anything other than a rule of thumb, it indicates that we may investigate the interplay of λ and N_s should we wish to understand the effects on the dynamics of a finite system size.

In Figs. 5.7.3 (b) and (d), we show the results of calculations of the absolute value of the Fourier transform of $\lim_{t_0 \rightarrow -\infty} \text{Re}[C^{(\times)}(t + \tau, t)]$ with respect to τ . This is done for each value of N_s in Fig. 5.7.2 by fixing $t = 2000$ and evaluating a diagonal time slice of each plot shown there for $\tau \in [-200, 200]$. These time slices are shown in Fig. 5.7.6 (a) ($\lambda = 0.1$) and (c) ($\lambda = 0.5$). From Eqs. (3.4.1) and (3.4.15), the quantity plotted in Figs. 5.7.3 (b) and (d) satisfies the following identity:

$$\mathcal{F}[\text{Re}[C^{(\times)}(\tau + t, t)]; \Omega] = \frac{P_{LR}(\Omega) + P_{RL}(\Omega)}{2} \quad (5.7.2)$$

We are therefore simply plotting the absolute value of the average symmetrized cross-correlations in Figs. 5.7.3 (b) and (d). In Fig. 5.7.3 (b), we plot this for $\lambda = 0.1$, and observe oscillating resonant frequencies at values of $n\Omega_{N_s}$ for some intrinsic frequency Ω_{N_s} that depends on the length of the wire. We find that Ω_{N_s} decreases with increasing wire length. For example, the main $N_s = 5$ resonance occurs at $\Omega_5 \simeq 0.15$, corresponding to a time of $2\pi/\Omega_5 \simeq 40 \simeq 2\tau_{max}$, i.e. the distance between peaks on Fig. 5.7.3 (a) and 5.7.2 (b). This is to be expected from the heuristic relation (5.7.1) and the contour plots of Fig. 5.7.2. When we increase the intersite coupling to $\lambda = 0.5$ in Fig. 5.7.3 (d), we find that the position of the main resonance, for each value of N_s , shifts by a factor of roughly 5, and the frequency range over which resonances are observed increases from roughly 0.5 to 2.5. Thus we conclude that these peaks can be attributed to wire traversal events, as they scale with N_s and λ in the fashion predicted by the heuristic relation (5.7.1). It can also be seen by comparing Figs. 5.7.3 (b) and (d) that the higher frequency

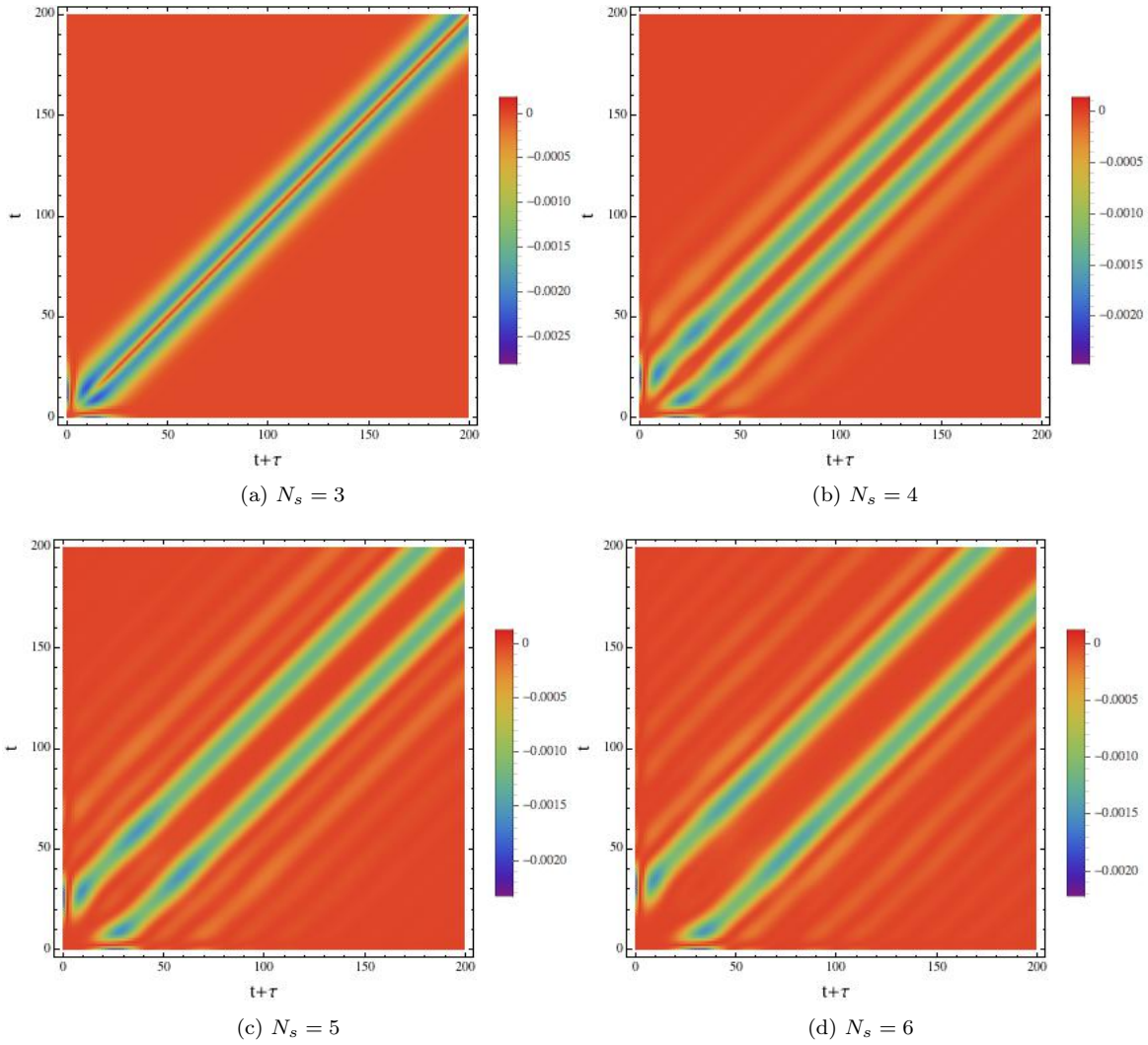


Figure 5.7.2: Plots of $\text{Re} [C^{(\times)}(t + \tau, t)]$ for $V = V_L = -V_R = 5$, $\lambda = 0.1$, $E = 1$, $\Gamma = 0.5$ where the number of sites is varied so that (a) $N_s = 3$, (b) $N_s = 4$, (c) $N_s = 5$ and (d) $N_s = 6$.

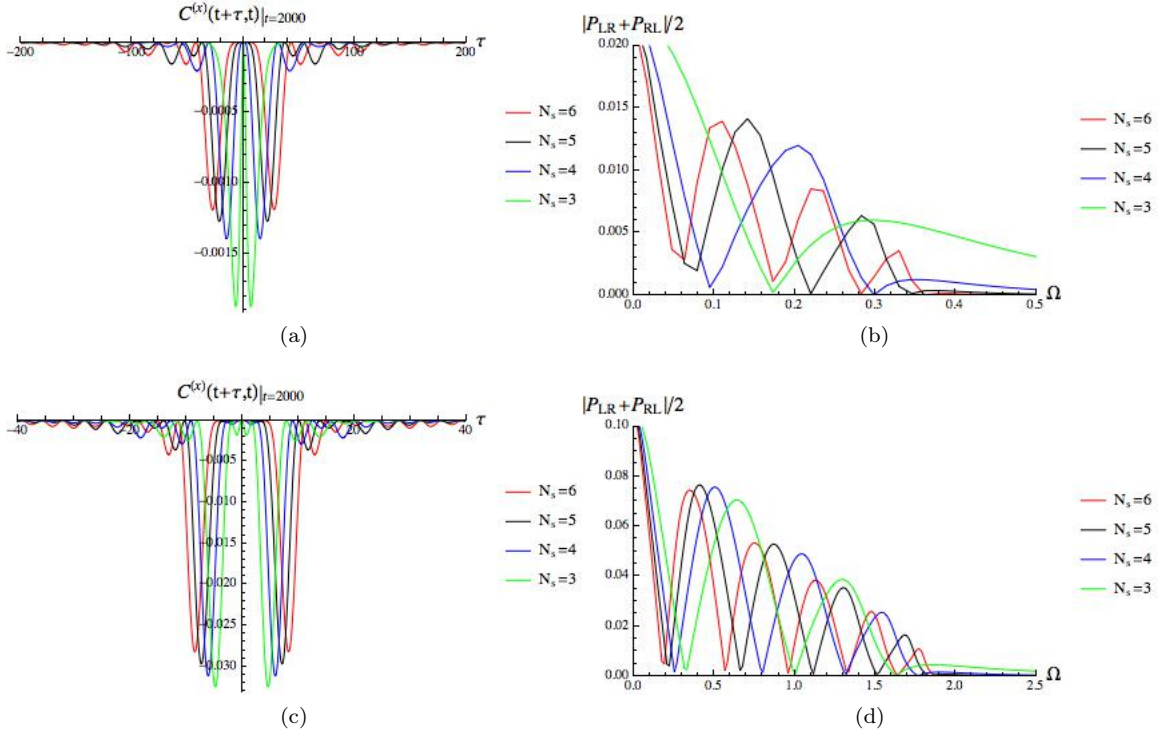


Figure 5.7.3: (a) Cross-section of $\text{Re}[C^{(\times)}(t+\tau, t)|_{t=2000}]$ for the relative time range $\tau \in [-200, 200]$, with $\lambda = 0.1$. (b) Plot of the low frequency end of the average symmetrized power spectrum of cross-correlations, $(P_{LR}(\Omega) + P_{RL}(\Omega))/2$ obtained as the numerical Fourier transform of the signal in (a). (c) Cross-section of $\text{Re}[C^{(\times)}(t+\tau, t)|_{t=2000}]$ for the relative time range $\tau \in [-40, 40]$, with $\lambda = 0.5$. (d) The low frequency region of $(P_{LR}(\Omega) + P_{RL}(\Omega))/2$ obtained from (c). We use the parameters $V = V_L = -V_R = 5$, $E = 1$, $\Gamma = 0.5$ throughout.

modes occurring at multiples of Ω_{N_s} are stronger and more numerous in the $\lambda = 0.5$ case than for $\lambda = 0.1$. These modes correspond to the subsidiary ‘ripples’ seen to emanate from the main resonances in Fig. 5.7.2. Physically, these ripples are due to internally reflected electrons, or ‘circular currents’ that contribute weakly to the cross-lead correlations in each lead when compared with the main influence of electrons propagating directly from the other lead.

5.7.2 AC-Driven Noise in the Molecular Wire

To understand how the timescale of the resonance occurring in the case of the perpendicular wire combines with an AC field, we will now compute the cross-correlations for the same type of driving that was studied in Ref. [2], where long transients were observed due to the relative sparsity of the level width matrix for a wire in the configuration of Fig. 1.4.1 (a). Specifically, we employ the bias (5.4.4) $V_L = 5$, $V_R = 5$, $A_L^{(1)} = 4 = A_R^{(1)}$, $A_L^{(2)} = 0 = A_R^{(2)}$, $\Omega_L = 1 = \Omega_R \equiv \Omega_D$, $p_1 = 1$, with the only difference between the leads coming from a symmetry-breaking phase: $\phi_L = 0$, $\phi_R = -\pi/2$.

In Fig 5.7.4 we exhibit the contour plot of $\text{Re}[C^{(\times)}(t+\tau, t)]$ with these model parameters, as was done in Fig. 5.7.2 for the constant bias switch-on. In similar fashion to the calculations exhibited in Fig. 5.7.4, we show this quantity for different numbers of atomic sites $N_s = 3, 4, 5, 6$, calculated with a summation over Bessel modes ranging from -6 to 6 . As for the static bias case, we see a very strong ‘ripple’ spreading out from the diagonal at all values of N_s with a maximum magnitude at some value of the relative time τ_{max} . We see in Figs. 5.7.4 (a)-(d) that τ_{max} increases linearly with increasing N_s , as in the constant bias case, but unlike that case the absolute value of the maximum oscillates with t with a period of $2\pi/\Omega_D$. We take this oscillating ‘ridge’ at particular values of τ to be

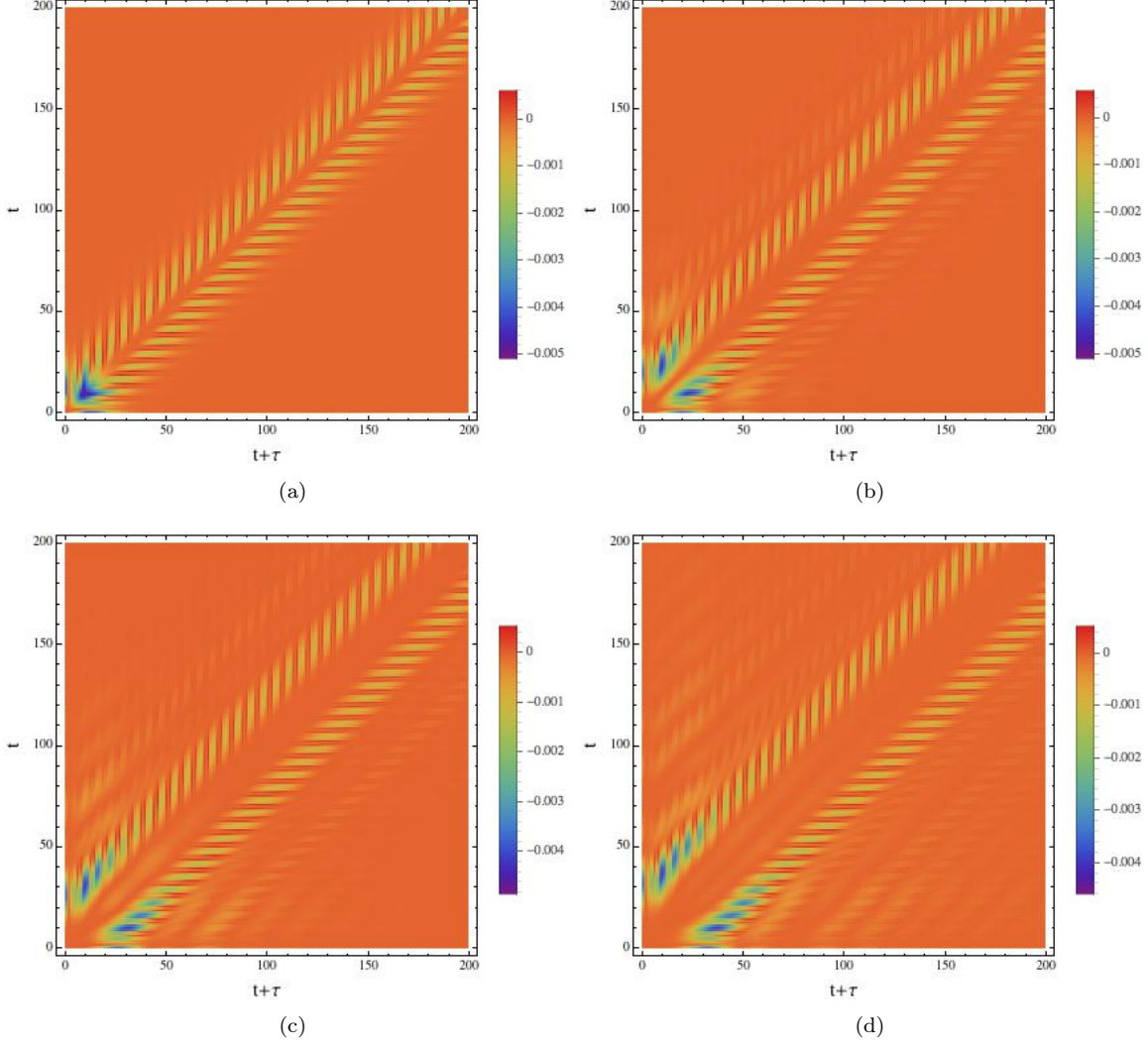


Figure 5.7.4: Contour plots of $\text{Re}[C^{(\times)}(t+\tau, t)]$, for (a) $N_s = 3$, (b) $N_s = 4$, (c) $N_s = 5$ and (d) $N_s = 6$, with model parameters $V_L = 5$, $V_R = 5$, $A_L^{(1)} = 4 = A_R^{(1)}$, $A_L^{(2)} = 0 = A_R^{(2)}$, $\Omega_L = 1 = \Omega_R \equiv \Omega_D$, $p_1 = 1 = p_2$, $\phi_L = 0$, $\phi_R = -\pi/2$.

indicative of the traversal time for electrons crossing the junction.

In Fig. 5.7.5 (a) we plot the $\tau = 0$ cross-correlation $C^{(\times)}(t, t)$ for different values of the end-site level width parameter Γ in a five-site wire. Similarly to Fig. 5.7.1 (a), we observe a resonance occurring in the absolute value of $C^{(\times)}(t, t)$ for the perpendicular five-site wire at most values of Γ , and the frequency of this resonance does not appear to be related to the driving frequency Ω_D (or even to the specific kind of applied bias) as it is unchanged from its position of $t_{res} \simeq 20$ in the static bias case considered in Fig. 5.7.1. After the resonance, the cross-correlation decays to a signal with a smaller amplitude, whilst retaining a complex periodic ‘ringing’ signal, as shown in the inset to Fig. 5.7.5 (a). In Fig. 5.7.5 (b), we again plot the measurement time Fourier transform $|\mathcal{F}[C^{(\times)}(t, t); \omega]|$. In addition to the peak at $\omega = \Omega_D$ corresponding to regular PAT processes, we observe an additional peak at a much lower frequency at the same position as in Fig. 5.7.1 (b), namely at $\omega_{res} \simeq 0.3\Omega_D$. We emphasize that this frequency should be distinguished from the resonance in the steady state correlations, Ω_{N_s} . The peak in Fig. 5.7.5 (b) becomes increasingly dominant as Γ is decreased from 5 to 1. In Fig. 5.7.5 (c) we plot $C^{(\times)}(t, t)$ for $\Gamma \in [0.05, 1]$. It is seen that the resonance at $\omega_{res} \simeq 0.3\Omega_D$ continues to grow as Γ decreases, before saturating in the region of

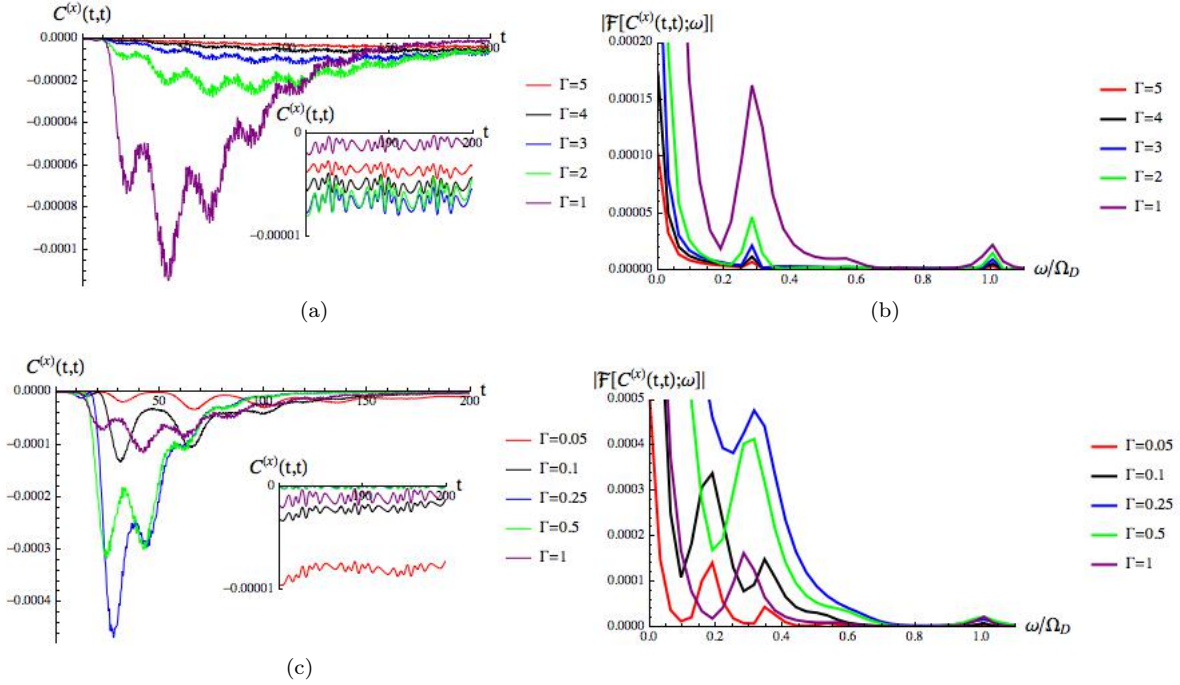


Figure 5.7.5: (a) Plot of $C^{(\times)}(t, t)$ for $\Gamma \in [1, 5]$. (b) Plot of the low-frequency end of the absolute value of the Fourier transform $\mathcal{F}[C^{(\times)}(t, t); \omega]$ for the same parameters as (a), in units of the fundamental driving frequency Ω_D . (c) Plot of $C^{(\times)}(t, t)$ for $\Gamma \in [0.05, 1]$. (d) Plot of the low-frequency end of $|\mathcal{F}[C^{(\times)}(t, t); \omega]|$ for the same parameters as (c). Parameters chosen are $V_L = 5$, $V_R = 5$, $A_L^{(1)} = 4 = A_R^{(1)}$, $A_L^{(2)} = 0 = A_R^{(2)}$, $\Omega_L = 1 = \Omega_R \equiv \Omega_D$, $\phi_L = 0$, $\phi_R = -\pi/2$, $N_s = 5$, $\lambda = 0.1$.

$\Gamma = 0.25$, whereupon the resonance decays into a less singular form. This is reflected in the frequency spectrum of this signal, shown in Fig. 5.7.5 (d), which shows how the resonance continues to grow before reaching the saturation value of Γ and splitting into two smaller resonant peaks as Γ tends to 0.

The frequency of the resonance in Figs. 5.7.5 (b) and (d) is located at about $0.3 - 0.35\Omega_D$ regardless of whether the bias is AC or DC, and seems to be only moderately affected by changes in Γ . We therefore suspect that it is due to the finite size and intrinsic properties of the wire. In Fig. 5.7.6, we present calculations of the cross-correlation in the same system, this time varying the hopping parameter λ and keeping the coupling parameter fixed at $\Gamma = 0.5$. Fig. 5.7.6 (a) shows that, as λ is doubled from 0.1 to 0.2, the time at which the resonance kicks in is approximately halved, before being scaled down by a factor of $\sim 2/3$ as λ is further increased to 0.3. This is reflected in the Fourier Transform of these signals shown in Fig. 5.7.6 (b), which show that the position of the resonant frequency increases linearly with increasing λ , as expected from the heuristic relation (5.7.1). As we continue to increase the coupling parameter, the duration of the transient resonance becomes shorter until it approaches the time of 2π , i.e. the time period of the fundamental driving frequency $\omega_{res} = \Omega_D$ at around $\lambda = 0.3$. For values of the coupling greater than this, we see indeed in Fig. 5.7.6 (c) that that timescale of the transient becomes smaller than the timescale associated with the driving. The frequency spectrum of cross-correlations, shown in Fig. 5.7.6 (d), contains peaks at $\omega_{res} \simeq 1.4\Omega_D$ (when $\lambda = 0.4$) and $\omega_{res} \simeq 1.75\Omega_D$ (when $\lambda = 0.5$), corresponding to a continuation of the linear dependence of the transient resonant frequency on λ . However, when we cross into the regime of $\lambda/\Gamma > 1$ (purple line), this resonance has been submerged beneath the growing resonances at integer values of ω/Ω_D , a fact which is reflected in the strongly oscillating signal of the purple line in Fig. 5.7.6 (c). These resonances continue into the high-frequency part of the spectrum beyond the narrow window exhibited here, and are due to PAT processes.

The calculations presented here point to a rather clear physical interpretation of the transient behaviour of cross-

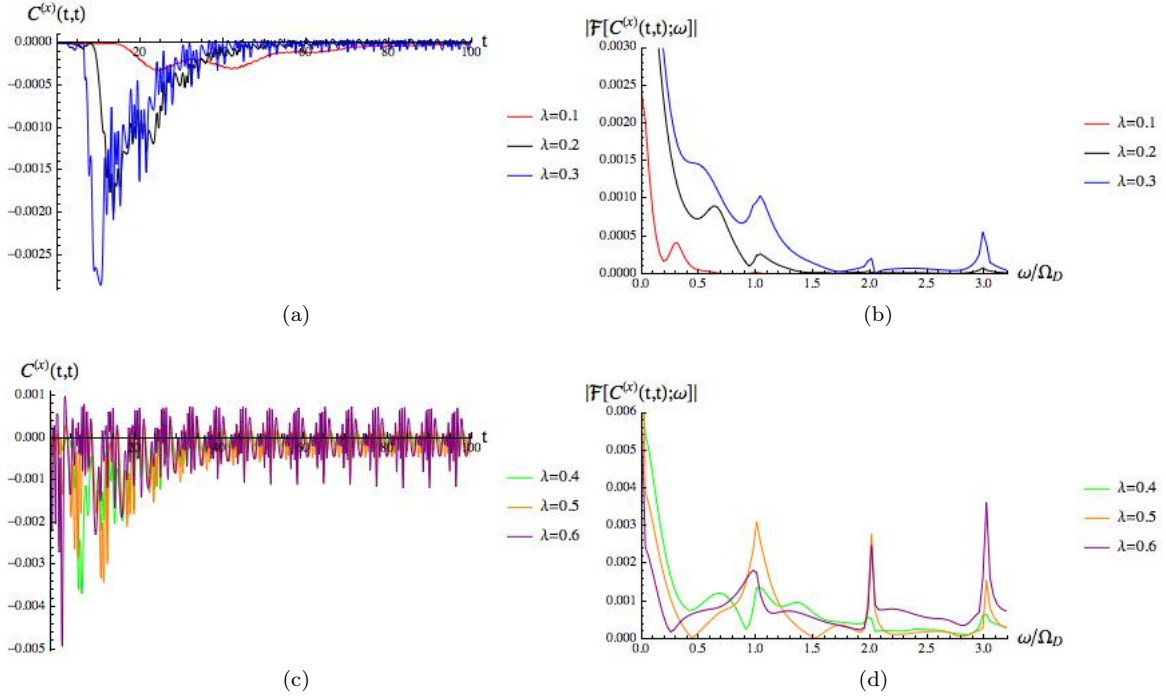


Figure 5.7.6: (a) Plot of $C^{(\times)}(t, t)$ for $\lambda \in [0.1, 0.3]$. (b) Plot of the low-frequency end of the absolute value of the Fourier transform $\mathcal{F}[C^{(\times)}(t, t); \omega]$ for the same parameters as in (a), in units of the fundamental driving frequency Ω_D . (c) Plot of $C^{(\times)}(t, t)$ for $\lambda \in [0.4, 0.6]$. (d) Plot of the low-frequency end of $|\mathcal{F}[C^{(\times)}(t, t); \omega]|$ for the same parameters as in (c). Parameters chosen are $V_L = 5$, $V_R = 5$, $A_L^{(1)} = 4 = A_R^{(1)}$, $A_L^{(2)} = 0 = A_R^{(2)}$, $\Omega_L = 1 = \Omega_R \equiv \Omega_D$, $\phi_L = 0$, $\phi_R = -\pi/2$, $N_s = 5$.

correlations in extended systems. There are three factors which compete to determine how long electrons take to cross the nanojunction: the strength of the end-site coupling Γ , the length of the wire $N_s - 1$ and the internal hopping parameter λ . When $\Gamma/\lambda > 1$, the molecular wire is more resistant to propagating electrons than the molecule-electrode interface. Although the large value of Γ tends to reduce the lifetime of molecular modes, the small value of λ makes it difficult for tunneling between sites to occur. This means that the time taken for electrons to traverse the molecular region is significantly longer than the timescale of the external driving field, and so the currents in each lead, $I_L(t)$ and $I_R(t)$ become more strongly correlated at about the time taken for electrons to propagate between the leads following the switch-on. This explains the resonant ‘kick’ at $t_{res} \simeq 20$ in Figs. 5.7.5 (a) and (c), which remains at this time so long as $\Gamma > \lambda$. However, as Γ is decreased to the weak coupling regime of $\Gamma/\lambda < 1$, we enter a regime in which it is energetically easier to tunnel between molecular sites than across the molecule-lead interface. This increases the likelihood of internal reflection or circular currents, and leads to the splitting of the single frequency peak in Fig. 5.7.5 (d) into two smaller peaks.

The position of the resonance in frequency space is determined by λ and N_s . Physically, as the coupling between molecular sites is increased, it becomes increasingly easier for electrons to traverse the wire. In the DC case we saw that increasing the value of λ increases the strength of reflected currents within the molecular wire. In the AC case, we found that in the regime of $\lambda \sim \Gamma \sim \Omega_D$, the time taken for electrons to pass from lead L to lead R is smaller than the rate at which photon-assisted electrons tunnel from the lead onto the molecule. In this regime, the electrons can travel between leads in less time than it takes for the signal driving them to undergo an appreciable change.

Once the resonance in $C^{(\times)}(t, t)$ has died out, a steady state is achieved which is oscillatory in the case of an AC bias, and stationary in the case of a DC bias. In the latter case, we saw in Section 5.7.1 the emergence of a regime in which each lead at time t felt the influence of the other most strongly at a time shifted by τ_{max} , which was roughly equal to the time t_{res} , and which changed with N_s and λ in the same way as t_{res} . This suggests the existence of a time delay for information to propagate between the L and R leads that shows up in the low frequency power spectrum, and in the equal time cross-correlations. The question of how to define the traversal time for electrons tunneling across a nanostructure has been the subject of much debate, with a variety of different definitions proposed, mainly based on the rate of change of wavepacket phase with respect to momentum [152, 308]. The results presented here point to a new method of determining this time for large molecular structures, namely, by identifying the low frequency resonances in the transient of $C^{(\times)}(t, t)$, or in the steady-state Fourier transform of $C^{(\times)}(t + \tau, t)$ with respect to the time difference τ .

Chapter 6

Quantum Transport in Response to a Fluctuating Bias

6.1 Introduction

So far the time-dependent response of molecular junctions to a deterministic bias has been the subject of our numerical investigations. In this Chapter, the stochastically driven systems discussed in Section 1.4.2.3 will be studied theoretically, which can be done within our formalism as the time-dependent bias is arbitrary. In Chapter 2 we proved the physically intuitive equivalence between shifting all the molecular energies by a time-dependent quantity, and shifting all the lead energies by an equal and opposite quantity. This fact enables us to treat stochasticity in the bias and in the molecular energies on the same formal footing.

Modern derivations of the Nyquist theorem use a Langevin equation approach to solve for the electric current, in which the stochastic bias acts as the generalized fluctuating force [160]. In Section 6.2 we consider the quantum-statistical analogue to the Langevin equation, in which the time-dependent inhomogeneities in the Kadanoff-Baym equations fluctuate in time. The bias in each lead contains a Gaussian stochastic part with negative exponential correlation function, characterised by the correlation time τ_c and fluctuation strength D . From a general expression for the current averaged with respect to the fluctuating bias, we first consider the quasistatic limit of large τ_c , and find an exact analytical formula for the current average. This expression is of the LB-type in the steady state limit, so that a closed expression can be found for an effective transmission function, which reduces to the formula in [241] for transmission through a fluctuating dot level. Next, we obtain a general formula for the average current for any τ_c , expressed in powers of $D\tau_c$. This new formula contains the transient which follows the switch-on of the noisy bias. In addition, those terms due to the system preparation can also be identified and are shown to vanish at long times, which demonstrate once again the equivalence of the partitioned and partition-free approaches at long times, even when the driving field is stochastic. The resulting formula for the current also has the particular virtue that it takes an asymptotic (long time) value which is of the LB form (1.4.7), and we can therefore extract an effective transmission function from it. In the $\tau_c \rightarrow 0$ limit of white noise fluctuations, this transmission function again reduces to the one published in [241].

We next present a novel numerical scheme for calculating the current response to a noisy bias, based on the Matsubara expansion of the current formula which removes all frequency integrals. This massively increases the computational efficiency of this method and makes fast calculation of noisy transport through complex nanostructures a real possibility. We show that for arbitrary extended systems, the fluctuations effectively modify the complex poles of the Fermi distribution function, so that the effect of fluctuations is equivalent to a thermal ‘smearing’ of

resonances in the transmission function. We interpret this as a *generalized fluctuation-dissipation relation* for quantum transport. Section 6.2 ends with a demonstration that our current formula satisfies the Memory-loss Theorem, and we go on to find direct counter-proofs to each of the main claims of Ref. [244]. Finally, in Section 6.3 we apply this numerical scheme to the problem of tunnelling through the five-site molecular wire illustrated in Fig. 1.4.1, in both the transient and steady state regimes. We find that there is a transition from nonlinear to Ohmic behaviour in the $I - V$ characteristics of the steady-state current as the fluctuation parameter D is increased. In addition, we observe for the first time the existence of a stochastic resonance effect in the conductance spectrum of the molecular wire.

6.2 Quantum Model of the Stochastic Bias

6.2.1 Classical Model and the Quantum Analogy

The problem of transport through a classical circuit with a stochastic applied driving bias has been studied using the Langevin equation method. In the simplest case, one solves the equation which encodes Ohm's Law for the current [232, 160]:

$$L \frac{dI}{dt} + RI(t) = V(t) \quad (6.2.1)$$

Here, L and R denote the inductance and resistance of the circuit, respectively. In the simplest case, the driving bias $V(t)$ is zero on average, but 'flickers' around this average value so that small bursts of current can be observed through the conductor. Taking $I(t_0) = I_0$, the solution to (6.2.1) is easily seen to be:

$$I(t) = I_0 e^{-\frac{t-t_0}{\tau_r}} + \frac{R}{L} \int_{t_0}^t d\bar{t} V(\bar{t}) e^{-\frac{t-\bar{t}}{\tau_r}} \quad (6.2.2)$$

Here we have defined the circuit relaxation time $\tau_r \equiv \frac{L}{R}$. If the experiment is carried out over a long enough time, the current averaged across realizations of the experiment will be equal to zero. It is then assumed that the bias is a Gaussian zero-mean process, and that the autocorrelation function of $V(t)$ is localized, such that its statistical weight integrated over all times is proportional to some fixed parameter D which quantifies the fluctuations of the bias. From these assumptions the current can be found, along with the time-dependent variance of the current, and both contain modes which decay on a timescale of $\tau_r = L/R$. One can also derive the following well-known result, a version of the *second fluctuation-dissipation theorem* [309, 219]

$$4DL^2 = J_V(\omega = 0) = 4Rk_B T \quad (6.2.3)$$

where $J_V(\omega)$ is the power spectrum of the bias fluctuations defined for positive frequencies. The expression (6.2.3) states the direct equivalence of the resistance of the conductor R and fluctuations of the bias, quantified by D , which at first sight appear to have a disconnected physical origin. These observations provide us with qualitative indications of the behaviour to look for in the analogous nanojunction. To study such a junction, we specialize the formalism described in Chapter 2 to the situation in which a bias in each lead is switched on at t_0 before fluctuating about some mean value V_α . The stochastic bias in lead α has the form:

$$V_\alpha(t > t_0) = V_\alpha + V^s(t) \quad (6.2.4)$$

Here, $V^s(t)$ is assumed to be a zero-mean, stationary, Gaussian stochastic process. This means that even-ordered

statistical moments can be decomposed into products of pair correlation functions, and odd-ordered moments vanish:

$$\overline{V^s(t)} = 0 \quad (6.2.5)$$

$$\overline{V^s(t_1) V^s(t_2)} = \overline{V^s(t_1 - t_2) V^s(0)} = C(t_1 - t_2) \quad (6.2.6)$$

$$\overline{V^s(t_1) \dots V^s(t_{2n})} = \sum_p C(t_{p_1} - t_{p_2}) \dots C(t_{p_{2n-1}} - t_{p_{2n}}) \quad (6.2.7)$$

$$\overline{V^s(t_1) \dots V^s(t_{2n+1})} = 0 \quad (6.2.8)$$

$\sum_p$ denotes a summation over all permutations of pairs of the time variables, and the bar denotes the average taken with respect to the stochastic bias. From the discussion in Section 2.6.1, this is equivalent to assuming that the driving term $V_C(t)$ on the right-hand side of the Kadanoff-Baym equations is stochastic, and equal to $-V^s(t)$, with a constant bias V_α switched on in each lead. In analogy with the classical approach in [160], we assume that

$$\int_{-\infty}^{\infty} d\tau \overline{V^s(\tau) V^s(0)} = 2D \quad (6.2.9)$$

where D is some parameter characterizing the magnitude of bias fluctuations. The time-dependent stochastic bias enters into our formula for the current via exponential factors of the form

$$e^{i\varphi^s(t_1, t_2)} \equiv \exp \left(i \int_{t_2}^{t_1} d\tau V^s(\tau) \right) \quad (6.2.10)$$

so we make use of the following general theorem for taking the average of these [310]:

$$\overline{e^{\pm i\varphi^s(t_2, t_1)}} \equiv \overline{\exp \left(\pm i \int_{t_1}^{t_2} d\tau V^s(\tau) \right)} = \exp \left[-\frac{1}{2} \int_{t_1}^{t_2} d\tau_1 \int_{t_1}^{t_2} d\tau_2 C(\tau_1 - \tau_2) \right] \quad (6.2.11)$$

Note that $C(\tau_1 - \tau_2)$ is independent of the sign on $V^s(t)$ so that an expression containing an average of the form (6.2.11) will be identical to one in which all energies on the molecule are shifted by $\pm V^s(t)$. To proceed further with numerical implementations, one needs to assume a specific functional form for $C(\tau_1 - \tau_2)$. In the simplest case, the white noise correlation function is assumed:

$$C(\tau_1 - \tau_2) = 2D\delta(\tau_1 - \tau_2) \quad (6.2.12)$$

Noting that the value of the function (6.2.11) must be invariant under the exchange $t_1 \leftrightarrow t_2$, we see that for the white noise stochastic bias it must be given by:

$$\overline{e^{\pm i\varphi^s(t_2, t_1)}} = e^{-D|t_1 - t_2|} \quad (6.2.13)$$

One may also choose a correlation function which involves a parameter $\omega_c = 1/\tau_c$, defining a finite correlation time τ_c , over which the bias is statistically correlated:

$$C(\tau_1 - \tau_2) = D\omega_c e^{-\omega_c|\tau_1 - \tau_2|} \quad (6.2.14)$$

This correlator arises e.g. in approximate microscopic models of molecular energy level fluctuations caused by electron-phonon interactions, in which case ω_c is a measure of the phononic band width [311, 312]. It should be noted that this means of incorporating the effects of a phononic environment on the molecule is valid only for T greater than the Debye temperature [313]. Inserting (6.2.14) into (6.2.11) gives:

$$\overline{e^{\pm i\varphi^s(t_2, t_1)}} = \exp \left\{ -D \left[|t_1 - t_2| - \frac{1}{\omega_c} \left(1 - e^{-\omega_c |t_1 - t_2|} \right) \right] \right\} \quad (6.2.15)$$

In the case of the white noise the correlation time is zero. Notice that the expression (6.2.15) tends to the white noise expression (6.2.13) in the $\omega_c \rightarrow \infty$ limit, and that (6.2.15) tends to 1 when $\omega_c \rightarrow 0$. Also, we observe that either case satisfies (6.2.9). In practice, values for the fluctuation parameter D may be determined from experiments that measure the two-time correlation function. We could also permit D to have some dependence on ω_c [314]. For example, in the Gauss-Markov model of exciton transport [311, 312, 315], and in Ref. [241] the correlation function (6.2.14) with $D = \sigma^2/\omega_c$ is used, where $\sigma = \sqrt{(V^s(t))^2}$ is the standard deviation of molecular site fluctuations. By the arguments in the previous section, this model is formally equivalent to the one we are considering with a fluctuating bias in the leads. Using the fact that

$$e^{\pm i\varphi^s(t_2, t_1)} e^{\pm i\varphi^s(t_1, t_3)} = e^{\pm i\varphi^s(t_2, t_3)} \quad (6.2.16)$$

we can perform the average over the stochastic bias on the leads in formula (2.6.11) and write in expanded form the bias-averaged current:

$$\begin{aligned} \overline{I_\alpha(t)} = & \frac{1}{\pi} \int d\omega f(\omega - \mu) \text{Tr}_C \mathbf{\Gamma}_\alpha \left\{ 2\text{Re} \left[i e^{i(\omega + V_\alpha - \mathbf{h}_{CC}^{eff})(t-t_0)} \overline{e^{i\varphi^s(t, t_0)}} \mathbf{G}^r(\omega) + \int_{t_0}^t d\tau e^{i(\omega + V_\alpha - \mathbf{h}_{CC}^{eff})(t-\tau)} \overline{e^{i\varphi^s(t, \tau)}} \right] \right. \\ & - e^{-i\mathbf{h}_{CC}^{eff}(t-t_0)} \sum_\gamma \left[\mathbf{G}^r(\omega) \mathbf{\Gamma}_\gamma \mathbf{G}^a(\omega) + 2\text{Re} \left[i \mathbf{G}^r(\omega) \mathbf{\Gamma}_\gamma \int_{t_0}^t d\tau e^{i(\omega + V_\gamma - \mathbf{h}_{CC}^{eff})(\tau-t_0)} \overline{e^{i\varphi^s(\tau, t_0)}} \right] \right. \\ & \left. \left. + \int_{t_0}^t d\tau \int_{t_0}^t d\bar{\tau} e^{-i(\omega + V_\gamma - \mathbf{h}_{CC}^{eff})(\tau-t_0)} \mathbf{\Gamma}_\gamma e^{i(\omega + V_\gamma - \mathbf{h}_{CC}^{eff})(\bar{\tau}-t_0)} \overline{e^{-i\varphi^s(\tau, \bar{\tau})}} \right] e^{i\mathbf{h}_{CC}^{eff}(t-t_0)} \right\} \quad (6.2.17) \end{aligned}$$

where the averages of the exponential bias-containing terms are given by (6.2.15). This general formula is the central result of this paper. We drop the CC notation on Green's functions defined in the molecular region basis for notational simplicity. In the last term of Eq. (6.2.17), the double integral is in general no longer separable into single integrals over the variables $\tau, \bar{\tau}$ due to the presence of the phase average which binds these variables into a single function of the difference $\tau - \bar{\tau}$. This leads to slight mathematical complications which will be addressed in Sections 6.2.2 and 6.2.3.

6.2.2 The quasistatic limit

Before proceeding to develop the full theory for a Gaussian colour noise with correlation function given by (6.2.14), we present results for the quasistatic limit of large τ_c . This corresponds to a stochastic bias that undergoes fluctuations over a very long time scale relative to the intrinsic timescales of the nanojunction. This case was addressed in Ref. [241] for the single-level CC region, so it provides an important check on the validity of our

theory. Expanding the exponent in (6.2.15) in powers of ω_c and keeping only the first term, we find that the phase factor is effectively replaced by a Gaussian:

$$\overline{e^{\pm i\varphi^s(t_2, t_1)}} \simeq \exp \left[-\frac{1}{2} D\omega_c |t_2 - t_1|^2 \right] \quad (6.2.18)$$

Notice that in the limit of $\omega_c \rightarrow 0$, (6.2.18) tends to 1, because in this limit $V^s(t)$ is frozen at its mean value of 0 and therefore this case is equivalent to the limiting case of a static bias switch-on process. This expression is then substituted into (6.2.17) and all time integrals can be analytically performed. This is done by projecting the current formula onto the right and left eigenvectors of the non-Hermitian matrix $\mathbf{h}_{CC}^{eff}$, introduced in Eq. (2.5.19), and the details of this analysis are included in Appendix B.2. Here we simply point out that in the long-time limit Eq. (B.2.5) reduces to an expression which is of the LB type:

$$\lim_{t_0 \rightarrow -\infty} \overline{I_\alpha(t)} = \frac{1}{\pi} \sum_\gamma \int d\omega [f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)] T_{\gamma\alpha}(\omega) \quad (6.2.19)$$

with

$$T_{\gamma\alpha}(\omega) = \sqrt{\frac{\pi}{2D\omega_c}} \sum_{j,k} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \left[e^{-\frac{(\omega - \bar{\varepsilon}_j)^2}{2D\omega_c}} \left[1 + \operatorname{erf} \left(i \frac{(\omega - \bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}} \right) \right] + c.c., j \leftrightarrow k} \right] \quad (6.2.20)$$

where we denote $c.c., j \leftrightarrow k$ to denote the complex conjugation of the preceding term with indices j and k exchanged. At first sight, this expression bears little resemblance to the formula obtained in [241] for the high τ_c transmission probability, which is a convolution integral of Gaussian and Lorentzian functions. To illustrate the connection with their work, we specialize to a system consisting of a quantum dot sandwiched between two terminals, such that $\bar{\varepsilon}_j = \varepsilon_0 - i\frac{\Gamma}{2}$, where ε_0 is the dot energy, Γ is a scalar and $\bar{\varepsilon}_j - \bar{\varepsilon}_k^* = -i\Gamma$. In this case the transmission probability for electrons to pass from lead γ to lead α becomes

$$T_{\gamma\alpha}(\omega) = \sqrt{\frac{2\pi}{D\omega_c}} \frac{\Gamma_\alpha \Gamma_\gamma}{\Gamma} \mathbb{V} \left(\frac{\Gamma}{2\sqrt{2D\omega_c}}, \frac{-(\omega - \varepsilon_0)}{\sqrt{2D\omega_c}} \right) = \frac{1}{\sqrt{2\pi D\omega_c}} \int_{-\infty}^{\infty} d\varepsilon' \frac{\Gamma_\alpha \Gamma_\gamma}{(\omega - \varepsilon_0 - \varepsilon')^2 + \Gamma^2/4} \exp \left(-\frac{\varepsilon'^2}{2D\omega_c} \right) \quad (6.2.21)$$

where

$$\mathbb{V}(a, b) \equiv \frac{a}{\pi} \int_{-\infty}^{\infty} dz \frac{e^{-z^2}}{(z - b)^2 + a^2} = \operatorname{Re} \left[e^{(a+ib)^2} [1 - \operatorname{erf}(a + ib)] \right] \quad (6.2.22)$$

is the *Voigt function* [316, 317].

If one makes the replacement $D \rightarrow \sigma^2/\omega_c$, one sees that the expression (6.2.21) is identical to the formula (12) in Ref. [241], which was obtained by completely different means. We emphasize that our approach is much more general than that of German *et al.*, because it generalizes their formula for the transmission function to multiple leads and a multi-level Hamiltonian. Most significantly for the present work, it enables us to study the effect of a strongly correlated energy fluctuation on the transport in all time regimes, for both the partitioned and partition-free switch-on processes.

6.2.3 Expansion for arbitrary τ_c

6.2.3.1 Effective transmission and the white noise limit

A general theory of fluctuating-bias driven transport must include calculation of the current and transmission of a system for all values of the correlation time τ_c , including as a special case the white noise limit described by (6.2.12) when $\tau_c \rightarrow 0$. To this end, we expand the colour noise phase average (6.2.15) in powers of $D\tau_c$:

$$\overline{e^{\pm i\varphi^*(t_2, t_1)}} = \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} e^{-(D+m\omega_c)|t_2-t_1|} \quad (6.2.23)$$

To derive the bias-averaged current for arbitrary values of τ_c , one inserts (6.2.23) into (6.2.17), and evaluates the subsequent formula in the left/right eigenbasis as was done for Eq. (B.2.5). Once again using the relation (B.2.4), it is possible to split the formula for the time-dependent current into a part that converges to a fixed value and a part that decays to zero with increasing $t - t_0$:

$$\begin{aligned} \overline{I_\alpha(t)} &= \frac{1}{\pi} \sum_{\gamma \neq \alpha} \int d\omega [f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)] T_{\gamma\alpha}(\omega, D, \omega_c) \\ &+ \frac{1}{\pi} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \int d\omega f(\omega - \mu) \left\{ 2\text{Re} \left[\sum_j \frac{\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} i \frac{e^{i(\omega + V_\alpha - \varepsilon_j + i(D+m\omega))(t-t_0)} (V_\alpha + i(D+m\omega_c))}{(\omega - \bar{\varepsilon}_j)(\omega + V_\alpha - \bar{\varepsilon}_j + i(D+m\omega_c))} \right] \right. \\ &\quad - \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \left[\frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \left(\frac{\delta_{n0}}{\omega - \bar{\varepsilon}_j} - \frac{1}{(\omega + V_\gamma - \bar{\varepsilon}_j + i(D+m\omega_c))} \right) \right. \\ &\quad \left. \left. + \frac{[e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} - e^{i(\omega + V_\gamma - \varepsilon_j + i(D+m\omega))(t-t_0)}]}{(\omega + V_\gamma - \bar{\varepsilon}_k^* + i(D+m\omega_c))} \left(\frac{1}{\omega - \bar{\varepsilon}_j} - \frac{1}{(\omega + V_\gamma - \bar{\varepsilon}_j + i(D+m\omega_c))} \right) + c.c.j \leftrightarrow k \right] \right\} \quad (6.2.24) \end{aligned}$$

where $T_{\beta\alpha}(\omega, D, \omega_c)$ is an effective transmission given by a sum of Lorentzians centred on $(\bar{\varepsilon}_j + \bar{\varepsilon}_k^*)/2$ with a level width that increases with D :

$$\begin{aligned} T_{\gamma\alpha}(\omega, D, \omega_c) &= \sum_{j,k} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*) \\ &\times \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \frac{i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*) + 2(D+m\omega_c)}{\left(\omega - \frac{\bar{\varepsilon}_j + \bar{\varepsilon}_k^*}{2}\right)^2 + \frac{1}{4}(i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*) + 2(D+m\omega_c))^2} \quad (6.2.25) \end{aligned}$$

In Appendix B.3, the current in Eq. (6.2.24) is re-written in terms of a summation over special functions, which arise from the evaluation of the frequency integrals in this formula. We now focus on the long time limit when the resulting bias averaged current converges to a finite value given by a LB type expression containing an effective transmission probability depending upon both D and ω_c :

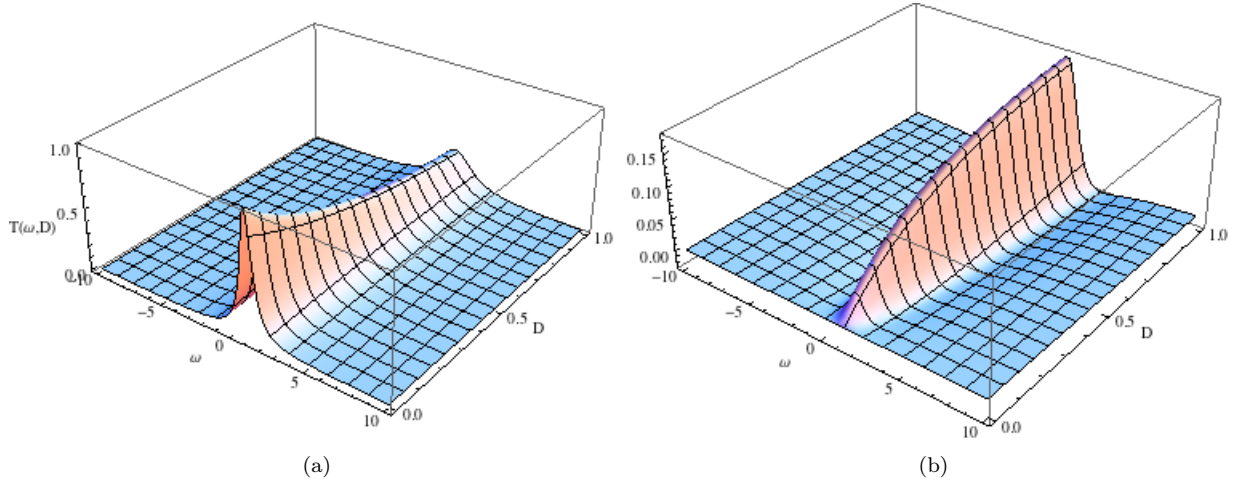


Figure 6.2.1: (a) Variation of the frequency-dependent transmission function as the fluctuation parameter D is increased from 0 to 1. (b) Setting $\omega_c = 1$, we plot the difference $T(\omega, D, \omega_c) - T(\omega, D, \omega_c \rightarrow \infty)$. Both plots assume coupling parameters $\Gamma_L = 0.5 = \Gamma_R$, and dot energy $\varepsilon_0 = 1$.

$$\lim_{t_0 \rightarrow -\infty} \overline{I_\alpha(t)} \equiv I_\alpha^{LB}(D, \omega_c) = \frac{1}{\pi} \sum_\gamma \int d\omega [f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)] T_{\gamma\alpha}(\omega, D, \omega_c) \quad (6.2.26)$$

We note that those modes of the current which die out, are, as in Ref. [1], exactly those which result from the preparation of the system, and therefore the asymptotic bias-averaged current satisfies the Theorem of Equivalence; in this limit it has the same value whether one takes the partitioned or the partition-free approach [189]. If the additional assumption is made that all the level width matrices are proportional, i.e. $\mathbf{\Gamma}_\gamma = x_\gamma \mathbf{\Gamma}$, then the summation indices decouple and (6.2.25) is re-expressible as:

$$T_{\gamma\alpha}(\omega, D, \omega_c) = x_\gamma \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \text{Tr}_C [\mathbf{\Gamma}_\alpha \mathbf{G}^r(\omega + i(D + m\omega_c)) (\mathbf{\Gamma} + 2(D + m\omega_c)) \mathbf{G}^a(\omega - i(D + m\omega_c))] \quad (6.2.27)$$

From this result we can establish a second connection with published work, by taking the white noise limit ($\omega_c \rightarrow \infty$) of $T_{\gamma\alpha}(\omega, D, \omega_c)$ and once again considering the simple case of the single level system studied in Section 6.2.2. In this limit, all terms in the expansion (6.2.27) of the transmission probability vanish with the exception of the $n = 0$ mode:

$$\lim_{\omega_c \rightarrow \infty} T_{\gamma\alpha}(\omega, D, \omega_c) = \frac{\Gamma_\alpha \Gamma_\gamma}{\Gamma} \frac{\Gamma + 2D}{(\omega - \varepsilon_0)^2 + (\Gamma/2 + D)^2} \quad (6.2.28)$$

This agrees exactly with the formula (15) in Ref. [241]. Clearly the effect of large fluctuations of the bias about its mean value is to flatten the transmission function and therefore eliminate the resonance at frequencies close to ε_0 . The resonance is sharpest at $D = 0$, in which case the transmission (6.2.28) assumes the well-known Breit-Wigner form [241, 128], and the resulting current formula is given exactly by the steady state LB formula. We remark in passing that the analytic results of Ref. [211] lead to the same effective transmission as Eq. (6.2.28) under the appropriate limits.

In Fig. 6.2.1 (a) we plot the transmission function (6.2.28) for a two-lead system with symmetric coupling $\Gamma_L = 0.5 = \Gamma_R$, and dot energy $\varepsilon_0 = 1$. The transmission function is a probability distribution in frequency space, so that

by virtue of the Heisenberg energy-time uncertainty principle, we interpret a narrow distribution as corresponding to eigenmodes of the dot with a long lifetime. In all previous treatments of steady state quantum transport, it has effectively been assumed that $D = 0$ so that this lifetime is given by approximately $\tau_{el} \sim 2/\Gamma$. However, here the bias is not assumed perfectly static, but is instead allowed to fluctuate about its fixed value, and the lifetime of molecular modes is decreased to $\tau_{el} \sim \frac{1}{\Gamma/2+D}$. This is clearly illustrated by Fig. 6.2.1 (a), where this decrease of temporal uncertainty is mirrored by a complete flattening out of the transmission function at all frequencies. The qualitative effects of this on the $I - V$ characteristics of a system with white noise fluctuations will be discussed in Section 6.3.

6.2.3.2 Particle Number

Using identical techniques to the derivation of Eq. (B.3.1), one can obtain the bias-averaged density of electrons on the l -th site of the molecule as:

$$\begin{aligned}
\overline{\rho_{ll}(t)} &= -i \langle l | \mathbf{G}^<(t, t) | l \rangle \\
&= \frac{1}{\pi} \text{Re} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \sum_{j,k,\gamma} \frac{\langle l | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle \langle \varphi_k^R | l \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \\
&\quad \times \left[\frac{\delta_{n0}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\frac{i\pi}{2} + e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu) \right) \right] \right. \\
&\quad \left. + \frac{[1 - e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}]}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\gamma + i(D + m\omega_c)) \right) \right. \\
&\quad \left. + \frac{e^{-i(\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c))(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j - V_\gamma - i(D + m\omega_c)} [\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu)) - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c)))] \right. \\
&\quad \left. + \frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j - V_\gamma - i(D + m\omega_c)} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c)) \right) \right] \right. \\
&\quad \left. + \frac{e^{-i(\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c))(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} [\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c))) - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c)))] \right. \\
&\quad \left. + \frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c)) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c)) \right) \right] \right] \\
&\quad \left. \right] \quad (6.2.29)
\end{aligned}$$

One can show that in the long time limit the site density is given by the expression:

$$\begin{aligned}
\lim_{t_0 \rightarrow -\infty} \overline{\rho_{ll}(t)} &= \frac{1}{\pi} \text{Re} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \sum_{j,k,\gamma} \frac{\langle l | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle \langle \varphi_k^R | l \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)} \\
&\quad \times \left[\frac{i\pi}{2} + \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\alpha + i(D + m\omega_c)) \right) \right] \quad (6.2.30)
\end{aligned}$$

This gives the following constant value for the total particle number (recalling the factor of 2 arising from spin degeneracy and using completeness of the molecular orbitals):

$$\lim_{t_0 \rightarrow -\infty} \overline{N_C(t)} = \lim_{t_0 \rightarrow -\infty} \sum_l^{N_s} \overline{\rho_{ll}(t)} \quad (6.2.31)$$

$$\begin{aligned} &= \frac{1}{\pi} \text{Re} \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \\ &\quad \times \left[i\pi + 2\Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\alpha + i(D + m\omega_c)) \right) \right] \end{aligned} \quad (6.2.32)$$

We can make a general statement about Eq. (6.2.30) in the limit of large D , as the digamma function vanishes in this limit, giving:

$$\lim_{t_0 \rightarrow -\infty, D \rightarrow \infty} \overline{\rho_{ll}(t)} = \frac{1}{\pi} \text{Re} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \sum_{j,k,\gamma} \frac{\langle l | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle \langle \varphi_k^R | l \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_k^* - \bar{\varepsilon}_j)} \frac{i\pi}{2} \quad (6.2.33)$$

Using the idempotency relation (2.5.20), the relation $\langle \varphi_j^L | \Gamma | \varphi_k^R \rangle = -i(\bar{\varepsilon}_k^* - \bar{\varepsilon}_j) \langle \varphi_j^L | \varphi_k^R \rangle$ and the following identity for the summation (enabling us to remove it as a constant prefactor)

$$\sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} = e^{D(1-1)/\omega_c} = 1 \quad (6.2.34)$$

we can see that the long-time site density converges to a state of exactly half-filling in the limit of very strong fluctuations:

$$\lim_{t_0 \rightarrow -\infty, D \rightarrow \infty} \overline{\rho_{ll}(t)} = \frac{1}{2} \quad (6.2.35)$$

where the l -th state was assumed to be normalized, $\langle l | l \rangle = 1$. This behaviour was observed numerically in Ref. [211], but in Eq. (6.2.35) we have obtained the far stronger result of a rigorous proof which holds for all systems, independently of molecular structure.

6.2.3.3 Fluctuation-Dissipation

We showed in Chapter 2 that in the steady state following the switch-on of a static bias, the transmission function can be expressed in terms of Green's functions of the CC region, and this transmission was given in Eq. (2.8.16). On inspection one can see that for a single level dot in the $D \rightarrow 0$ limit equation (6.2.28) reduces exactly to the formula (2.8.16) for the transmission function. Therefore, for the case of the quantum dot, the effect of adding a stochastic part to the bias is identical to the effect of adding another lead to the junction with self-energy $-iD\mathbf{I}$, although the two sources of dissipation on the dot are physically distinct. More generally, if one considers the structure of the summand in (6.2.27), it is strikingly similar to that of (2.8.16). The expression (6.2.27) is identical to a weighted sum of transmission functions of the form found in (2.8.16) for a molecule whose coupling to each lead $\gamma \neq \alpha$ is enhanced:

$$\Gamma_\gamma \rightarrow \Gamma_\gamma + x_\gamma 2(D + m\omega_c) \mathbf{I} \quad (6.2.36)$$

The relation (6.2.36) relates the self-energy, which describes the broadening and dephasing of molecular eigenmodes, to the fluctuation of the bias placed across the molecular junction. This is analogous to the Nyquist theorem, which

relates fluctuations in the bias to the dissipative quantity R . However, in contrast to the classical circuit, in the quantum case the fluctuations make a modification to the ‘frictional’ term $\mathbf{\Gamma}$ which is *additive*. Formally, the effects are similar to the self-energies used in phenomenological theories of the electron-phonon coupling strength, in which the influence of the e-ph coupling is equivalent to that of a fictitious probe coupled to the system [318, 319].

The relation (6.2.36) applies only to systems satisfying the condition that $\mathbf{\Gamma}_\gamma = x_\gamma \mathbf{\Gamma}$, which should hold for very small or dot-like systems, but in other circumstances it is not exact and should only be used to guide physical intuition. It would be desirable to find a general principle that relates the smearing out of quantum features in the transport to the fluctuations in the bias (or, equivalently, of energy levels in the molecule), valid for arbitrary $\mathbf{\Gamma}_\gamma$. This can be done if we expand the Fermi function into a sum of N_p simple poles defined in the complex energy plane using Eq. (4.2.2). The full formula for the time-dependent current in terms of special functions obtained from a Matsubara expansion is given in Eq. (B.3.1) of Appendix B.3, and the detailed implementation of these formulas using the Padé parameters is described in Appendix A.3. If the temperature of the system is increased then each pole ζ_l/β is shifted further away from the real axis; therefore a uniform shift of all the poles tends to flatten out the Fermi function around $x = 0$, and to ‘smear’ out quantum effects in this regime. Inserting Eq. (4.2.2) into Eq. (6.2.26) and performing the resulting contour integrals, we obtain the following formula for the current in terms of the poles:

$$I_\alpha^{LB}(D, \omega_c) = \frac{2i}{\beta} \sum_\gamma (V_\alpha - V_\gamma) \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c}\right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \sum_{j,k} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \\ \times \lim_{N \rightarrow \infty} \sum_{l=1}^N \eta_l \left[\frac{1}{\left(\bar{\varepsilon}_j - V_\alpha - \mu - i\left(D + m\omega_c + \frac{\zeta_l}{\beta}\right)\right) \left(\bar{\varepsilon}_j - V_\gamma - \mu - i\left(D + m\omega_c + \frac{\zeta_l}{\beta}\right)\right)} + c.c._{j \leftrightarrow k} \right] \quad (6.2.37)$$

In the white noise limit, (6.2.37) is exactly equal to the regular LB formula in Eq. (4.3.9) of Chapter 4, in which all poles of the Fermi function undergo the shift

$$\frac{\zeta_l}{\beta} \rightarrow \frac{\zeta_l}{\beta} + D \quad (6.2.38)$$

so that the formal effect of the fluctuating white noise bias is therefore to shift all of the poles of the Fermi function lying on the imaginary frequency axis by a constant value D . We expect that this will generate similar physics to an increase in temperature, as the latter change also has the effect of increasing the magnitude of the positive and negative imaginary poles $\pm \frac{\zeta_l}{\beta}$. For the general case of the coloured noise, we can assert the following result:

The asymptotic value of the average current through a molecule subject to bias fluctuations with magnitude D and correlation time τ_c is a weighted sum of LB-type formulas evaluated with Fermi functions whose poles are shifted as

$$\frac{\zeta_l}{\beta} \rightarrow \frac{\zeta_l}{\beta} + D + m/\tau_c \quad (6.2.39)$$

where m is an integer.

Although this statement is valid for fluctuations described by the correlation function (6.2.14) and hence as such is not completely general, it can obviously be generalized to a correlation function fitted to a sum of negative exponentials and can therefore be used to describe a vast number of Gaussian stochastic processes. We therefore expect that the effect of a non-zero stochastic bias should affect its resistance in a similar (but not identical) way to a temperature increase: at large temperatures, Eq. (6.2.37), implies a linear dependence of the resistance on temperature, as in the Nyquist theorem. An exact formula for the multi-level resistance is further illustrated by considering the resistance of the single-level model in Section 6.3. We note in passing that in Ref. [1] we identified

those terms in the current which arise from either the initial condition for the lesser Green's function or from vertical contour convolutions. These terms contain information on the way the system was prepared, as they arise from the Matsubara Hamiltonian. One can see during the derivation of Eq. (B.3.1) that those terms which are *not* preparation dependent conform to the relation in Eq. (6.2.39). So we conclude: *the relation (6.2.39) is also true for all the time-dependent modes of the lesser Green's function and current which arise from real-time convolutions taken on the horizontal part of the Konstantinov-Perel' contour.*

Finally, we can conclude from the LB-type structure of Eq. (6.2.37) that, if there is no net bias across the junction, i.e. $V_\alpha = V_\gamma$ for all γ , then no current can flow, regardless of the molecular structure. A *ratchet* is a structure described by a spatially periodic potential $V(x)$ which lacks reflection symmetry, and is of interest for the understanding of transport processes in biological systems, which can efficiently transport molecules across a system with no applied potential or thermal gradient [320, 92, 93, 231]. Substantial work has been done on directed noise-induced transport resulting from broken symmetries [314, 234, 223, 225]. In particular, it was shown that in ratchet structures a net current can be established from fluctuating forces, given that the fluctuations are non-Gaussian and that all odd statistical moments of the fluctuations are vanishing [314, 234]. Furthermore, Łuczka *et al.* demonstrated that if the structure is reflection symmetric, then there is no current unless the fluctuations are *asymmetric*, i.e. with odd-ordered moments that are non-zero [223, 225]. Consistently with Eq. (6.2.37), this work implies that the quantum ratchet effect cannot be observed in any system if the net bias is zero and the fluctuations are Gaussian. However, in the published work it was usually assumed that the fluctuations were spatially homogeneous. By contrast, one can show with a straightforward extension (via the replacement $V^s(t) \rightarrow V_\alpha^s(t)$) of our formalism that one could generate a net current with zero net bias if the fluctuations in each lead are of a different magnitude, even if they are Gaussian. In this case the fluctuation parameter D acquires a lead index α and the formula for $I_\alpha^{LB}(D, \omega_c)$ would no longer be of the LB type. The resulting current is a kind of stochastic ‘pump’ as it results from a stochastic dynamical asymmetry in the fluctuating lead Fermi levels, even though there is zero net bias [271]. As we are not focusing on asymmetry effects here, we defer proper investigation of this stochastic pump to a future work.

6.2.3.4 Multistability and Asymptotics

In Ref. [189] two key theorems of noninteracting quantum transport were established. The first, known as the Theorem of Equivalence, states that the *long-time limit* of the current response to an arbitrary time-dependent bias is the same for both the partitioned and the partition-free approaches. Our TD-NEGF formula was shown [1] to satisfy this theorem, and so any asymptotic formulas for the current derived in this paper are valid in either framework. The second, called the Memory-loss Theorem, states that if the bias $V_\alpha(t)$ tends to a static value V_α as $t - t_0 \rightarrow \infty$, the current also possesses a unique asymptotic value which is a function of V_α [189]. In Ref. [1], we proved that our formula satisfies this theorem as well and that the value of the asymptotic current is given by an expression of the LB form. A recent paper on transport through a fluctuating level [244] has brought these theorems into question by suggesting that tunneling through a fluctuating energy level can generate multistability in the long-time current in a manner that violates the Memory-loss Theorem.

Specifically Ref. [244] considered tunneling through a single fluctuating level of energy ε_0 , which is symmetrically coupled to left and right leads, so that the level width matrices become scalars obeying $\Gamma_L = \frac{\Gamma}{2} = \Gamma_R$. They calculated the symmetrized current, which in our formalism can be written as follows:

$$\overline{I_{LR}(t)} \equiv \frac{\overline{I_L(t)} - \overline{I_R(t)}}{2} = \frac{1}{2\pi} \int d\omega f(\omega - \mu) \text{Re} \left[i\Gamma e^{i\omega(t-t_0)} \left(\overline{e^{i\psi_L(t,t_0)} S_L(t, t_0; \omega)} - \overline{e^{i\psi_R(t,t_0)} S_R(t, t_0; \omega)} \right) \right] \quad (6.2.40)$$

where S_L, S_R are scalar functions defined as in Eq. (2.5.88) and the effective Hamiltonian $\mathbf{h}_{CC}^{eff} \rightarrow h^{eff} = \varepsilon_0 - i\Gamma/2$. Numerical simulations on this model are reported in [244] which appear to provide support for the following propositions: (i) If the noise on the level is white, then there is no effect on the asymptotic current, even if the noise is present at all times, including in the asymptotic limit. (ii) If the noise on the level is coloured and switched on during the transient regime $t \in [t_0, 2/\Gamma]$ following the switch-on, then the asymptotic current is suppressed with respect to its LB value, even if the noise is switched off subsequent to the transient regime. (iii) Any kind of noise switched on only after the transient regime has elapsed (i.e. for $t > 2/\Gamma$) can have no effect on the asymptotic current. In this work a partitioned approach is used within the WBLA, and in addition to the lead-dot coupling, the dot energy acquires a stochastic time-dependence $V(t)$ at time t_0 . The method used to establish (i)-(iii) was based on a numerical time-stepping scheme, which calculates long-time currents for different trajectories of $V(t)$ before averaging across the resulting ensemble for the ensemble average of the current.

Clearly, claim (ii) of the above violates the Memory-loss theorem because it implies that one can have a static bias in the long time limit without the corresponding relaxation to a unique value of the current. In addition, (i) implies that one can have a level which is constantly undergoing fluctuations due to interactions with its environment, but if they are completely uncorrelated in time then there is no effect on the transport. (iii) also implies this, but in addition implies that correlated fluctuations also have no effect if they are switched on after the crucial initial period. A complete theory of transport through a fluctuating level must be able to address these rather fundamental claims.

The formula (6.2.28) is proof that white noise fluctuations on a dot energy level can affect the asymptotic value of the current passing through it, so long as $\lim_{\tau_c \rightarrow 0} D \neq 0$. This contradicts claim (i) of Ref. [244], where it was asserted that the electrons do not ‘see’ the fluctuations in the energy level and so therefore the transport is unaffected. However, there are good physical reasons to suppose the contrary - we have already discussed numerical work in the Introduction where fluctuations lead to changes in the steady-state current [211, 243]. Physically, one can see that during the transport process, a dot energy with white noise can jump frequently to values far from the mean energy ε_0 . This means that, in the time it takes for an electron to hop across the junction, the energy gradient across the junction can switch sign and the electron has an equal probability to hop in any direction. There is no longer a resonance at ε_0 because electrons with this energy are no longer ‘privileged’ in the transport process with respect to electrons of other energies. In Fig. 6.2.1 (b) we illustrate the effect of a finite correlation frequency of $\omega_c = 1$ on the transport through the single level system, by plotting the difference in the transmission (6.2.25) and the white noise transmission function (6.2.28). We find that as D is increased this difference grows larger, before flattening out, so that the effect of colour noise on the transmission is to slow down its decay with increasing fluctuation strength. Physically, this means that the energies on the dot are not completely random, so there are still some ‘privileged’ energy values at which the electron will be transported.

Claim (ii) is straightforward to check. Choosing the time t_u as the upper bound of the transient regime, we can simply set $V_\alpha^s(t) = 0$ for any $t > t_u$ (so that $V_\alpha(t) = V_\alpha$ is constant at these times) and evaluate the long time limit of the main ingredient of the current (2.6.11):

$$\lim_{t \rightarrow \infty} \overline{e^{i\omega(t-t_0)} e^{i\psi_\alpha(t,t_0)} \mathbf{S}_\alpha(t, t_0; \omega)} = \mathbf{G}^r(\omega + V_\alpha) \quad (6.2.41)$$

Indeed, the first term in $e^{i\omega(t-t_0)} e^{i\psi_\alpha} \mathbf{S}_\alpha$ contains the time-decaying exponent $e^{i(\omega \mathbf{1} - \mathbf{h}_{CC}^{eff})(t-t_0)} \sim e^{-\frac{1}{2}\Gamma(t-t_0)}$, which vanishes in the $t \rightarrow \infty$ limit. In the second term,

$$-i \int_{t_0}^t d\tau e^{i(\omega \mathbf{1} - \mathbf{h}_{CC}^{eff})(t-\tau)} e^{-i\varphi_\alpha(t,\tau)}$$

we split the integral by the time t_u . The integral over the interval $\bar{t} \in [t_0, t_u]$ vanishes because $e^{-i\mathbf{h}^{eff}(t-\tau)}$ goes to zero for all τ in this integrand. The second integral taken over the interval $\bar{t} \in [t_u, t]$ can be easily calculated yielding

$$-\mathbf{G}^r(\omega + V_\alpha) \left[e^{i((\omega + V_\alpha)\mathbf{1} - \mathbf{h}_{CC}^{eff})(t-t_0)} - 1 \right]$$

As the exponential term tends to zero at long times, we immediately obtain (6.2.41). Replacing $e^{i\omega(t-t_0)}e^{i\psi_\alpha}\mathbf{S}_\alpha$ with $\mathbf{G}^r(\omega + V_\alpha)$ in the formula (2.6.11) for the current, we recover the LB formula. Hence, at long times the unique value of the current corresponding to the stationary result is established even if the color noise is only present during the transient. Although this is sufficient to contradict claim (ii) on its own, it is actually a much weaker condition than the Memory-loss theorem, which implies that the bias could fluctuate in any way at any finite time, so long as it takes a static value asymptotically, and the value of the current will be a unique function of that value. This theorem can be proven for any system within the WBLA by recognizing that the time t_u can be taken infinitesimally close to t , resulting in the LB value for the asymptotic current even in this case. Thus, we have explicitly verified the Memory-loss theorem for any TD bias within the WBLA and ultimately demonstrated that claim (ii) of Ref. [244] is false. As this theorem is true for any realization of the ensemble defined by the noisy bias $V_\alpha^s(t)$, it is also true for the ensemble average, which explains the limit (6.2.41).

The equation for the current contains the transient following the switch-on of the noisy bias, and we can therefore use it to verify the validity of claim (iii). We can easily check this by setting $V_\alpha^s(t) = 0$ for $t \in [t_0, t_u]$ and choosing $V_\alpha^s(t)$ as a generic colour noise characterized by the parameters D, ω_c . The following limit can then be calculated using the same methods as in Section 6.2.3, and considering the convergence of the integrand in the regions $\tau \in [t_0, t_u]$ and $\tau \in [t_u, t]$:

$$\lim_{t \rightarrow \infty} e^{i\omega(t-t_0)} \overline{e^{i\psi_\alpha(t,t_0)} S_\alpha(t, t_0; \omega)} = \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} G^r(\omega + V_\alpha + i(D + m\omega_c)) \quad (6.2.42)$$

This result is clearly not equal to the final value of $G^r(\omega + V_\alpha)$, which would result from a static bias switch-on process. We note that our conclusion is strongly supported by the numerical work published in Ref. [211]. Therefore, claim (iii) of Ref. [244] is also contradicted because it implies that a constantly fluctuating bias switched on outside the transient period should result in the LB current.

6.3 Numerics

To get an idea of how the voltage-dependence of the current varies with the bias fluctuations, we consider the current through a molecular wire consisting of $N_s = 5$ atoms, coupled to two leads L and R in the perpendicular configuration illustrated in Fig. 5.4.3 (a). Additionally, we choose the chemical potential $\mu = 0$ and the matrix elements $E = 1, \lambda = 0.1, \Gamma_{11} = 0.5 = \Gamma_{55}$ which define the energy and time scales in arbitrary units. The mean values of the fluctuating bias are written $\overline{V_L(t)} \equiv V_L$ and $\overline{V_R(t)} \equiv V_R$.

We first consider the effects of white noise on the $I-t$ characteristics of the system, using the formula (B.3.1) with $\tau_c = 0, E = 1, V_L = 10$ and $V_R = 0$, and using the Padé expansion with $N_p = 20$ to evaluate all special functions. In Fig. 6.3.1 (a), we plot as a function of both the time t and fluctuation parameter D the long time average of the symmetrized current, defined (similarly to Eq. (5.4.13)) for an arbitrary coupling to the leads as:

$$\overline{I_{LR}(t)} \equiv \frac{\overline{I_L(t)} - \overline{I_R(t)}}{2} \quad (6.3.1)$$

Whereas for low D there is an oscillatory ‘ringing’ transient signal following the switch-on of the bias, for strong

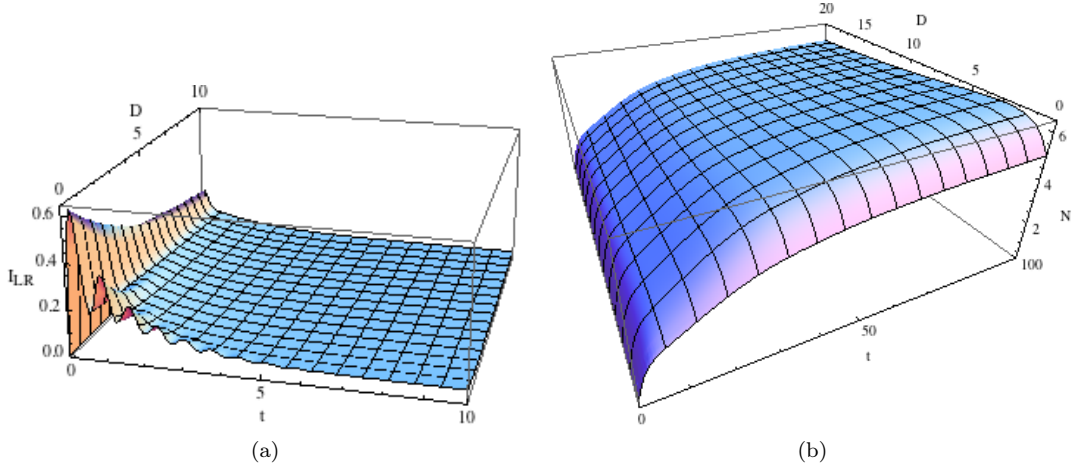


Figure 6.3.1: (a) The time-dependent symmetrized current $\overline{I_{LR}}(t)$ computed as a function of D using parameters $k_B T = 0.1$, $V_L = 10$, $V_R = 0$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = 1$, $\lambda = 0.1$. (b) The time-dependent bias-averaged particle number $\overline{N_C}(t)$ in the molecular wire.

fluctuations these oscillations are washed out. The time-dependent effects of the fluctuation on the decay of modes can be clearly seen in the general formula (B.3.1). The timescale of the decaying modes is influenced by the imaginary part of the complex eigenvalues $\bar{\epsilon}_j = h_j - i\gamma_j$, from which the decay time can be given roughly as $\tau \equiv \text{Max}\{1/\gamma_j\}$ [2]. In addition to terms for which this is the only source of decay, we note the existence of modes with prefactors of the form $e^{-n\pi k_B T}$ for integer n , so that an increase in temperature has the dynamical effect of pushing the system more rapidly towards its stationary state. Fluctuations on the bias or energy levels increase the rate of decay in these modes of the current, which acquire a prefactor of $e^{-(D+m\omega_c)(t-t_0)}$ for the m -th term of the summation. The fluctuations therefore speed up the loss of stable molecular eigenmodes into the leads in a similar (but not exactly equivalent) way to the temperature and the level width Γ , consistently with the discussion of Eqs. (6.2.36) and (6.2.39) given above.

In Fig. 6.3.1 (b), we show the time dependence of the bias average $\overline{N_C}(t)$ of the particle number $N_C(t) \equiv -2i \text{Tr}_C [\mathbf{G}^<(t, t)]$, which can be evaluated from Eq. (6.2.29) using the same methods as for the current. The central region undergoes a fast filling process before asymptoting long after the most dramatic oscillations in the current have died down, at $t \sim 100$. This timescale is due to the sparsity of the level width matrix, as discussed in Ref. [2] and Chapter 5. The plot in Fig. 6.3.1 (b) shows that the steady-state value of $\overline{N_C}$ approaches the half-filled value of 5 as D is increased. This behaviour is implicit in the half-filling result of Eq. (6.2.35), which gives

$$\lim_{t_0 \rightarrow -\infty, D \rightarrow \infty} \overline{N_C}(t) = \lim_{t_0 \rightarrow -\infty, D \rightarrow \infty} 2 \sum_{l=1}^{N_s} \overline{\rho_{ll}}(t) = N_s \quad (6.3.2)$$

i.e. the bias-averaged particle number equals half the number of available states (in a spin degenerate system) for any value of ω_c .

Now we move to the steady-state regime and focus on the effects of white noise on the $I - V$ characteristics of the system, using the formula (B.3.2). Fixing $V_R = 0$, we vary V_L so that the molecular chain energy levels are always located in the bias window where the transport occurs. In Fig. 6.3.2(a), we plot as a function of both the bias $V = V_L - V_R$ and fluctuation parameter D the long time average of $\overline{I_{LR}}(t)$. In order to focus solely on the effects of the fluctuations we set $k_B T = 0.1$. Whereas the characteristic nonlinear step-like structure is observed at low values of D [67, 321, 322, 323, 324, 66], there appears to be a smooth transition to a linear $I - V$ relation as the magnitude of the bias fluctuations are increased.

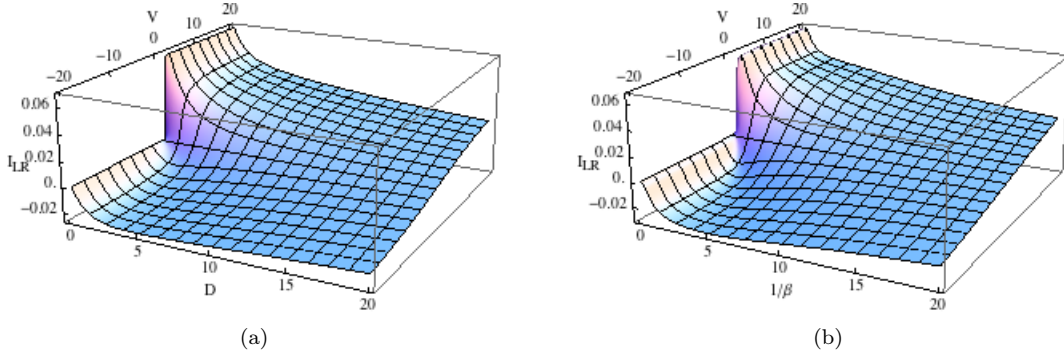


Figure 6.3.2: (a) The symmetrized current as a function of voltage V and fluctuation D , with $k_B T = 0.1$, $V_R = 0$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = 1$, $\lambda = 0.1$. (b) The current in the left lead as a function of V and $k_B T$, with $D = 0.1$ and all other parameters as in (a).

In order to rationalize this behaviour, we consider the zero temperature limit of (6.2.26) for arbitrary noise. The problem of transport with site fluctuations at low temperature is of specific interest in the Anderson insulator problem considered in Ref. [247]. It also provides us with guidance on the qualitative features one may expect to see in the current as a function of the bias and the fluctuation parameters D and ω_c . The formula (6.2.26) in this limit assumes the form:

$$\lim_{T \rightarrow 0} I_\alpha^{LB}(D, \omega_c) = \frac{2}{\pi} \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle i (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \times \left[\arctan \left(\frac{V_\alpha + \mu - (\bar{\varepsilon}_j + \bar{\varepsilon}_k^*)/2}{D + m\omega_c + i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)/2} \right) - \arctan \left(\frac{V_\gamma + \mu - (\bar{\varepsilon}_j + \bar{\varepsilon}_k^*)/2}{D + m\omega_c + i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)/2} \right) \right] \quad (6.3.3)$$

It is worth comparing this expression with Eq. (1.4.31) of Chapter 1. Whereas there the effect of a periodic driving field was to replace the current with a weighted sum of arctan functions with shifted *bias*, here the effect of a stochastic driving field is to replace the current with a weighted sum of arctan functions with shifted *level width*. As D is increased, the region in which the arctan is approximately linear also increases, and the current's dependence on the bias becomes exactly linear, as can be seen from the $D \gg V_{\alpha/\gamma}$ limit of (6.3.3):

$$\lim_{T \rightarrow 0, D \gg V_{\alpha/\gamma}} I_\alpha^{LB}(D, \omega_c) \simeq \frac{4}{\pi} \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle i (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \times \left[\sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \frac{1}{2(D + m\omega_c) + i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \right] (V_\alpha - V_\gamma) \quad (6.3.4)$$

The obtained expression shows that the fluctuations drive a transition from nonlinearity in the $I - V$ characteristic current to an Ohmic regime. It also demonstrates that, when the noise is white, I_α^{LB} tends to 0 in the $D \rightarrow \infty$ limit, i.e. there is zero net current across the nanojunction. This explains the approach of $\overline{N_C(t)}$ to the half-filling value in the steady state and high D limits: in a given time interval, electrons have an equal probability of tunneling from the α lead onto the molecule or in the opposite direction due to the random flipping of the sign on the potential gradient, so their probability of occupying the molecular region must be 1/2. In addition, this non-linear to linear transition contradicts another key claim of Ref. [244], where it was stated that no change in the shape of the $I - V$ characteristic results from the fluctuating level, except that the amplitude of the current signal is suppressed.

To provide some physical insight into this behaviour, we plot in Fig. 6.3.2 (b) the $I - V$ characteristics of the same molecular chain system with the fluctuation parameter kept fixed at $D = 0.1$, and we instead vary $k_B T$. Interestingly, this case leads to qualitatively similar results to Fig. 6.3.2 (a), in that the current plotted appears not only to have very similar absolute values, but it also approaches linearity. As discussed in Section 6.2.3 for both dynamical and static modes of the current, the effect of raising the magnitude of the fluctuations is physically similar to raising the temperature throughout the system, explaining the classical behaviour at large values of D .

One might intuitively think that the loss of coherence due to increasing fluctuations in the bias/molecular energies always tends to weaken the current signal. However, when systems possess some sort of activation threshold for a transport process, and a nonlinear dependence on the input signal [325], it is possible for a noisy environment to actually enhance the output signal, in a phenomenon known as *stochastic resonance* [227, 228, 229, 231]. Notice in Figs. 6.3.2 (a-b) that for $V > 1$, the current is always decreasing with D , whereas when $V < 1$, the current possesses a negative maximum for a particular value of D before approaching zero. In the latter case, we see that the current is a non-monotonic function of D , as it approaches a negative resonant peak for a particular value of D , before decaying to zero. This behaviour was seen for a single level system in Ref. [211] and is also similar to results obtained for the Langevin dynamics of Brownian particles in the asymmetric problems discussed in Section 6.2.3.3 [221, 222, 326, 226]. We emphasize that whereas the resonance of this Brownian particle occurs in ‘noise rectifiers’ with zero applied bias, we are instead discussing this the effects of noise on a system with a non-zero average bias. One can interpret the stochastic resonance in Fig. 6.3.2 either in terms of the fluctuating bias or in terms of fluctuating levels. When $V > 1$, the molecular wire energies are always located within the $[V_L, V_R]$ transport window, whereas for $V < 1$, E is always above this window. Taking the bias to fluctuate, one should have in mind a picture of the system where increasing D causes the entire bias window to fluctuate until it overlaps with the molecular energy levels, at which point the transport is enhanced. If the fluctuations are located in the molecular levels, a qualitative interpretation of the resonance derives from the effective broadening of the spectral density of states due to a modified level width (note, however, that Eq. (6.2.36) is not strictly valid in this multi-level system as Γ_L is not proportional to Γ_R) [238, 211].

In Fig. 6.3.3 (a), we plot for $\tau_c = 0$ the bias-dependence of the conductance

$$G(V; D, \omega_c) \equiv \frac{\partial \overline{I_{LR}}(t \rightarrow \infty)}{\partial V} \quad (6.3.5)$$

obtained from the long-time limit of $\overline{I_{LR}}(t)$ for the same parameters considered in Fig. 6.3.2 (a). We see (as observed in Ref. [241]) that the conductance behaves similarly to the transmission function for this system, with a central peak at $V_L = 1$, because at this point the chain energy E overlaps with the bias window. This peak then decays with increasing D , and in understanding the high- D limit it is useful to once again consider the symmetric single level system of Section 6.2.3.1. In this model one can use Eq. (6.3.4) to show that, for white noise with a large fluctuation magnitude, the zero-temperature effective resistance $R = G^{-1}$ is given by the constant:

$$R = \frac{\pi(\Gamma + 2D)}{\Gamma} \quad (6.3.6)$$

The physics when D is large in our theory is therefore qualitatively similar to the physics of the Nyquist theorem, where R scales linearly with D . However, the most interesting feature of Fig. 6.3.3 (a) is the existence of a D -dependent resonant peak occurring for $D \sim 1$ at all voltages far from the main resonance. This conductance illustrates that the fluctuations have two effects on the transport, which compete with each other in enhancing/destroying the current signal. The main peak always decreases with increasing D , as this defines the bias at which resonant tunneling is enabled, and increasing the fluctuations broadens the energy levels involved in this quantum process. To illustrate the basic mechanism here, in Fig. 6.3.3 (b) we plot $G(V; D, \omega_c \rightarrow \infty)$ for $V_R = 2$

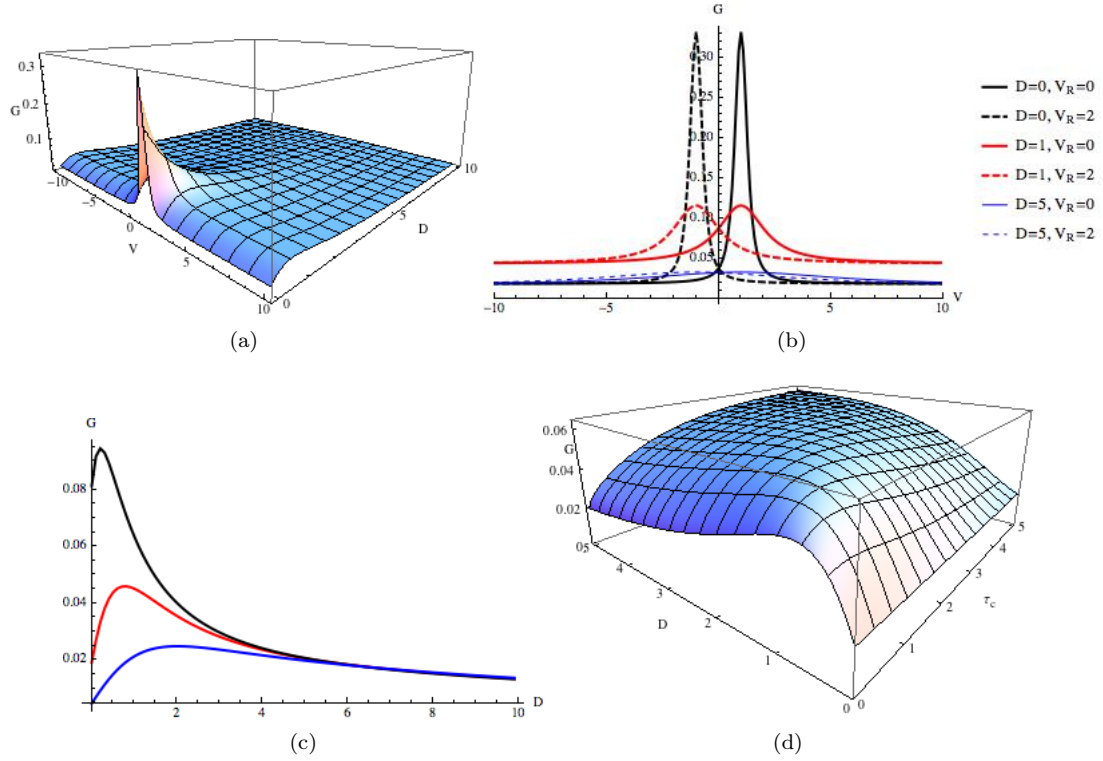


Figure 6.3.3: (a) $G(V; D, \omega_c \rightarrow \infty)$ at $V_R = 0$, varying V_L . (b) $G - V$ characteristics at $D = 0$ (black), $D = 1$ (red), $D = 5$ (blue) for $V_R = 0$ (full line) and $V_R = 2$ (dashed line). (c) D -dependence of the conductance at $V = 10$, for $|E - V_R| = 0.5$ (black), $|E - V_R| = 1$ (red) and $|E - V_R| = 2$ (blue). (d) $G(V; D, \omega_c \rightarrow \infty)$ as a function of both D and τ_c at $V_L = 10$, $V_R = 0$. All plots use the parameters $k_B T = 0.1$, $\Gamma_{11} = 0.5$, $\Gamma_{55} = 0.5$, $E = 1$, $\lambda = 0.1$

(dashed lines) beside the conductance for $V_R = 0$ (solid lines) in the molecular wire system. This exchanges the positions of V_R and E without altering the magnitude of $|E - V_R|$. Hence, the position of the main conductance peak is shifted to $V = -1$, but at large V the conductance is independent of the bias, and is instead enhanced at an intermediate value of D (red curves). This value of D corresponds to an optimal spread in energy levels achieved at the point where they overlap with the transport window, without being so large that there is a complete loss of phase in the transport (i.e. when a very small statistical weight is assigned to resonant energies) [238]. In Fig. 6.3.3 (c) the D -dependence of the conductance at $V = 10$ is shown for different values of the gap $|E - V_R|$. The resonant peak occurs when $D \sim |E - V_R|$, i.e. the noise provides the extra energy required for the molecular wire to enter the transport window. This may have applications in devices where resonant tunneling is not viable in practice, and the value of the voltage can only be controlled to lie within a certain range. Such devices may be tuned so that their conductance is stochastically enhanced for most values of the potential difference. Finally, in Fig. 6.3.3 (d) we plot for the same parameters as in Fig. 6.3.3 (a) the $V = 10$ conductance as a function of D and τ_c . In the limit $\tau_c \rightarrow 0$, the white noise conductance shown in Fig. 6.3.3 (c) is recovered, with the resonance at $D \sim |E - V_R|$. As τ_c is increased, this resonance is shifted to a value that is greater than $|E - V_R|$, and the rate of decay with increasing D is slowed down in behaviour that is reminiscent of the effect of colour noise on the transmission function, as illustrated above in Fig. 6.2.1 (b). In the quasistatic limit of large τ_c , the conductance decays to its $D = 0$ value, as taking $\tau_c \rightarrow \infty$ is equivalent to the zero D (frozen bias) limit in Eq. (6.2.18). However, when the ratio $D/\tau_c \sim 1$, the rate of decay to the frozen bias limit with increasing τ_c is slowed down, indicating that there is competition between very strong fluctuations and increasing correlation time in the quasistatic regime. This is also apparent from the general Eq. (6.2.25), as increasing D tends to cause spreading in the effective transmission whereas increasing τ_c has the opposite effect. This behaviour in the conductance is similar to that observed in Ref. [314] for the current through a ratchet driven by fluctuations with the same correlation function as Eq. (6.2.14).

Chapter 7

Conclusions and Future Outlook

The theoretical work of this thesis contains a number of novel results, which can now be summarized in order.

In Chapter 2 we generalized the time-dependent partition-free LB formalism of Refs. [128, 172] to be able to deal with an arbitrarily time-dependent bias. This involved an exact solution of the Kadanoff-Baym equations within the WBLA for each matrix ‘block’ of the time-dependent noninteracting Hamiltonian discussed in Section 2.2. In particular it enabled us to write down the specific functional form of the lesser and greater Green’s functions of two times defined on the molecular region, in Eq. (2.5.89). This exact and novel solution was published in Ref. [1], and it enabled us to write down a generalized LB formula for the current, Eq. (2.6.11), valid for a partition-free switch-on and arbitrary bias, temperature, and molecular structure. A continuity equation expressing dynamical charge conservation in the nanojunction was also derived. The generalized TD-bias TD-LB current formula was then shown to reduce exactly to previously published work under the limits of a constant bias and at long times after the switch-on.

Then in Chapter 3, and still working within the WBLA, we extended the LB theory of time-dependent current fluctuations in nanojunctions to a partition-free theory that was valid for arbitrary time-dependent biases, using the solutions for the Green’s functions in the two-time plane from the previous Chapter. The key result in this Chapter is Eq. (3.3.5), which expresses the two-time non-symmetrized current correlation function in terms of known matrix functions. For completeness we then showed how under the long time and constant bias limits this formula can be used to reproduce several published results on the quantum noise. In particular, we could generalize published results on frequency-dependent power spectra (for a constant bias switch-on) from single-level quantum dot systems to molecular junctions of arbitrary structure.

Up to this point, the work presented was purely analytical, but for realistic applications it is necessary to provide an efficient scheme for actually getting numbers out of the new formulas. So, in Chapter 4, it was proven that all frequency integrals appearing in the current and current noise could be analytically removed by utilising a simple pole expansion of the Fermi functions appearing in the integrand. This enabled us to replace the formulas (2.5.89) and (2.6.11) with Eqs. (4.2.14) and (4.3.8), respectively. It also enabled the replacement of the matrices (3.3.6) and (3.3.8) with those in Eqs. (4.4.3) and (4.4.4). The formulas in Chapter 4 are given as a sum over left/right eigenvectors and they are suitable for direct programming. Calculations of the current, greater/lesser Green’s functions and current correlations scale with the system size N_s as $\alpha_s N_s^2$, where the parameter α_s is minimized by the removal of all frequency integrals. The current and current correlations are ‘single-shot’ memoryless functions defined on the single and double time domains, making them ideal for parallelization.

Periodically driven molecular transport is a subfield of nanoscience in its own right. In Chapter 5 we presented some new results - both analytic and numerical - on the electronic response of molecular junctions with an AC bias applied

to the leads. This first involved a set of calculations on a periodically driven single-site molecule which showed both a ‘ringing’ in the transient current signal and a periodically repeated ‘ringing’ at long times after t_0 . The frequency of this ringing was identified with the gap between the dot energy and the fixed part of the driven lead’s Fermi level. Comparing the current computed from the new TD-LB method with the current computed from the LB formula at each value of the driving bias, we found the two calculations to differ except in the very low frequency case, when the driving parameters are varied adiabatically with respect to the internal electronic timescales of the molecular junction. One advantage of an analytic current response formula is that it can be used to analyse generic classes of driving field. In Section 5.3 we focused on the question of how to generate a time-averaged ‘pump current’ through the nanojunction with a periodically varied driving field. By splitting up the driving bias into separate harmonics, a set of conditions was derived for generating a pump current that included the breaking of TR symmetry in one of the harmonics. We refer to this result as the *quantum pump symmetry theorem*. Next, we studied the physics contained in the biharmonic bias of Eq. (5.4.4), which was chosen to satisfy the quantum pump symmetry theorem because it can be used to simulate some recent experiments. Lengthy formulas were derived for the current, lesser/greater Green’s functions and matrices appearing in the current correlation within this model. They involved the removal of all time integrals and replacement thereof with nested summations over Bessel functions. These formulas are ‘single-shot’ functions of one or two times, and the main computational bottleneck in their evaluation comes from the nested Bessel function summations. Thus we have for this model achieved the objective of a computational method that scales with time and system size in the same way as the static bias partition-free approaches discussed in Section 1.4.2.1. We then presented numerical results for the switch-on of a constant bias in single level and molecular wire nanojunctions, and found that the relative magnitude of the steady state and transient current signals depended strongly on the system size. Finite-size dependence was also observed in calculations of the current response to an AC bias in a molecular wire in Section 5.4.4. In Section 5.5, the pump current was calculated in a single site model driven by a quantum dot as a function of the symmetry-breaking phase, the frequency and a lead-independent shift in Fermi level. Calculations were then performed of the cross-lead current correlations both in the full two-time plane and for the $\tau = 0$ case in a molecular wire. We found in Section 5.7.1 that the magnitude of cross-correlations was maximized for a correlation delay time τ_{max} , which was seen to increase linearly with increasing number of sites N_s and with $1/\lambda$, where λ represents the inter-site coupling. This points to an interpretation of τ_{max} as the traversal time for electronic information to cross the nanojunction. In addition, a resonance was observed in the $\tau = 0$ cross-correlation at a time t_{res} that could be orders of magnitude greater than the time taken for electrons to tunnel onto the molecule. We then moved on in Section 5.7.2 to the first calculations of partition-free cross-lead current correlations in AC-driven molecular wires. As for the case of the constant bias, a resonance was observed in the $\tau = 0$ cross-correlations of the driven system at some time t_{res} , and in the two-time cross-correlations at a time difference of τ_{max} , indicating that these times are independent of the particular bias chosen. Both times were found to scale linearly with N_s and $1/\lambda$, pointing once again to a signature of the transit time in the cross-correlations. Therefore we anticipate that our method can be used to determine electron traversal times in large systems in a rather more precise way than that offered by heuristic arguments.

In Chapter 6 the specific problem of stochastic driving in molecular junctions was studied. The TD-NEGF formalism developed in the earlier chapters made no assumptions about the kind of time-dependence in the spatially homogeneous driving field, making it ideal for a treatment of this problem. First it was shown that the effect of the time-fluctuating molecular levels can be incorporated into the time-dependent bias on the leads of the junction, and hence both effects can be treated on the same mathematical footing. Then, we assumed that either the bias or molecular energies fluctuate in time around some time-constant values with a correlation function given by a single exponential time-decaying function corresponding to a coloured noise with strength D and correlation time τ_c . Under the $\tau_c \rightarrow 0$ limit the noise is white. Simplified analytical expressions were worked out in each case (white and coloured noise, for long and transient times) which enable straightforward implementation for realistic systems

instead of restricting ourselves to single-level molecules. Then an exact expansion of the bias-averaged current in powers of $D\tau_c$ was obtained. In the long-time limit, the current resulting from a noisy time-dependence has the LB form, and from this an exact formal relation was derived between the conductance, the temperature and the fluctuation strength, which we interpret as a quantum analogue to the classical Nyquist theorem relating the electrical resistance of a conductor to the temperature and the strength of the bias fluctuations. We also discussed in detail a number of claims made in the literature [244] concerning the long time behaviour of the current in the junction due to initial fluctuations of the molecular levels. We find that, at least within the model considered, both the initial preparation of the system and initial bias (or energy levels) fluctuations do not affect the long-time behaviour of the current, i.e. our equations do satisfy the Memory-loss theorem [189]. Consequently, we were able to prove the claims made in Ref. [244] to be false. Analytic results, as well as the results of our numerical calculations, performed on a simple five site atomic chain bridging two electrodes, show that the $I - V$ characteristic of the molecular wire goes from being nonlinear at small D to being linear at large D . We find that for very large D the conductance is suppressed, as would be expected from the classical Nyquist theorem. However, there exist intermediate values of D at which the conductance may actually be enhanced, due to a finite energy threshold that needs to be crossed for electronic states to enter the transport window. This ‘stochastic resonance’ occurs due to a trade-off between quantum coherence and classical noise, although similar physics can be seen in the noise-assisted transport of Brownian particles in spatially asymmetric systems. Compared with numerical approaches to this problem, which must average across many realisations of the stochastic bias, our method provides a massive computational speed-up. It will therefore be an exact benchmark and source of ideas for the qualitative effects of noise on transport through interacting systems, or systems that go beyond the WBLA.

This thesis has answered several questions, but raised just as many which will be addressed in future studies. Within the WBLA, it may be possible to make analytical progress with the Kadanoff-Baym equations for other forms of time-dependence than those considered here, for example by including a dipole-type coupling to molecular sites of the kind considered in Ref. [92]. So far, we have considered the problems of stochastic and AC driving fields in isolation from each other. However, the work done in Chapters 5 and 6 may be combined to investigate the interplay of AC driving frequencies with the inverse correlation time and fluctuation strength in an analytically exact way. The stochastic resonance effect was initially studied in driven systems [227, 228], and we anticipate the appearance of frequency and amplitude-dependent resonances in the transport for different values of τ_c and D , in similar fashion to studies which add a driving term to the classical Langevin equation [233, 235, 226, 236, 237, 231]. The solutions obtained in this thesis will be competitive with the very fastest methods for simulating the time-dependent current and current noise in large, complex molecular structures, as they enable us to move between multiple time scales with no change in the computational complexity involved. Their real impact will come in software packages where, for given parameter ranges that allow one to assume the WBLA, they are used in optimally fast calculations of transport properties such as the current, pump current, time-dependent noise and traversal time. Development of this software is ongoing.

Appendix A

Useful Integral Identities and Special Functions

A.1 Identity for Converting Matsubara Summations into Fermi Integrals

In this appendix, we prove a useful formula for converting summations over Matsubara frequencies into integrals over the entire real frequency axis. We start from the Fermi function, which has simple poles at the complex frequencies $\omega_n = \frac{i(2n+1)\pi}{\beta}$:

$$\begin{aligned} f(z) &= \frac{1}{e^{\beta z} + 1} = \frac{e^{-i\frac{(2n+1)\pi}{\beta}}}{e^{[\beta(z - i\frac{(2n+1)\pi}{\beta})]} + e^{-i\frac{(2n+1)\pi}{\beta}}} \\ &= - \left[1 + \beta \left(z - i\frac{(2n+1)\pi}{\beta} \right) + \frac{\beta^2}{2} \left(z - i\frac{(2n+1)\pi}{\beta} \right)^2 + \dots - 1 \right]^{-1} \\ &= - \frac{1}{\beta \left(z - i\frac{(2n+1)\pi}{\beta} \right)} \left[1 + \frac{\beta}{2} \left(z - i\frac{(2n+1)\pi}{\beta} \right) + \dots \right]^{-1} \end{aligned}$$

It follows that the residual of the Fermi function at any of these poles is given by:

$$\text{Res}(z = \omega_n) = \lim_{z \rightarrow i\frac{(2n+1)\pi}{\beta}} f(z) \left(z - i\frac{(2n+1)\pi}{\beta} \right) = -\frac{1}{\beta} \quad (\text{A.1.1})$$

Now, consider the contour Γ_a shown in Fig. 3(a), which encloses the Matsubara frequencies on an anticlockwise path about the imaginary frequency axis. Given a function $Q(z)$ which is analytic on and within this contour, the Residue Theorem implies the following identity [128]:

$$\int_{\Gamma_a} \frac{dz}{2\pi} Q(z) e^{-z\tau} \left\{ \begin{array}{l} f(z) \\ -e^{\beta z} f(z) \end{array} \right\} = -\frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{-\omega_n \tau} \quad (\text{A.1.2})$$

Here, the second row in the curly bracket holds because $e^{\beta \omega_n} = -1$. Now, if $\beta > \tau > 0$, $\lim_{z \rightarrow \pm\infty} e^{(\beta-\tau)z} f(z) = 0$, and we can deform the contour Γ_a into Γ_b shown in Fig. 3(b):

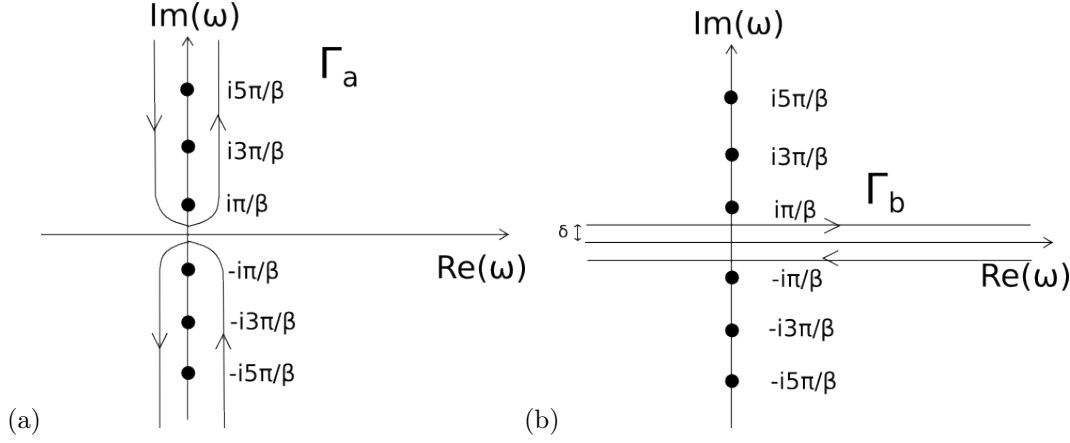


Figure A.1.1: The contours in the complex frequency plane used for the simplification of Matsubara summations.

$$\frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{-\omega_n \tau} = \int_{\Gamma_b} \frac{dz}{2\pi} Q(z) e^{(\beta-z)\tau} f(z) \quad (\text{A.1.3})$$

If, however, $0 > \tau > -\beta$, $\lim_{z \rightarrow +\infty} e^{-\tau z} f(z) = \lim_{z \rightarrow \infty} e^{-(\beta+\tau)z} = 0$, and $\lim_{z \rightarrow -\infty} e^{-\tau z} f(z) = 0$, as τ is negative. Therefore we can write:

$$\frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{-\omega_n \tau} = - \int_{\Gamma_b} \frac{dz}{2\pi} Q(z) e^{-z\tau} f(z) \quad (\text{A.1.4})$$

These conditions are summarized in the formula:

$$\frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{-\omega_n \tau} = \int_{\Gamma_b} \frac{dz}{2\pi} Q(z) e^{-z\tau} f(z) [\theta(\tau) e^{\beta z} - \theta(-\tau)] \quad (\text{A.1.5})$$

Introducing the small positive parameter 0^+ , from the contour Γ_b one can see that the following expressions hold:

$$\begin{aligned} \frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{-\omega_n 0^+} &= \int_{\Gamma_b} \frac{dz}{2\pi} Q(z) e^{-z 0^+} f(z) e^{\beta z} \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - f(\omega)) e^{-\omega 0^+} [Q(\omega + i0^+) - Q(\omega - i0^+)] \end{aligned} \quad (\text{A.1.6})$$

$$\begin{aligned} \frac{i}{\beta} \sum_{n=-\infty}^{\infty} Q(\omega_n) e^{\omega_n 0^+} &= - \int_{\Gamma_b} \frac{dz}{2\pi} Q(z) e^{z 0^+} f(z) \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) e^{\omega 0^+} [Q(\omega - i0^+) - Q(\omega + i0^+)] \end{aligned} \quad (\text{A.1.7})$$

A.2 Integral Identities and Special Functions

When we manipulate the equations for the current, greater/lesser Green's functions and current noise into a form that is suitable for numerical integration, several identities are useful which map from Fermi function integrals

to special functions. The first of these special functions is the *digamma function* $\Psi(z)$, defined as the logarithmic derivative of the complex gamma function $\Gamma(z)$ [154]:

$$\Psi(z) \equiv \frac{d \ln \Gamma(z)}{dz} = -\gamma - \frac{1}{z} + \sum_{n=1}^{\infty} \left[\frac{1}{n} - \frac{1}{n+z} \right] \quad (\text{A.2.1})$$

Here, $\gamma \equiv \lim_{N \rightarrow \infty} \sum_{n=1}^N \left(\frac{1}{n} - \ln(N) \right)$ is the Euler-Mascheroni constant. This function satisfies the property

$$\Psi(z_1) - \Psi(z_2) = -\sum_{n=0}^{\infty} \left(\frac{1}{n+z_1} - \frac{1}{n+z_2} \right) \quad (\text{A.2.2})$$

Or, equivalently,

$$\frac{\Psi(z_1) - \Psi(z_2)}{z_1 - z_2} = \sum_{n=0}^{\infty} \frac{1}{(n+z_1)(n+z_2)} \quad (\text{A.2.3})$$

A key integral occurring in the greater/lesser Green's functions is:

$$\int d\omega \frac{f(\mp(\omega - \mu))}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} \quad (\text{A.2.4})$$

To carry out this integral, the Fermi function is first expanded into the simple pole expansion of Eq. (4.2.2):

$$\begin{aligned} \int d\omega \frac{f(\mp(\omega - \mu))}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} &= \frac{1}{2} \int d\omega \frac{1}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} \\ &\pm \lim_{N_p \rightarrow \infty} \sum_{l=1}^{N_p} \frac{\eta_l}{\beta} \int d\omega \left(\frac{1}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)(\omega - \mu + i\frac{\zeta_l}{\beta})} + \frac{1}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)(\omega - \mu - i\frac{\zeta_l}{\beta})} \right) \end{aligned} \quad (\text{A.2.5})$$

All three terms in this integral can be evaluated using the Residue Theorem. In the first term, we take a semicircular contour of integration which may lie in the upper or lower half of the complex frequency plane. In the second and third terms, the presence of the poles at $\omega = \mu - i\frac{\zeta_l}{\beta}$ ($\omega = \mu + i\frac{\zeta_l}{\beta}$) mean that the contour is chosen in the upper (lower) half plane. This gives:

$$\int d\omega \frac{f(\mp(\omega - \mu))}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} = \frac{1}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[i\pi \pm \lim_{N_p \rightarrow \infty} \frac{2\pi i}{\beta} \sum_{l=1}^{N_p} \eta_l \left[\frac{1}{i\frac{\zeta_l}{\beta} + (\bar{\varepsilon}_k^* - \mu)} - \frac{1}{i\frac{\zeta_l}{\beta} - (\bar{\varepsilon}_j - \mu)} \right] \right] \quad (\text{A.2.6})$$

When expressing this integral analytically, it is useful to do so in terms of the digamma function, which can be evaluated numerically in a number of different ways. This can be done by choosing the Matsubara parameters $\eta_l = 1$ and $\zeta_l = \pi(2l - 1)$, which finally gives:

$$\int d\omega \frac{f(\mp(\omega - \mu))}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} = \frac{1}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[i\pi \mp \left[\Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu) \right) \right] \right] \quad (\text{A.2.7})$$

The second key special function used in this thesis is the *Hurwitz-Lerch Transcendent*, which is formally defined in Eq. 4.2.6. Using the definition (4.2.6), the following identities are easily established:

$$\sum_{n=0}^{\infty} \frac{e^{-An}}{n+B} = \Phi(e^{-A}, 1, B) \quad (\text{A.2.8})$$

$$\sum_{n=1}^{\infty} \frac{e^{-An}}{n+B} = e^{-A} \Phi(e^{-A}, 1, B+1) \quad (\text{A.2.9})$$

We use this function to represent second kind of frequency integral occurring in the expanded greater/lesser Green's function, Eq. (4.2.1):

$$\int d\omega \frac{f(\mp(\omega - \mu))}{\omega - \bar{\varepsilon}_k^*} e^{-i\omega(\tau - t_0)} \quad (\text{A.2.10})$$

This is once again expanded in simple poles of the Fermi function:

$$\int d\omega \frac{f(\mp(\omega - \mu))}{\omega - \bar{\varepsilon}_k^*} e^{-i\omega(\tau - t_0)} = \int d\omega \left[\frac{1}{2} - \lim_{N_p \rightarrow \infty} \sum_{l=1}^{N_p} \frac{\eta_l}{\beta} \left(\frac{1}{\omega - \mu + i\frac{\zeta_l}{\beta}} + \frac{1}{\omega - \mu - i\frac{\zeta_l}{\beta}} \right) \right] \frac{e^{-i\omega(\tau - t_0)}}{\omega - \bar{\varepsilon}_k^*} \quad (\text{A.2.11})$$

Due to the existence of the additional pole at $\omega = \bar{\varepsilon}_k^*$ in the upper-half plane, the integral (A.2.11) may be evaluated using the Residue Theorem with a semicircular contour taken in the lower half plane. The first and last terms on the right-hand side of Eq. (A.2.11) are then equal to zero, and one obtains

$$\int d\omega \frac{f(\mp(\omega - \mu))}{\omega - \bar{\varepsilon}_k^*} e^{-i\omega(\tau - t_0)} = \pm \frac{2\pi i}{\beta} e^{-i\mu(\tau - t_0)} \sum_{l=1}^{N_p} \eta_l \frac{e^{-\frac{\zeta_l}{\beta}(\tau - t_0)}}{i\frac{\zeta_l}{\beta} + \bar{\varepsilon}_k^* - \mu} \quad (\text{A.2.12})$$

We then substitute the Matsubara parameters in for η_l and ζ_l , and use the identity (A.2.9) with $A = \frac{2\pi}{\beta}(\tau - t_0)$ and $B = \frac{1}{2} + \frac{\beta}{2\pi i}(\bar{\varepsilon}_k^* - \mu)$ to finally obtain the result

$$\int d\omega \frac{f(\mp(\omega - \mu))}{\omega - \bar{\varepsilon}_k^*} e^{-i\omega(\tau - t_0)} = \pm e^{-i\mu(\tau - t_0)} \bar{\Phi}(\tau - t_0, \beta, \bar{\varepsilon}_k^* - \mu) \quad (\text{A.2.13})$$

where for compactness, we introduce the notation:

$$\bar{\Phi}(\tau, \beta, z) \equiv \exp\left(-\frac{\pi\tau}{\beta}\right) \Phi\left(e^{-\frac{2\pi\tau}{\beta}}, 1, \frac{1}{2} + \frac{\beta z}{2i\pi}\right) \quad (\text{A.2.14})$$

The final species of integral appearing in Eq. (4.2.1) is the following:

$$\int d\omega f(\mp(\omega - \mu)) e^{-i\omega(\tau - \bar{\tau})} \quad (\text{A.2.15})$$

Once again we make the substitution of the Padé expansion into the integrand of Eq. (A.2.15), to get

$$\int d\omega f(\mp(\omega - \mu)) e^{-i\omega(\tau - \bar{\tau})} = \pi\delta(\tau - \bar{\tau}) - \lim_{N_p \rightarrow \infty} \sum_{l=1}^{N_p} \frac{\eta_l}{\beta} \int d\omega e^{-i\omega(\tau - \bar{\tau})} \left(\frac{1}{\omega - \mu + i\frac{\zeta_l}{\beta}} + \frac{1}{\omega - \mu - i\frac{\zeta_l}{\beta}} \right) \quad (\text{A.2.16})$$

where the first term is evaluated using the identity (2.4.15). Thus one ends up with a summation over integrals of the form:

$$\int d\omega \frac{2e^{-i\omega(\tau - \bar{\tau})}(\omega - \mu)}{(\omega - \mu)^2 + \left(\frac{\zeta_l}{\beta}\right)^2} \quad (\text{A.2.17})$$

When the times in the exponent are not equal, this can be evaluated using Jordan's Lemma [282], which for $\bar{\tau} > \tau$

($\tau > \bar{\tau}$) involves taking an anticlockwise (clockwise) path of integration over a semicircular contour in the upper (lower) complex frequency plane enclosing the pole at $\omega = \mu + i\frac{\zeta_l}{\beta}$ ($\omega = \mu - i\frac{\zeta_l}{\beta}$). At $\tau = \bar{\tau}$, the integral (taken over the full frequency range $[-\infty, \infty]$) in Eq. (A.2.17) is not defined, so one can replace it with the limiting value:

$$\lim_{L \rightarrow \infty} \int_{-L}^L d\omega \frac{2(\omega - \mu)}{(\omega - \mu)^2 + \left(\frac{\zeta_l}{\beta}\right)^2} = \lim_{L \rightarrow \infty} \frac{1}{2} \left[\text{Log} \left(\frac{\beta^2 (L - \mu)^2}{\zeta_l^2} + 1 \right) - \text{Log} \left(\frac{\beta^2 (L + \mu)^2}{\zeta_l^2} + 1 \right) \right] = 0 \quad (\text{A.2.18})$$

We therefore have the identity

$$\int d\omega f(\mp(\omega - \mu)) e^{-i\omega(\tau - \bar{\tau})} = \left[\pi \delta(\tau - \bar{\tau}) \mp \frac{2\pi i}{\beta} \lim_{N_p \rightarrow \infty} \sum_{l=1}^{N_p} \eta_l \left[\theta(\tau - \bar{\tau}) e^{-\frac{\zeta_l}{\beta}(\tau - \bar{\tau})} - \theta(\bar{\tau} - \tau) e^{-\frac{\zeta_l}{\beta}(\bar{\tau} - \tau)} \right] \right] e^{-i\mu(\tau - \bar{\tau})} \quad (\text{A.2.19})$$

where in the summation term the step functions are implemented using the half-maximum convention of Eq. (1.5.62), which means that this term vanishes for $\tau = \bar{\tau}$. If one inserts the Matsubara parameters for η_l and ζ_l into Eq. (A.2.19), one gets, for example:

$$\lim_{N_p \rightarrow \infty} \sum_{l=1}^{N_p} \eta_l e^{-\frac{\zeta_l}{\beta}(\tau - \bar{\tau})} = \sum_{l=0}^{\infty} e^{-\frac{\pi}{\beta}(2l+1)(\tau - \bar{\tau})} = \frac{1}{2} \text{cosech} \left(\frac{\pi}{\beta} (\tau - \bar{\tau}) \right) \quad (\text{A.2.20})$$

where we have simply summed up the infinite geometric series in the right hand equality. For compactness, we therefore define a new function $\text{cosech} \left(\frac{\pi}{\beta} (t_1 - t_2) \right) \Big|_{t_1 \neq t_2}$, using the Padé parameters, as

$$\text{cosech} \left(\frac{\pi}{\beta} (t_1 - t_2) \right) \Big|_{t_1 \neq t_2} \simeq 2 \sum_{l=1}^{N_p} \eta_l \left[\theta(t_1 - t_2) e^{-\frac{\zeta_l}{\beta}(t_1 - t_2)} - \theta(t_2 - t_1) e^{-\frac{\zeta_l}{\beta}(t_2 - t_1)} \right] \quad (\text{A.2.21})$$

where the subscript indicates that it is equal to zero when $t_1 = t_2$. The approximation in Eq. (A.2.21) becomes exact when $N_p \rightarrow \infty$. We note that the Padé expansion in Eq. (A.2.21) diverges less rapidly than the true cosech in the region of $t_1 \sim t_2$, so it is advantageous to use this expansion when evaluating the double integral of Eq. (4.2.7) with a numerical routine. Thus, we can finally write the integral (A.2.19) in a rather compact manner:

$$\int d\omega f(\mp(\omega - \mu)) e^{-i\omega(\tau - \bar{\tau})} = \left[\pi \delta(\tau - \bar{\tau}) \mp \frac{\pi i}{\beta} \text{cosech} \left(\frac{\pi}{\beta} (\tau - \bar{\tau}) \right) \right] \Big|_{\tau \neq \bar{\tau}} e^{-i\mu(\tau - \bar{\tau})} \quad (\text{A.2.22})$$

A.3 Padé Parameters and Implementation of the Special Functions

The Padé expansion of the Fermi function $f(x) = (e^{\beta x} + 1)^{-1}$ provides a means of closely approximating it with a fit to an $[N_p - 1/N_p]$ polynomial fraction [288, 289]:

$$f\left(\frac{x}{\beta}\right) = \frac{1}{2} - x \Phi^F(x^2) \simeq \frac{1}{2} - x \frac{P_{N_p-1}(x^2)}{Q_{N_p}(x^2)} \quad (\text{A.3.1})$$

where P_j, Q_j denote polynomials of order j . An exact form of the Fermi function is given in terms of hyperbolic functions:

$$f\left(\frac{x}{\beta}\right) = \frac{1}{2} \left(1 - \frac{\sinh\left(\frac{x}{2}\right)}{\cosh\left(\frac{x}{2}\right)} \right) \quad (\text{A.3.2})$$

Now, defining the hypergeometric function

$$F(a; x) \equiv {}_0F_1(a; x) = \sum_{n=0}^{\infty} \frac{x^n}{(a)_n n!} = \sum_{n=0}^{\infty} \frac{x^n \Gamma(a)}{\Gamma(a+n) n!} \quad (\text{A.3.3})$$

where

$$(a)_n \equiv \begin{cases} 1, & n = 0 \\ a(a+1) \dots (a+(n-1)), & n > 0 \end{cases} \quad (\text{A.3.4})$$

it can be shown that $\sinh(z) = zF\left(\frac{3}{2}; \frac{z^2}{4}\right)$ and $\cosh(z) = F\left(\frac{1}{2}; \frac{z^2}{4}\right)$, so that we can rewrite Eq. (A.3.2) as

$$f\left(\frac{x}{\beta}\right) = \frac{1}{2} \left(1 - \frac{x F\left(\frac{3}{2}; \frac{x^2}{16}\right)}{F\left(\frac{1}{2}; \frac{x^2}{16}\right)} \right) \quad (\text{A.3.5})$$

Then, using the recurrence relation

$$F(a-1; x) = F(a; x) + \frac{x}{a(a-1)} F(a+1; x) \quad (\text{A.3.6})$$

one can write $\Phi^F(x^2)$ in the form of a continued fraction up to the M -th iteration:

$$\Phi_M^F(x^2) = \left[\frac{1/4}{1 + \frac{x^2/4}{3 + \frac{x^2/4}{5 + \dots}}} \right] \equiv \left[\frac{1/4}{b_1 +}, \frac{x^2/4}{b_3 +}, \dots, \frac{x^2/4}{b_M} \right] \equiv \frac{A_M(x^2)}{B_M(x^2)} \quad (\text{A.3.7})$$

where we also define $b_j \equiv 2j - 1$. In general, it can be shown that, if $\Phi_{2N_p}^F = A_{2N_p}/B_{2N_p}$, then A_{2N_p} is a polynomial of order $N_p - 1$ while B_{2N_p} is a polynomial of order N_p [289], so that one can make an approximation to the Fermi function in the form:

$$f\left(\frac{x}{\beta}\right) \simeq \frac{1}{2} - x \Phi^F(x^2) = \frac{1}{2} - x \sum_{l=1}^{N_p} \frac{2\eta_l}{x^2 + \zeta_l^2} \quad (\text{A.3.8})$$

This is equivalent to the imaginary pole expansion in Eq. (4.2.2), and it remains to find a numerical method for determining the parameters η_l and ζ_l for a given N_p . Using Cramer's rule for expanding determinants [282], it is possible to expand the '11' element of the inverse of some $M \times M$ matrix $\mathbf{C} = \|c_{ij}\|$, and this is given by the continued fraction expansion:

$$(\mathbf{C}^{-1})_{11} = \left[\frac{1}{c_{11}-}, \frac{c_{12}c_{21}}{c_{22}-}, \dots, \frac{c_{M-1M}c_{MM-1}}{c_{MM}} \right] \quad (\text{A.3.9})$$

Thus, defining the components of the matrices $\mathbf{A}$, $\mathbf{B}$ as $A_{ij} = b_i \delta_{ij}$ and $B_{ij} = \delta_{ij \pm 1}$, we obtain yet another representation of the Femi function:

$$f\left(\frac{x}{\beta}\right) \simeq \frac{1}{2} \left(1 - \frac{x}{2} \left(\mathbf{A} + \frac{ix}{2} \mathbf{B} \right)_{11}^{-1} \right) \quad (\text{A.3.10})$$

The singular values of x in this equation are therefore the poles of $\Phi_{2N_p}^F(x^2)$, i.e. these are the values of x for which $|\mathbf{A} + \frac{ix}{2} \mathbf{B}| = 0$, which is equivalent to solving the eigenproblem

$$\mathbf{A} |\lambda_j\rangle = \lambda_j |\lambda_j\rangle \quad (\text{A.3.11})$$

where $\mathbf{\Lambda} = \mathbf{A}^{-\frac{1}{2}} \mathbf{B} \mathbf{A}^{-\frac{1}{2}}$ has elements $\Lambda_{ij} = \frac{\delta_{ij \pm 1}}{\sqrt{b_i b_j}}$ and eigenvalues $\lambda_j = \frac{2i}{x_j}$. This gives us the poles x_j of the Padé expansion. Due to the symmetry of $\mathbf{\Lambda}$, its eigenvalues must all be real, i.e. we have $x_j = \pm i \zeta_j$, $\lambda_j = \pm \frac{2}{\zeta_j}$ as the roots of $\Phi_{2N_p}(x^2)$, occuring at $x^2 = -\zeta_j^2$. It is then possible to write the numerator and denominator in (A.3.1) in the product form:

$$\Phi_{2N_p}(x^2) = \frac{P_{N_p-1}(x^2)}{Q_{N_p}(x^2)} = \frac{p_{N_p-1}}{q_{N_p}} \frac{\prod_{k=1}^{N_p-1} (x^2 + \alpha_k^2)}{\prod_{k=1}^{N_p} (x^2 + \zeta_k^2)} = \sum_{l=1}^{N_p} \frac{2\eta_l x}{x^2 + \zeta_l^2} \quad (\text{A.3.12})$$

Here, the $\pm i\alpha_k$ give roots of the numerator $P_{N_p-1}(x^2)$, and p_j, q_j denote the coefficient of the j -th power term in the polynomials P_{N_p-1}, Q_{N_p} . From the third equality in Eq. (A.3.12), one can then identify the residues as:

$$2\eta_i = \lim_{x^2 \rightarrow -\zeta_i^2} \left[(x^2 + \zeta_i^2) \sum_{l=1}^{N_p} \frac{2\eta_l x}{x^2 + \zeta_l^2} \right] = \frac{p_{N_p-1}}{q_{N_p}} \frac{\prod_{k=1}^{N_p-1} (\alpha_k^2 - \zeta_i^2)}{\prod_{\substack{k=1 \\ k \neq i}}^{N_p} (\zeta_k^2 - \zeta_i^2)} \quad (\text{A.3.13})$$

It can be shown [288, 289] that

$$\frac{p_{N_p-1}}{q_{N_p}} = b_2 + b_4 + \dots + b_{2N_p} = N_p b_{N_p+1} \quad (\text{A.3.14})$$

It remains to find the negative roots of the numerator polynomial $P_{N_p-1}(x^2)$. We can invert Eq. (A.3.7) to obtain the inverse ratio

$$\frac{B_M}{A_M} = 4 \left(b_1 + \frac{x^2}{4} \left(\mathbf{C} + \frac{ix}{2} \mathbf{D} \right)_{11}^{-1} \right) \quad (\text{A.3.15})$$

where

$$\mathbf{C} = \begin{pmatrix} b_2 & 0 & 0 & 0 \\ 0 & b_3 & 0 & 0 \\ 0 & 0 & \ddots & \vdots \\ 0 & 0 & \dots & b_M \end{pmatrix} \quad (\text{A.3.16})$$

is an $M-1 \times M-1$ matrix, and so is $\mathbf{D}$, with elements $D_{ij} = \delta_{ij \pm 1}$. As for the denominator roots, the roots x_i of Eq. (A.3.15) are found when $|\mathbf{C} + \frac{ix}{2} \mathbf{D}| = 0$, which is equivalent to solving the eigenproblem

$$\mathbf{\Sigma} |\sigma_j\rangle = \sigma_j |\sigma_j\rangle \quad (\text{A.3.17})$$

where we have introduced $\mathbf{\Sigma} = \mathbf{C}^{-1} \mathbf{D} \mathbf{C}^{-1}$ with elements $\Sigma_{ij} = \frac{\delta_{ij \pm 1}}{\sqrt{b_{i+1} b_{j+1}}}$. The roots of the numerator x_i are pure imaginary, and related to eigenvalues σ_j of $\mathbf{\Sigma}$ as $\sigma_j = \frac{2i}{x_j}$. So $x_j = \pm i \alpha_j$ for some α_j , which means the roots of $Q_{N_p-1}(x^2)$ are negative and located at $x^2 = -\alpha_j^2$. This is the final quantity needed for the representation of the Fermi function in terms of a Padé expansion, and we summarize the full algorithm for computing the η_l and ζ_l of this expansion in the boxed Algorithm A.1.

In Table A.1, we tabulate the values of ζ_l and η_l for $N_p = 20$ in the first and third columns, respectively. In the middle column, the ratio of these poles to the Matsubara frequencies $\omega_l = \pi(2l-1)$ is shown. In contrast to the Matsubara expansion, the ζ_l of the Padé expansion are spaced unevenly along the imaginary axis, and the residues η_l are all real and positive-valued. In either representation, the Fermi function has poles distributed symmetrically along the imaginary axis in the upper and lower half-planes.

Algorithm A.1

1. Choose N_p . Define $M_p \equiv 2N_p$.
2. Defining $b_j = 2j - 1$, solve the eigenproblem of the real symmetric $M_p \times M_p$ matrix:

$$\Lambda_{mn} = \frac{\delta_{m,n\pm 1}}{\sqrt{b_m b_n}} \quad (\text{A.3.18})$$

to get the nonzero eigenvalues

$$\lambda_l \equiv \pm \frac{2}{\zeta_l} \quad (\text{A.3.19})$$

where ζ_l define the *Padé frequencies*.

3. Solve the eigenproblem of the real symmetric $M_p \times M_p$ matrix:

$$\Sigma_{mn} = \frac{\delta_{m,n\pm 1}}{\sqrt{b_{m+1} b_{n+1}}} \quad (\text{A.3.20})$$

to get the nonzero eigenvalues

$$\sigma_l \equiv \pm \frac{2}{\alpha_l} \quad (\text{A.3.21})$$

4. Using the ζ_l and α_l defined in Eqs. (A.3.19) and (A.3.21), construct the object

$$\eta_l = \frac{N_p b_{N_p+1}}{2} \frac{\prod_{k=1}^{N-1} (\alpha_k^2 - \zeta_l^2)}{\prod_{\substack{k=1 \\ k \neq l}}^{N_p} (\zeta_k^2 - \zeta_l^2)} \quad (\text{A.3.22})$$

5. The Fermi function for the given N_p is then approximated as

$$f(x) = \frac{1}{e^{\beta x} + 1} \simeq \frac{1}{2} - \sum_{l=1}^{N_p} \eta_l \left(\frac{1}{\beta x + i\zeta_l} + \frac{1}{\beta x - i\zeta_l} \right) \quad (\text{A.3.23})$$

, where the ζ_l are given by Eq. (A.3.19) and the η_l are given by Eq. (A.3.22).

ζ_l	ζ_l/ω_l	η_l
3.14159	1	1
9.42478	1	1
15.708	1	1
21.9911	1	1
28.2743	1	1
34.5575	1	1
40.8407	1	1
47.1239	1	1
53.4071	1	1
59.6903	1	1.00001
65.9746	1.00002	1.00084
72.3098	1.00074	1.02665
79.2216	1.00868	1.21807
88.2477	1.04037	1.70439
101.304	1.11194	2.51662
121.036	1.24281	3.8983
152.953	1.47534	6.59481
211.472	1.92325	13.117
349.595	3.00756	36.7563
1044.58	8.52563	332.187

Table A.1: Table of the Padé parameters for the Padé expansion of the Fermi function of order $N_p = 20$. In the first column, the complex poles ζ_l appearing in the denominators of the summation term in Eq. (4.2.2) are listed. In the second column, the ratio of these poles to the Matsubara frequencies $\omega_l = \pi(2l - 1)$ is shown. In the third column, the residues of the Fermi expansion η_l appearing as a prefactor in the summation term of Eq. (4.2.2) are listed.

In Fig. A.3.1, we make a comparison of the Padé and Matsubara schemes at different values of N_p (with chemical potential $\mu = 0$) for the inverse temperatures $\beta = 0.1$ ((a)), $\beta = 1$ ((b)) and $\beta = 10$ ((c)). The Figures (a)-(c) show that the Padé expansion is superior to the Matsubara expansion at all temperatures considered, as it converges to the exact Fermi function (shown in red) at lower values of N_p . This is related to the fact that the poles in the Padé scheme are not evenly distributed along the imaginary axis - effectively in the Padé scheme one is systematically adding back the difference in the exact and approximate values of the Fermi function when one truncates (4.2.3) at some finite term. Fig. A.3.1 also shows that convergence of the Padé approximation to the exact Fermi function is faster at high temperatures. Generally speaking, whereas the Padé expansion converges to the exact Fermi function at all temperatures by $N_p = 20$, the Matsubara expansion may not converge satisfactorily for N_p as high as 1000000. When actually implementing the digamma function in code, we note that in the context of this thesis it always appears in a difference of digammas with the form of Eq. (A.2.2). Thus, all constants appearing in the identity (A.2.1) cancel out and we can use the numerical definition of the digamma:

$$\Psi(z) \equiv -2\pi i \sum_{l=1}^{N_p} \frac{\eta_l}{\beta z + i\zeta_l} \quad (\text{A.3.24})$$

It must be emphasized here that this identification is only valid when the digamma appears in the difference in Eq. (A.2.2) and cannot be taken as the value of $\Psi(z)$ in all contexts. When implementing the function $\bar{\Phi}(\tau, \beta, z)$ in Eq. (4.2.5), we use the identity:

$$\bar{\Phi}(\tau, \beta, z) \equiv 2\pi i \sum_{l=1}^{N_p} \frac{\eta_l e^{-\frac{\zeta_l}{\beta}\tau}}{\beta z + i\zeta_l} \quad (\text{A.3.25})$$

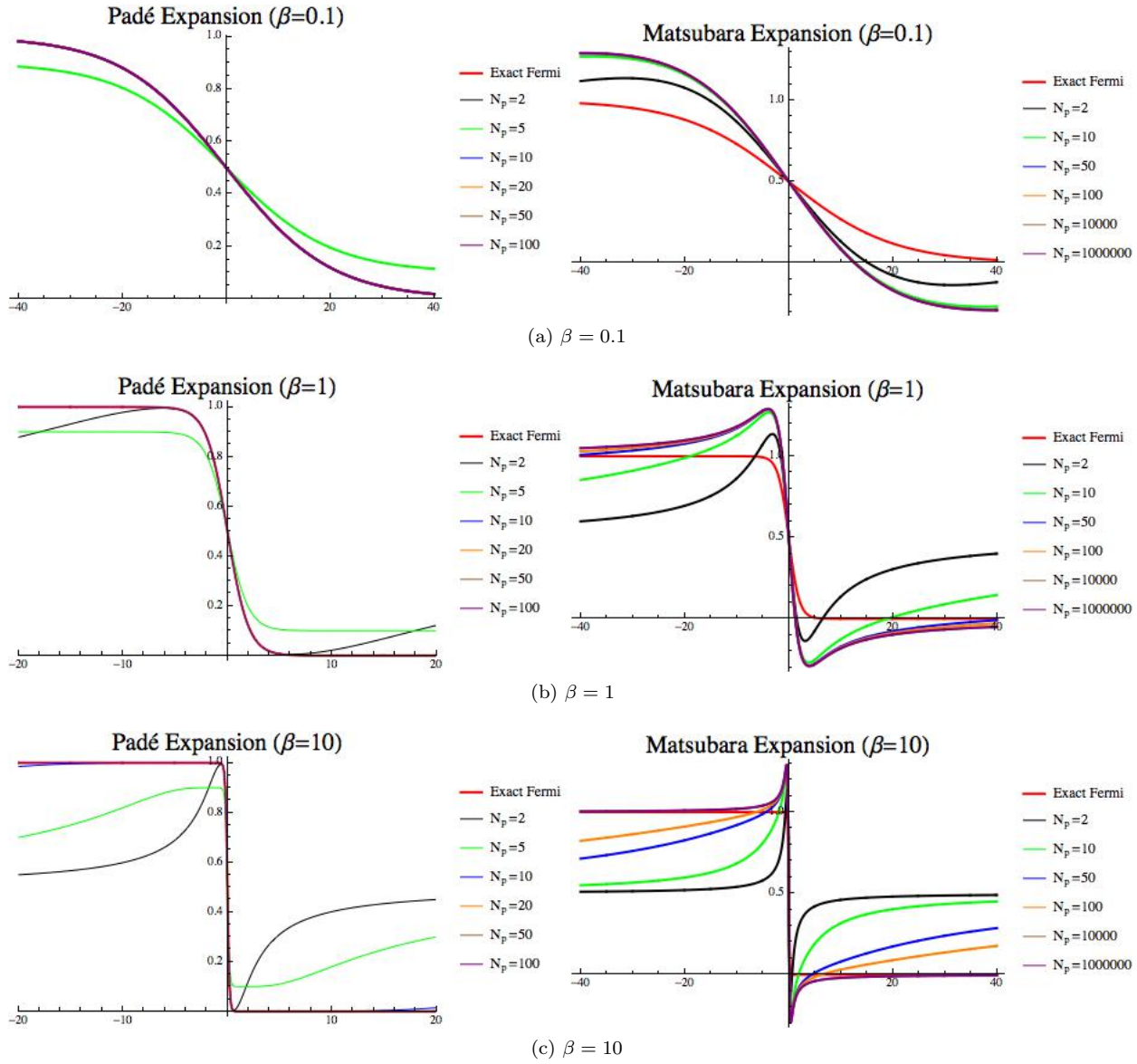


Figure A.3.1: The exact (thick red line) Fermi function plotted for different values of the inverse temperature β , in comparison with the Padé and Matsubara approximations to the Fermi function for various values of N_p .

By contrast with the digamma function, this expression for the Hurwitz-Lerch special function is general and becomes exact in the limit of $N_p \rightarrow \infty$. In both Eq. (A.3.24) and Eq. (A.3.25), we set $N_p = 20$, in accordance with the discussion of Fig. (A.3.1) above.

Appendix B

Details of the Current Implementations for Different Models

B.1 Formulas for the Current and Current Correlation in the Biharmonic Model

When we substitute Eq. (5.4.5) into Eq. (4.2.14), we obtain the following result for the greater and lesser Green's functions:

$$\begin{aligned}
\mathbf{G}^{\geq}(t_1, t_2) = & \frac{1}{2\pi} \sum_{\gamma, k, j} \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \mathbf{\Gamma}_\gamma |\varphi_k^L\rangle \langle \varphi_k^R|}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \left\{ \pm \frac{\pi}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\theta(t_1 - t_2) e^{-i\bar{\varepsilon}_j(t_1 - t_2)} + \theta(t_2 - t_1) e^{i\bar{\varepsilon}_k^*(t_2 - t_1)} \right] \right. \\
& + \frac{i e^{-i\bar{\varepsilon}_j(t_1 - t_0)} e^{i\bar{\varepsilon}_k^*(t_2 - t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi\left(\frac{1}{2} + \frac{\beta}{2i\pi}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2i\pi}(\bar{\varepsilon}_j - \mu)\right) \right] \\
& + i \sum_{r, s} J_r \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \right) J_s \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_\gamma} \right) \left[\frac{e^{-ir\phi_\gamma} e^{i \frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \sin \phi_\gamma}}{\bar{\varepsilon}_j - \bar{\varepsilon}_k^* - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)} \right. \\
& \times \left[e^{-i\bar{\varepsilon}_j(t_1 - t_0)} e^{i\bar{\varepsilon}_k^*(t_2 - t_0)} \left[\Psi\left(\frac{1}{2} + \frac{\beta}{2\pi i}(\bar{\varepsilon}_k^* - \mu)\right) - \Psi\left(\frac{1}{2} + \frac{\beta}{2\pi i}(\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))\right) \right] \right. \\
& \left. \left. + e^{i\bar{\varepsilon}_k^*(t_2 - t_0)} e^{-i(\mu + V_\gamma + \Omega_\gamma(p_1 r + p_2 s))(t_1 - t_0)} \left[\bar{\Phi}(t_1 - t_0, \beta, \bar{\varepsilon}_k^* - \mu) - \bar{\Phi}(t_1 - t_0, \beta, \bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)) \right] \right] \right. \\
& \left. + \frac{e^{ir\phi_\gamma} e^{-i \frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \sin \phi_\gamma}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)} \left[e^{-i\bar{\varepsilon}_j(t_1 - t_0)} e^{i\bar{\varepsilon}_k^*(t_2 - t_0)} \right. \right. \\
& \left. \left. \times \left[\Psi\left(\frac{1}{2} - \frac{\beta}{2\pi i}(\bar{\varepsilon}_j - \mu)\right) - \Psi\left(\frac{1}{2} - \frac{\beta}{2\pi i}(\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))\right) \right] \right] \right]
\end{aligned}$$

$$\begin{aligned}
& +e^{-i\bar{\varepsilon}_j(t_1-t_0)}e^{i(\mu+V_\gamma+\Omega_\gamma(p_1r+p_2s))(t_2-t_0)}\left[\bar{\Phi}(t_2-t_0,\beta,-(\bar{\varepsilon}_j-\mu))-\bar{\Phi}(t_2-t_0,\beta,-(\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s)))\right]\Bigg] \\
& +i\sum_{r,r',s,s'}J_r\left(\frac{A_\gamma^{(1)}}{p_1\Omega_\gamma}\right)J_{r'}\left(\frac{A_\gamma^{(1)}}{p_1\Omega_\gamma}\right)J_s\left(\frac{A_\gamma^{(2)}}{p_2\Omega_\gamma}\right)J_{s'}\left(\frac{A_\gamma^{(2)}}{p_2\Omega_\gamma}\right)\frac{e^{-i(r-r')\phi_\gamma}}{\bar{\varepsilon}_j-\bar{\varepsilon}_k^*-\Omega_\gamma(p_1(r-r')+p_2(s-s'))} \\
& \times\left[e^{-i\bar{\varepsilon}_j(t_1-t_0)}e^{i\bar{\varepsilon}_k^*(t_2-t_0)}\left[\Psi\left(\frac{1}{2}+\frac{\beta}{2\pi i}(\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s))\right)-\Psi\left(\frac{1}{2}-\frac{\beta}{2\pi i}(\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s'))\right)\right]\right. \\
& +e^{i\bar{\varepsilon}_k^*(t_2-t_0)}e^{-i(\mu+V_\gamma+\Omega_\gamma(p_1r+p_2s))(t_1-t_0)}\left[\bar{\Phi}(t_1-t_0,\beta,\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s))\right. \\
& \left.-\bar{\Phi}(t_1-t_0,\beta,\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s'))\right] \\
& +e^{-i\bar{\varepsilon}_j(t_1-t_0)}e^{i(\mu+V_\gamma+\Omega_\gamma(p_1r'+p_2s'))(t_2-t_0)}\left[\bar{\Phi}(t_2-t_0,\beta,-(\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s)))\right. \\
& \left.-\bar{\Phi}(t_2-t_0,\beta,-(\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s')))\right] \\
& +\theta(t_1-t_2)\left[e^{-i\Omega_\gamma(p_1r+p_2s)(t_1-t_0)}e^{i\Omega_\gamma(p_1r'+p_2s')(t_2-t_0)}e^{-i(\mu+V_\gamma)(t_1-t_2)}\right. \\
& \times\left[\bar{\Phi}(t_1-t_2,\beta,\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s'))-\bar{\Phi}(t_1-t_2,\beta,\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s))\right] \\
& +e^{-i\bar{\varepsilon}_j(t_1-t_2)}e^{-i\Omega_\gamma(p_1(r-r')+p_2(s-s'))(t_2-t_0)}\left[\Psi\left(\frac{1}{2}-\frac{\beta}{2\pi i}(\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s))\right)\right. \\
& \left.-\Psi\left(\frac{1}{2}+\frac{\beta}{2\pi i}(\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s))\right)\right]\Bigg] \\
& +\theta(t_2-t_1)\left[e^{-i\Omega_\gamma(p_1r+p_2s)(t_1-t_0)}e^{i\Omega_\gamma(p_1r'+p_2s')(t_2-t_0)}e^{-i(\mu+V_\gamma)(t_1-t_2)}\right. \\
& \times\left[\bar{\Phi}(t_2-t_1,\beta,-(\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s')))-\bar{\Phi}(t_2-t_1,\beta,-(\bar{\varepsilon}_j-\mu-V_\gamma-\Omega_\gamma(p_1r+p_2s))\right] \\
& +e^{i\bar{\varepsilon}_k^*(t_2-t_1)}e^{-i\Omega_\gamma(p_1(r-r')+p_2(s-s'))(t_1-t_0)}\left[\Psi\left(\frac{1}{2}-\frac{\beta}{2\pi i}(\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s'))\right)\right. \\
& \left.-\Psi\left(\frac{1}{2}+\frac{\beta}{2\pi i}(\bar{\varepsilon}_k^*-\mu-V_\gamma-\Omega_\gamma(p_1r'+p_2s'))\right)\right]\Bigg]\Bigg\} \tag{B.1.1}
\end{aligned}$$

The formula for the current in lead α can be similarly derived by inserting Eq. (5.4.5) into Eq. (4.3.8), giving the following:

$$\begin{aligned}
I_\alpha(t) = & \frac{1}{\pi} \sum_j \left\{ 2\text{Re} \left[\frac{\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[i e^{i \frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} (\sin(p_1 \Omega_\alpha (t-t_0) + \phi_\alpha) - \sin \phi_\alpha)} e^{i \frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \sin(p_2 \Omega_\alpha (t-t_0))} \sum_{r,s} J_r \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_s \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) e^{-ir\phi_\alpha} \right. \right. \\
& \times \left[e^{-i(\bar{\varepsilon}_j - \mu - V_\alpha)(t-t_0)} [\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))) - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu))] \right. \\
& \left. \left. \left. + e^{-i\Omega_\alpha(p_1 r + p_2 s)(t-t_0)} \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right) \right] \right] \right\} \\
& - \sum_{\gamma,k} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \left[\frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu) \right) \right] \right. \\
& \left. + \sum_{r,s} J_r \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \right) J_s \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_\gamma} \right) \left[\frac{e^{-ir\phi_\gamma} e^{i \frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \sin \phi_\gamma}}{\bar{\varepsilon}_j - \bar{\varepsilon}_k^* - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)} \right. \right. \\
& \times \left[e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} \left[\Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)) \right) \right] \right. \\
& \left. \left. + e^{i(\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))(t-t_0)} [\bar{\Phi}(t-t_0, \beta, \bar{\varepsilon}_k^* - \mu) - \bar{\Phi}(t-t_0, \beta, \bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))] \right] \right] \\
& + \frac{e^{ir\phi_\gamma} e^{-i \frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \sin \phi_\gamma}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)} \left[e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)) \right) \right] \right. \\
& \left. \left. + e^{-i(\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))(t-t_0)} [\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu)) - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)))] \right] \right] \\
& + \sum_{r,r',s,s'} J_r \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \right) J_{r'} \left(\frac{A_\gamma^{(1)}}{p_1 \Omega_\gamma} \right) J_s \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_\gamma} \right) J_{s'} \left(\frac{A_\gamma^{(2)}}{p_2 \Omega_\gamma} \right) \frac{e^{-i(r-r')\phi_\gamma}}{\bar{\varepsilon}_j - \bar{\varepsilon}_k^* - \Omega_\gamma(p_1(r-r') + p_2(s-s'))} \\
& \times \left[e^{-i\Omega_\gamma(p_1(r-r') + p_2(s-s'))(t-t_0)} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)) \right) \right. \right. \\
& \left. \left. - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r' + p_2 s')) \right) \right] \right. \\
& \left. e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} \left[\Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r' + p_2 s')) \right) \right] \right. \\
& \left. + e^{i(\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))(t-t_0)} [\bar{\Phi}(t-t_0, \beta, \bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s)) \right.
\end{aligned}$$

$$\begin{aligned}
& -\bar{\Phi}(t-t_0, \beta, \bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r' + p_2 s'))] \\
& + e^{-i(\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r' + p_2 s'))(t-t_0)} [\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu - V_\gamma - \Omega_\gamma(p_1 r + p_2 s))) \\
& - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_k^* - \mu - V_\gamma - \Omega_\gamma(p_1 r' + p_2 s')))] \} \tag{B.1.2}
\end{aligned}$$

To evaluate the two-time current correlation function in Eq. (3.3.5) for the biharmonic driving model, it is necessary to evaluate the integral appearing in the expression (4.4.7) for $\Lambda_\beta^+(t_2, t_1)$. Expanding the integrand using Eq. (5.4.5), we obtain:

$$\begin{aligned}
& \int_{t_0}^{t_1} d\tau e^{i\bar{\varepsilon}_j^*(t_1-\tau)} e^{-i\mu(t_2-\tau)} e^{-i\psi_\beta(t_2,\tau)} \text{cosech}\left(\frac{\pi}{\beta}(t_2-\tau)\right) \Big|_{t_2 \neq \tau} \\
& = \frac{\beta}{\pi} e^{i\bar{\varepsilon}_j^*(t_1-t_0)} e^{-i(\mu+V_\beta)(t_2-t_0)} e^{-i\frac{A_\beta^{(1)}}{p_1\Omega_\beta} \sin(p_1\Omega_\beta(t_2-t_0)+\phi_\beta)} e^{-i\frac{A_\beta^{(2)}}{p_2\Omega_\beta} \sin(p_2\Omega_\beta(t_2-t_0))} \sum_{r,s} J_r \left(\frac{A_\beta^{(1)}}{p_1\Omega_\beta}\right) J_s \left(\frac{A_\beta^{(2)}}{p_2\Omega_\beta}\right) e^{ir\phi_\beta} \\
& \times \left\{ \theta(t_1-t_2) e^{-i(\bar{\varepsilon}_j^*-\mu-V_\beta-\Omega_\beta(p_1 r+p_2 s))(t_2-t_0)} \left[\Psi\left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))\right) \right. \right. \\
& \left. \left. - \Psi\left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))\right) \right] - \bar{\Phi}(t_2-t_0, \beta, \bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s)) \right. \\
& \left. e^{-i(\bar{\varepsilon}_j^*-\mu-V_\beta-\Omega_\beta(p_1 r+p_2 s))(t_1-t_0)} [\theta(t_1-t_2) \bar{\Phi}(t_1-t_2, \beta, -(\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))) \right. \\
& \left. \left. \theta(t_2-t_1) \bar{\Phi}(t_2-t_1, \beta, \bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s)) \right] \right\} \tag{B.1.3}
\end{aligned}$$

The integral in $(\Lambda_\beta^-)^\dagger(t_2, t_1)$ is obtained as the complex conjugate of Eq. (B.1.3), the integral in $\Lambda_\alpha^-(t_1, t_2)$ is obtained by exchanging indices $\alpha \leftrightarrow \beta$ and times $t_1 \leftrightarrow t_2$, and the integral in $(\Lambda_\alpha^+)^\dagger(t_1, t_2)$ is obtained as the complex conjugate of the latter expression. Thus, one obtains for the full lambda matrices:

$$\begin{aligned}
\Lambda_\beta^+(t_2, t_1) & = \sum_j \frac{\mathbf{\Gamma}_\beta |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \left[-\frac{i}{2\pi} e^{i\bar{\varepsilon}_j^*(t_1-t_0)} e^{-i(\mu+V_\beta)(t_2-t_0)} e^{-i\frac{A_\beta^{(1)}}{p_1\Omega_\beta} \sin(p_1\Omega_\beta(t_2-t_0)+\phi_\beta)} e^{-i\frac{A_\beta^{(2)}}{p_2\Omega_\beta} \sin(p_2\Omega_\beta(t_2-t_0))} \right. \\
& \times \left[e^{i\frac{A_\beta^{(1)}}{p_1\Omega_\beta} \sin(\phi_\beta)} \bar{\Phi}(\beta, t_2-t_0, \bar{\varepsilon}_j^* - \mu) + \sum_{r,s} J_r \left(\frac{A_\beta^{(1)}}{p_1\Omega_\beta}\right) J_s \left(\frac{A_\beta^{(2)}}{p_2\Omega_\beta}\right) e^{ir\phi_\beta} \left\{ \theta(t_1-t_2) e^{-i(\bar{\varepsilon}_j^*-\mu-V_\beta-\Omega_\beta(p_1 r+p_2 s))(t_2-t_0)} \right. \right. \\
& \times \left[\Psi\left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))\right) - \Psi\left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))\right) \right] \\
& \left. \left. - \bar{\Phi}(t_2-t_0, \beta, \bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s)) \right\} \right.
\end{aligned}$$

$$\begin{aligned}
& + e^{-i(\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))(t_1 - t_0)} \left[\theta(t_1 - t_2) \bar{\Phi}(t_1 - t_2, \beta, -(\bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s))) \right. \\
& \left. + \theta(t_2 - t_1) \bar{\Phi}(t_2 - t_1, \beta, \bar{\varepsilon}_j^* - \mu - V_\beta - \Omega_\beta(p_1 r + p_2 s)) \right] - \theta(t_1 - t_2) \frac{e^{i\bar{\varepsilon}_j^*(t_1 - t_2)}}{2} \Big] \quad (\text{B.1.4})
\end{aligned}$$

$$\begin{aligned}
\Lambda_\alpha^-(t_1, t_2) &= \sum_j \frac{\mathbf{\Gamma}_\alpha |\varphi_j^L\rangle \langle \varphi_j^R|}{\langle \varphi_j^R | \varphi_j^L \rangle} \left[-\frac{i}{2\pi} e^{i\bar{\varepsilon}_j^*(t_2 - t_0)} e^{-i(\mu + V_\alpha)(t_1 - t_0)} e^{-i\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \sin(p_1 \Omega_\alpha(t_1 - t_0) + \phi_\alpha)} e^{-i\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \sin(p_2 \Omega_\alpha(t_1 - t_0))} \right. \\
&\times \left[e^{i\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \sin(\phi_\alpha)} \bar{\Phi}(\beta, t_1 - t_0, \bar{\varepsilon}_j^* - \mu) + \sum_{r,s} J_r \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_s \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) e^{ir\phi_\alpha} \left\{ \theta(t_2 - t_1) e^{-i(\bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))(t_1 - t_0)} \right. \right. \\
&\times \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right) \right] \\
&\left. \left. - \bar{\Phi}(t_1 - t_0, \beta, \bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right\} \right. \\
&\left. + e^{-i(\bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))(t_2 - t_0)} \left[\theta(t_1 - t_2) \bar{\Phi}(t_1 - t_2, \beta, \bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right. \right. \\
&\left. \left. + \theta(t_2 - t_1) \bar{\Phi}(t_2 - t_1, \beta, -(\bar{\varepsilon}_j^* - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))) \right] \right] + \theta(t_2 - t_1) \frac{e^{i\bar{\varepsilon}_j^*(t_2 - t_1)}}{2} \Big] \quad (\text{B.1.5})
\end{aligned}$$

$$\begin{aligned}
(\Lambda_\alpha^+)^{\dagger}(t_1, t_2) &= \sum_j \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \mathbf{\Gamma}_\alpha}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[\frac{i}{2\pi} e^{-i\bar{\varepsilon}_j(t_2 - t_0)} e^{i(\mu + V_\alpha)(t_1 - t_0)} e^{i\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \sin(p_1 \Omega_\alpha(t_1 - t_0) + \phi_\alpha)} e^{i\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \sin(p_2 \Omega_\alpha(t_1 - t_0))} \right. \\
&\times \left[e^{-i\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \sin(\phi_\alpha)} \bar{\Phi}(\beta, t_1 - t_0, -(\bar{\varepsilon}_j - \mu)) + \sum_{r,s} J_r \left(\frac{A_\alpha^{(1)}}{p_1 \Omega_\alpha} \right) J_s \left(\frac{A_\alpha^{(2)}}{p_2 \Omega_\alpha} \right) e^{-ir\phi_\alpha} \left\{ \theta(t_2 - t_1) e^{i(\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))(t_1 - t_0)} \right. \right. \\
&\times \left[\Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right) \right] \\
&\left. \left. - \bar{\Phi}(t_1 - t_0, \beta, -(\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))) \right\} \right. \\
&\left. + e^{i(\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))(t_2 - t_0)} \left[\theta(t_1 - t_2) \bar{\Phi}(t_1 - t_2, \beta, -(\bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s))) \right. \right. \\
&\left. \left. + \theta(t_2 - t_1) \bar{\Phi}(t_2 - t_1, \beta, \bar{\varepsilon}_j - \mu - V_\alpha - \Omega_\alpha(p_1 r + p_2 s)) \right] \right] - \theta(t_2 - t_1) \frac{e^{-i\bar{\varepsilon}_j(t_2 - t_1)}}{2} \Big] \quad (\text{B.1.6})
\end{aligned}$$

$$\begin{aligned}
(\Lambda_\beta^-)^\dagger(t_2, t_1) &= \sum_j \frac{|\varphi_j^R\rangle \langle \varphi_j^L| \Gamma_\beta}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[\frac{i}{2\pi} e^{-i\bar{\varepsilon}_j(t_1-t_0)} e^{i(\mu+V_\beta)(t_2-t_0)} e^{i\frac{A_\beta^{(1)}}{p_1\Omega_\beta} \sin(p_1\Omega_\beta(t_2-t_0)+\phi_\alpha)} e^{i\frac{A_\beta^{(2)}}{p_2\Omega_\beta} \sin(p_2\Omega_\beta(t_2-t_0))} \right. \\
&\times \left[e^{-i\frac{A_\beta^{(1)}}{p_1\Omega_\beta} \sin(\phi_\beta)} \bar{\Phi}(\beta, t_2-t_0, -(\bar{\varepsilon}_j-\mu)) + \sum_{r,s} J_r \left(\frac{A_\beta^{(1)}}{p_1\Omega_\beta} \right) J_s \left(\frac{A_\beta^{(2)}}{p_2\Omega_\beta} \right) e^{-ir\phi_\beta} \left\{ \theta(t_1-t_2) e^{i(\bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s))(t_2-t_0)} \right. \right. \\
&\times \left[\Psi \left(\frac{1}{2} + \frac{\beta}{2\pi i} (\bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s)) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2\pi i} (\bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s)) \right) \right] \\
&\left. \left. - \bar{\Phi}(t_2-t_0, \beta, -(\bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s))) \right. \right. \\
&\left. \left. + e^{i(\bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s))(t_1-t_0)} \left[\theta(t_1-t_2) \bar{\Phi}(t_1-t_2, \beta, \bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s)) \right. \right. \right. \\
&\left. \left. \left. + \theta(t_2-t_1) \bar{\Phi}(t_2-t_1, \beta, -(\bar{\varepsilon}_j-\mu-V_\beta-\Omega_\beta(p_1r+p_2s))) \right] \right] \right] + \theta(t_1-t_2) \frac{e^{-i\bar{\varepsilon}_j(t_1-t_2)}}{2} \Big] \quad (B.1.7)
\end{aligned}$$

B.2 Current for the quasistatic limit of stochastic driving

We first insert (6.2.18) in all places where the phase average appears. Next we make use of the idempotency relation in Eq. (2.5.20) (twice in the part containing the double time integral in the current formula (6.2.17), and once everywhere else), to give for the bias-averaged current:

$$\begin{aligned}
\overline{I_\alpha(t)} &= \frac{1}{\pi} \int d\omega f(\omega - V_\alpha - \mu) \text{Re} \left\{ \sum_j \frac{\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[i e^{-\frac{D\omega_c(t-t_0)^2}{2}} \frac{e^{i(\omega-\varepsilon_j)(t-t_0)}}{\omega - V_\alpha - \bar{\varepsilon}_j} \right. \right. \\
&\left. \left. + \sqrt{\frac{\pi}{2D\omega_c}} e^{-\frac{(\omega-\bar{\varepsilon}_j)^2}{2D\omega_c}} \left[\text{erf} \left(\sqrt{\frac{D\omega_c}{2}} (t-t_0) - i \frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}} \right) + \text{erf} \left(i \frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}} \right) \right] \right] \right\} \\
&- \frac{1}{\pi} \int d\omega \sum_{\beta,j,k} f(\omega - V_\beta - \mu) \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \left[\frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)}}{(\omega-\bar{\varepsilon}_j)(\omega-\bar{\varepsilon}_k^*)} \right. \\
&\left. + \sqrt{\frac{\pi}{2D\omega_c}} \left(i \frac{e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)} e^{-\frac{(\omega-\varepsilon_j)^2}{2D\omega_c}}}{\omega - V_\gamma - \bar{\varepsilon}_k^*} \left[\text{erf} \left(\sqrt{\frac{D\omega_c}{2}} (t-t_0) + i \frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}} \right) - \text{erf} \left(i \frac{(\omega-\bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}} \right) \right] + c.c.j \leftrightarrow k} \right) \right. \\
&\left. \left. + e^{-i(\bar{\varepsilon}_j-\bar{\varepsilon}_k^*)(t-t_0)} \int_0^{t-t_0} dx \int_0^{t-t_0} dy e^{-i(\omega-\bar{\varepsilon}_j)x} e^{i(\omega-\bar{\varepsilon}_k^*)y} e^{-\frac{D\omega_c}{2}(x-y)^2} \right] \right] \quad (B.2.1)
\end{aligned}$$

Here we use the notation $c.c.j \leftrightarrow k$ to denote the complex conjugation of the preceding term with indices j and k exchanged.

The double integral on the final line of Eq. (B.2.1) can be removed with the aid of the mathematical identity:

$$\int_0^A dx \operatorname{erf}(B(x+C)) e^{iDx} = \frac{1}{iD} \left[e^{iDA} \operatorname{erf}(B(A+C)) - \operatorname{erf}(BC) - e^{-iDC} e^{-\frac{D^2}{4B^2}} \left[\operatorname{erf}\left(B(A+C) - \frac{iD}{2B}\right) - \operatorname{erf}\left(BC - \frac{iD}{2B}\right) \right] \right] \quad (\text{B.2.2})$$

Following some tedious but mathematically trivial manipulations one finally ends with a closed expression for this double integral. To simplify the resulting formula, we note that because $\mathbf{\Gamma} = i(\mathbf{h}^{eff} - \mathbf{h}^{eff\dagger})$, the identity

$$\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_k^R \rangle = i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*) \langle \varphi_j^L | \varphi_k^R \rangle - \sum_{\gamma \neq \alpha} \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^R \rangle \quad (\text{B.2.3})$$

must be valid and so the following relation can be proven:

$$f_\alpha \sum_j \frac{\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} c_j - \sum_\gamma f_\gamma \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} c_j = \sum_{\gamma \neq \alpha} [f_\alpha - f_\gamma] \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} c_j \quad (\text{B.2.4})$$

In this expression f_γ can be any function of parameters which depend on the lead index γ . This leads us finally to re-express (B.2.1) as a sum of a term that decays to zero asymptotically and a term which is of the LB type:

$$\begin{aligned} \overline{I_\alpha(t)} &= \frac{1}{\pi} \sum_{\gamma \neq \alpha} [f(\omega - V_\alpha - \mu) - f(\omega - V_\gamma - \mu)] T_{\gamma\alpha}(\omega, t - t_0) \\ &+ \frac{1}{\pi} \operatorname{Re} \int d\omega f(\omega - V_\alpha - \mu) \left\{ \sum_j \frac{\langle \varphi_j^L | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} i e^{-\frac{D\omega_c}{2}(t-t_0)^2} \frac{e^{i(\omega - \bar{\varepsilon}_j)(t-t_0)}}{\omega - V_\alpha - \bar{\varepsilon}_j} \right. \\ &\quad \left. - \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \left[\frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{(\omega - \bar{\varepsilon}_j)(\omega - \bar{\varepsilon}_k^*)} \right] \right\} \\ &+ i \sqrt{\frac{\pi}{2D\omega_c}} \frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} e^{-\frac{(\omega - \bar{\varepsilon}_j)^2}{2D\omega_c}} (\bar{\varepsilon}_j - \omega + V_\gamma)}{(\omega - V_\gamma - \bar{\varepsilon}_k^*)(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \left[\operatorname{erf}\left(\sqrt{\frac{D\omega_c}{2}}(t-t_0) + i \frac{(\omega - \bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right) - \operatorname{erf}\left(i \frac{(\omega - \bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right) \right] \right] \Bigg\} \quad (\text{B.2.5}) \end{aligned}$$

where we make the definition of the time-dependent transmission probability:

$$\begin{aligned} T_{\gamma\alpha}(\omega, t - t_0) &= \sqrt{\frac{\pi}{2D\omega_c}} \sum_{j,k} \frac{\langle \varphi_k^R | \mathbf{\Gamma}_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \mathbf{\Gamma}_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \\ &\times \left[e^{-\frac{(\omega - \bar{\varepsilon}_j)^2}{2D\omega_c}} \left[\operatorname{erf}\left(\sqrt{\frac{D\omega_c}{2}}(t-t_0) - i \frac{(\omega - \bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right) + \operatorname{erf}\left(i \frac{(\omega - \bar{\varepsilon}_j)}{\sqrt{2\pi D\omega_c}}\right) \right] + c.c._{j \leftrightarrow k} \right] \quad (\text{B.2.6}) \end{aligned}$$

The LB term therefore depends on $t - t_0$ at finite times but has an asymptotically finite value given by the equation (6.2.20), while all other modes of the current vanish asymptotically. It should also be noted that in the long time limit all the dependence on the lead index γ goes into the Fermi function and level width matrix.

B.3 Current for arbitrary stochastic driving

For numerical implementations, it is useful to replace the frequency integrals in Eq. (6.2.24) with summations. This can be done by inserting Eq. (4.2.2) into the current formula and removing all time integrals explicitly, as discussed in Section 6.2.3.3. One can use either the Padé or Matsubara expansions to do this. If the Matsubara expansion is used, all integrals can be analytically carried out and the resulting summations expressed in terms of the special functions Ψ and $\bar{\Phi}$ discussed in Appendix B. The average current can then be expressed entirely in terms of embedded summations over special functions:

$$\begin{aligned}
\overline{I_\alpha(t)} = & \frac{2}{\pi} \text{Re} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \sum_j \left\{ i \frac{\langle \varphi_j^L | \Gamma_\alpha | \varphi_j^R \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\alpha - i(D + m\omega_c)) \right) \right. \right. \\
& + e^{-i(\bar{\varepsilon}_j - \mu - V_\alpha - i(D + m\omega_c))(t-t_0)} \left[\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu - V_\alpha - i(D + m\omega_c))) - \bar{\Phi}(\beta, t-t_0, -(\bar{\varepsilon}_j - \mu)) \right] \\
& - \sum_{k,\gamma} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle} \left[\frac{\delta_{n0} e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu) \right) \right. \\
& + \left. \frac{[e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)} - 1]}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c)) \right) \right. \\
& + \left. \frac{e^{-i(\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c))(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j - V_\gamma - i(D + m\omega_c)} \left[\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu)) - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c))) \right] \right. \\
& + \left. \frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j - V_\gamma - i(D + m\omega_c)} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c)) \right) \right] \right. \\
& + \left. \frac{e^{-i(\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c))(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c))) - \bar{\Phi}(t-t_0, \beta, -(\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c))) \right] \right. \\
& + \left. \left. \frac{e^{-i(\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)(t-t_0)}}{\bar{\varepsilon}_k^* - \bar{\varepsilon}_j} \left[\Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\gamma - i(D + m\omega_c)) \right) - \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c)) \right) \right] \right] \right\} \\
& \left. \right\} \quad (\text{B.3.1})
\end{aligned}$$

In the long time limit, one can use the theorem (B.2.4) to show that (B.3.1) reduces to the following form:

$$\begin{aligned}
\lim_{t_0 \rightarrow -\infty} \overline{I_\alpha(t)} = & \frac{1}{\pi} \sum_{n=0}^{\infty} \left(\frac{D}{\omega_c} \right)^n \sum_{m=0}^n \frac{(-1)^m}{(n-m)!m!} \sum_{j,k,\gamma} \frac{\langle \varphi_k^R | \Gamma_\alpha | \varphi_j^R \rangle \langle \varphi_j^L | \Gamma_\gamma | \varphi_k^L \rangle}{\langle \varphi_j^L | \varphi_j^R \rangle \langle \varphi_k^R | \varphi_k^L \rangle (\bar{\varepsilon}_j - \bar{\varepsilon}_k^*)} \\
& \times \left\{ \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\alpha - i(D + m\omega_c)) \right) - \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\alpha + i(D + m\omega_c)) \right) \right. \\
& - \Psi \left(\frac{1}{2} - \frac{\beta}{2i\pi} (\bar{\varepsilon}_j - \mu - V_\gamma - i(D + m\omega_c)) \right) + \Psi \left(\frac{1}{2} + \frac{\beta}{2i\pi} (\bar{\varepsilon}_k^* - \mu - V_\gamma + i(D + m\omega_c)) \right) \left. \right\} \quad (\text{B.3.2})
\end{aligned}$$

It can be easily seen, by inserting the Matsubara poles into the expression for $I_\alpha^{LB}(D, \omega_c)$, Eq. (6.2.37), that it is equivalent to (B.3.2). However, Eq. (B.3.2) allows for a much faster numerical implementation of the asymptotic current average.

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