Theory of Charge and Heat Transport Mechanisms in Nanodevices

by

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Abstract

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In this thesis, we pursue mechanisms in the nonequilibrium transport of charge and heat, to elucidate nanodevice operation, and explore fundamental theoretical questions. The thesis is divided into two parts. Part I explores in detail the role of incoherent effects on the charge transport behaviour of molecular junctions. Such effects, induced by molecular vibrations, solvent or other environmental effects, play a crucial role in many physical setups, but are difficult to simulate explicitly. We apply the Landauer-Büttiker probe technique, a phenomenological approach that incorporates incoherent effects at a low computational cost, and demonstrate the applicability of the technique by verifying that it captures a number of pertinent physical features, and achieves semi-quantitative agreement with experimental data. Going beyond this, we apply the probe method to a number of proposed physical setups. In stacked vs. alternating GC-rich ds-DNA, we find the even-odd effect in the experimentally observed conductance can be explained via a mixed coherent-incoherent transport mechanism. We find that in general, environmental interactions are destructive to the operation of molecular charge rectifiers, though in certain circumstances a weak rectifying behaviour might arise from many-body environmental effects.

In Part II of this thesis we shift our focus to heat transport, and particularly the operation of quantum heat machines. We begin with a study of the role of so-called noise-induced coherences on the operation of a quantum absorption refrigerator. While in the past quantum coherences have usually been found to boost power in such setups, we observe a complete shutdown of the device when coherences survive to the nonequilibrium steady-state. We then extend our analysis, developing a general approach that one can use to more easily discover the role of coherences in quantum heat machines. We conclude with the development of a new numerically exact approach, the iterative full-counting statistics path integral (iFCSPI), which is suitable for simulations of heat transport in nanodevices. The iFCSPI allows the calculation of the cumulants of heat transport, as well as strong-coupling and non-Markovian effects, provided it can be converged.
For Shannon, and our loving family.
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Contents

I Chapters 1 & 2: Charge Transport with Büttiker Probes

1 The Landauer-Büttiker Probe Technique: Behaviour and Applications

1.1 Introduction .................................................. 6
1.2 Model and Method .................................................. 9
  1.2.1 Model Hamiltonian ........................................ 9
  1.2.2 Büttiker probes ........................................... 11
  1.2.3 Structured environment .................................... 14
1.3 Transport Mechanisms ........................................... 15
  1.3.1 Coherent electrons: Ballistic motion and tunnelling ...... 15
  1.3.2 Bath-assisted transport .................................... 17
1.4 Results: Tunnelling to Hopping Conduction .................... 18
  1.4.1 Length dependence ........................................ 18
  1.4.2 Thermal activation ......................................... 19
  1.4.3 Environmental interaction strength ......................... 21
  1.4.4 Junction energetics ....................................... 22
  1.4.5 Structured environment results ............................ 23
1.5 Comparison to Experiments: ONI wires .......................... 24
1.6 Mixed Coherent/Incoherent Transport in ds-DNA ............... 27
  1.6.1 Molecular system: Stacked and alternating GC-DNA ....... 28
  1.6.2 ds-DNA results ........................................... 30
1.7 Conclusions .................................................... 33

2 Dissipative High Bias Conduction and Device Operation ........ 36

2.1 Introduction ................................................... 36
2.2 Voltage Probe Far From Equilibrium ............................ 37
2.3 Finite Bias Simulations ......................................... 38
  2.3.1 Current-voltage characteristics ............................ 38
  2.3.2 Inside the probes ......................................... 41
2.4 Tunnelling Diodes under Environmental Effects ................ 43
  2.4.1 Model ..................................................... 43
  2.4.2 Two-state diodes .......................................... 44
  2.4.3 Four-state diodes .......................................... 46
List of Figures

1.1 (a) A molecular wire with $N$ electronic sites (inter-site tunnelling $v$ and bridge height $\epsilon_B$) coupled to a thermal environment, represented by the shaded region surrounding the electronic states. The thermal bath, including molecular and external vibrational degrees of freedom, is characterized by its temperature $T$, spectral density function with a cutoff frequency $\Omega$ and electron-vibration coupling strength $\gamma_d$. (b) In this work we introduce the environment in a phenomenological manner by using the probe technique, attaching fictitious metal terminals to electronic sites. The figure illustrates voltage probes, characterized by their temperature and chemical potentials which are determined such that there is zero net charge current to each probe. ........................................... 10

1.2 Dominant transport mechanisms in the LBP molecular wire model. (a) Off-resonant tunnelling and (resonant) ballistic conduction when $\gamma_d = 0$. The blue line at the left end describes the Fermi distribution function of incoming electrons. (b) Illustration of bath (probe) assisted transport, depicting for simplicity a single probe. While all molecular orbitals are broadened, we explicitly demonstrate the broadening of two orbitals, those that are strongly coupled to the left and right metals. Incoming electrons of energy $\epsilon$, possibly at the tail of the broadening function, are scattered between the probes and the molecular states, then emitted to the $R$ lead. Energy conservation is imposed by the dephasing probe. ..................................................... 17

1.3 Electrical conductance as a function of molecular length $N$ at $T = 300$ K using different dephasing strengths, $\gamma_d=0$, 1, 10 and 100 meV, as indicated in the figure caption, (dephasing probe condition). (a) A semi-logarithmic plot demonstrates that $G$ decays exponentially with length in short chains at weak dephasing. (b)-(e) An inverse algebraic behaviour (1.31), $G^{-1} \propto N$, is established for long chains at large enough dephasing. Dominating transport mechanisms are marked in panel (a). ..................................................... 19

1.4 Temperature dependence of the electrical conductance for (a) $N = 4$-site wire and (b) $N = 10$-site wire, demonstrating tunnelling behaviour at low temperatures, ballistic-resonant activated conduction at high temperatures, and hopping behaviour when $\gamma_d \neq 0$, at low-intermediate temperatures. Parameters are $\epsilon_B = 0.5$, $v = 0.05$, and $\gamma_L = \gamma_R = 0.2$, $\Delta \mu = 0.001$ eV, dephasing probe condition. ..................................................... 20

1.5 Activation energy $E_A$, as resolved from Arrhenius plots as in Fig. 1.4, plotted against the bridge energy $\epsilon_B$, demonstrating a linear relationship. Parameters are indicated in Fig. 1.4. ..................................................... 20

1.6 Kramers-like behaviour of the electrical conductance with dephasing strength (dephasing probe). Parameters are indicated within the figure. ..................................................... 21
1.7 Conductance as a function of the bridge energy $\epsilon_B$. $v = 0.05$, $\gamma_{L,R} = 0.2$, $\gamma_d = 10^{-3}$ (dephasing probe) and $\Delta \mu = 0.01$ eV. ......................................................... 22

1.8 Analysis of bath-assisted conduction, $\gamma_d = 1$ meV. (a) At low temperatures $T = 150$ K and for high bridges an activation-less transport takes place. (b) At high temperatures $T = 350$ K the conductance is enhanced by a thermal factor. Panels (a1)-(a4) and (b1)-(b4) expose the ohmic-like behaviour in long wires, $v = 0.05$, $\gamma_{L,R} = 0.2$, $\Delta \mu = 0.01$ eV; dephasing probe condition (full symbols), voltage probe (empty symbols). ..................... 23

1.9 Electrical conductance as a function of length using structured (Debye-Drude form, Eq. 1.21) and unstructured ($\gamma_d$ is a constant) environments at high and low temperatures. At low temperatures the conductance is sensitive to the cutoff frequency $\Omega = 0.1$ eV. We used $v = 0.05$, $\epsilon_B = 0.5$, $\gamma_{L,R} = 0.2$, $\Delta \mu = 0.01$ eV and $\tilde{\gamma}_d = 1, 10^{-3}$ meV as indicated, dephasing probe condition. For unstructured environments we used $\gamma_d = 1, 10^{-3}$ meV, independent of energy. ................................................................. 24

1.10 Analysis of experimental results. We extracted data for the resistance of an ONI monolayer with $M \sim 100$ from Fig. 6 of Ref. [1], and multiplied it by $M = 100$ to approximate resistance per molecule. Top: a single ONI wire. (a)-(b) Experimental data (+) [1] as a function of molecular length, compared to probe-method simulations with $\gamma_d = 0, 0.2, 0.5$ meV, top to bottom (dotted lines with empty squares) assuming (a1)-(a2) $T = 300$ K and (b1)-(b2) $T = 280$ K. Panels (a1)-(b1) illustrate the tunnelling region for $N = 1 - 4$, panels (a2)-(b2) uncover the ohmic behaviour for $N > 5$. Dephasing-probe simulations were performed with $\epsilon_B = 0.8$ eV, $v = 0.22$ eV, $\gamma_{L,R} = 0.018$ eV, applied voltage $\Delta \mu = 0.01$ eV and dephasing strengths in the range $\gamma_d = 0 - 1$ meV. ......................................................... 25

1.11 Analysis of experimental results for the temperature dependence of conductance in ONI wires. Experimental data (+) [1] for $N = 7$ is compared to simulations with $\gamma_d = 0, 0.2, 0.4$ meV (empty squares, top to bottom). For reference, we also show the $N = 3$ case (◦) in which the resistance is independent of dephasing in the range $\gamma_d \sim 0 - 5$ meV (consistent with the experiment). Other parameters are the same as in Fig. 1.10. ..................... 26

1.12 Example of stacked and alternating DNA sequences investigated in this work. (a)-(b) and (c)-(d) are the ladder and simplified 1D models for alternating and stacked sequences, respectively. See Appendix B for site energies and tunnelling matrix elements. .................. 28

1.13 Ladder model. Resistance of (a) alternating (GC)$_n$ and (b) stacked G$_n$C$_n$ sequences, see Fig. 1.12 for the ladder model. Panel (c) overlays A and S simulations along with experimental results from Ref. [2]. Simulations were performed at room temperature, with $\gamma_d = 0.01, 0.03$ and 0.05 eV, $\gamma_{L,R} = 0.05$ eV. ................................. 30

1.14 Ladder model. Resistance of (a) alternating (GC)$_n$ and (b) stacked G$_n$C$_n$ sequences, panel (c) overlays A and S results. Parameters are the same as in Fig. 1.13, but we take $\gamma_{L,R} = 1$ eV. .................. 30

1.15 Energy spectrum for alternating (a1)-(a2) and stacked (s1)-(s2) ladder models, with $N = 4n + 4$ electronic states. Panels (a2) and (s2) zoom over the low-energy range. The dashed line marks the Fermi energy, and we set $\epsilon_F = \epsilon_G = 0$. ................................. 31

1.16 Density matrix map of the ladder model for (a) alternating and (b) stacked sequences. Parameters are $\gamma_{L,R} = 0.05$ eV, $\gamma_d = 0.03$ eV, room temperature, $\epsilon_F = \epsilon_G$. ................................. 32
2.1 (a) I-V characteristics with a linearly deformed bridge [Eq. (2.3)] with $N=6$ sites of height $\epsilon_B = 0.5$. Other parameters are intra-site coupling $v = 0.05$, leads coupling $\gamma_{L,R} = 0.2$, dephasing strength $\gamma_d = 0.001, 0.01, 0.1$ eV (organized bottom to top at low voltage), with dephasing probe (dashed) and voltage probe (full), and temperature for leads and probes $T = 298$ K. The dotted line at $\Delta \mu = 0.5$ eV marks the value beyond which molecular resonances appear within the bias window. Beyond $\Delta \mu = 1.0$ eV, more than half of the sites of the bridge are situated within the bias window. Zoom over (a2) $\gamma_d = 100$ meV, (a3) $\gamma_d = 1$ meV.

2.2 Magnitude of energy-resolved currents at the left and right contacts, calculated as the integrand of Eq. (1.7), and an analogous current at the right side. The voltage probe (top) permits energy dissipation, therefore the energy-resolved current leaving the left-high bias-lead (dark purple) is not the same as that arriving at the right low-bias lead (pink). The dephasing probe (bottom) does not allow dissipation, and the left and right energy-resolved currents are identical. Parameters are the same as in Fig. 2.1, $\gamma_d = 10$ meV. (a) and (d): Low voltage with off-resonant conduction. (b) and (e): Low-intermediate voltage with off-resonant conduction, and (c) and (f): High-bias simulations with resonant transmission.

2.3 Potential profile within voltage probes along the chain for $\gamma_d = 10$ meV in the R1, R2, R3 regions for (a), (b), (c), respectively. Parameters are the same as in Fig. 2.1.

2.4 Illustration of the examined tunnelling diode. Displayed are levels (a) at zero bias, (b) forward bias, providing a resonant situation beneficial for conductance, and (c) under reverse bias when levels are shifted away from each other resulting in small tunnelling currents.

2.5 Tunnelling diodes under inelastic effects with parameters corresponding to the 1,2-bis(4-(phenylethynyl)phenyl)ethane molecule (top panel), serving as the backbone of the diode. (a) IV characteristics of the junction, (b) rectification ratio $R$, and (c) level diagram showing the chemical potentials $\mu_{L,R}$ at the two leads (dashed lines) and the eigenenergies of $H$, Eq. (2.5) (full lines). Parameters here and throughout this subsection correspond to a two-state model of the molecule (top panel) with $\epsilon_1 = 0$, $\epsilon_2 = -0.329$, $v = 0.0109$, $\gamma_{L,R} = 0.03$, all in units of eV, and $\alpha = 0.55$ [3]; $T = 298$ K. $\gamma_d = 0, 0.01, 0.1, 0.3$ eV.

2.6 Energy resolved currents in the coherent limit $\gamma_d = 0$ (black) and under inelastic effects $\gamma_d = 0.05$ eV. In the latter case $|I_L(\epsilon)| \neq |I_R(\epsilon)|$, i.e. the current profile of electrons entering the junction is different from the one leaving it. The three panels follow the configurations of Fig. 2.4: (a) Low bias, when inelastic effects play a little role. (b) At peak voltage $\sim 0.6$ V the two states are in resonance, $\epsilon_1 + \alpha eV/2 \sim \epsilon_2 - \alpha eV/2 = -0.165$ eV. (c) At large negative voltages $-0.6$ V, $\epsilon_1 + \alpha eV/2=0.165$ eV and $\epsilon_2 - \alpha eV/2 = -0.49$ eV. In panels (b)-(c) we further depict the resolved current under the dephasing probe condition when energy relaxation is not allowed (dashed line). Parameters are the same as in Fig. 2.5.

2.7 Map of rectification ratios as a function of applied bias and metal-molecule hybridization (starting at values $\gamma_{L,R} = 1$ meV). (a) Coherent limit, (b) $\gamma_d = 10$ meV, and (c) $\gamma_d = 100$ meV. Parameters are the same as in Fig. 2.5.
2.8 Decline of rectifying behaviour due to environmental interactions with the parameters of Fig. 2.5. Filled symbols at the left boundary mark corresponding rectification ratios in the coherent $\gamma_d = 0$ limit. ................................................................. 48

2.9 Top: Scheme of a four-site diode in the site representation (left), and energy representation within each conjugated moiety (right). Bottom: Operation of the junction as a diode (a) IV characteristics, (b) rectification ratio, and (c) level diagram with (dashed lines) chemical potentials and (full lines) the four eigenenergies of the molecule. Parameters are $\epsilon_1 = 0$, $\epsilon_2 = -0.329$, $v = 0.0109$, $\gamma_L, R = 0.03$ eV, and $\alpha = 0.55$ as in Fig. 2.5, as well as $v_1 = v_2 = 0.03$ eV for the tunnelling energy within each conjugated unit. The temperature is set at $T = 298$ K and $\gamma_d$ was varied as indicated in the figure. ............... 49

2.10 Type 1 EID. Top: Schematic representation of a diode induced by inelastic effects. The electronic structure is symmetric, but hybridization strengths to the leads are different, illustrated by arrows of different colour at the edges. (a) Rectification ratio as a function of environmental coupling. (b) Potential profile within the voltage probes demonstrating the development of an asymmetry in the junction’s response to applied bias at peak value $\gamma_d = 0.16$ eV. Parameters are $\epsilon_B = 0.3$, $v = 0.05$, $\gamma_L, R = 0.2$ eV, $\gamma_L = 10 \times \gamma_R$, $T = 298$ K and $N = 3$, voltage probe condition. The dotted line identifies the symmetry axis. .......... 50

2.11 Type 2 EID. Top: Schematic representation of the diode. The electronic structure is spatially symmetric and $\gamma_L = \gamma_R$, but coupling strength to the surrounding environment assumes a certain profile, represented by the colour gradient of the bath, $\gamma_1 > \gamma_2 > \gamma_3$, with the integer standing for the site index left to right. (a) Rectification ratio as a function of coupling to the environment. Parameters are the same as in Fig. 2.10, with $\gamma_1 = 2\gamma_d$, $\gamma_2 = \gamma_d$, $\gamma_3 = \gamma_d/2$. (b) Potential profile within the probes, demonstrating the development of an asymmetry in the junction’s response to applied bias under inelastic effects at peak value $\gamma_d = 0.4$ eV. .................................................. 51

3.1 Diagram of the VETS in the local-site basis (left) and in the energy basis (right). The arrows represent interactions with the hot, cold and decoherence baths, denoted by $\Gamma_h, \Gamma_c$ and $\Gamma_d$ respectively. ................................................................. 61

3.2 Diagram of a three-level QAR (3lQAR). The arrows represent energy exchange processes with the hot, cold and work baths, denoted by $\Gamma_h, \Gamma_c$ and $\Gamma_w$ respectively. ..................... 63

3.3 Diagram of the four-level QAR in the local-site basis (left) and energy basis (right). The arrows represent interactions with the hot, cold, work and decoherence baths, denoted by $\Gamma_h, \Gamma_c, \Gamma_w$ and $\Gamma_d$ respectively. ................................................................. 64

3.4 Heat current in the VETS model. (a)-(d) Solution of the Redfield equation with an increasing decoherence strength between the excited states. (e) When decoherence is sufficiently strong, we retrieve the secular behaviour. $\gamma \equiv \gamma_{h,c} = 0.002$, $\omega_c = 50$, $T_h = 0.15$, $T_c = 0.1$, $T_d = 0.12$. .................................................. 66

3.5 (a) Contour plot of current in the VETS model as a function of the inter-site coupling $g$ and decoherence strength $\gamma_d$. (b) Demonstration of a non-monotonic $J_q$ vs. $\gamma_d$ behaviour. $\gamma \equiv \gamma_{h,c} = 0.002$, $\omega_c = 50$, $T_h = 0.15$, $T_c = 0.1$, $T_d = 0.12$, $\theta = 0.5$. ..................... 67

3.6 Heat current in the VETS model as a function of the inter-site coupling $g$. Parameters are the same as in Fig. 3.4, with $\theta = 0.5$, $\gamma \cdot \theta = 0.001$. ..................... 68
3.7 (a) Current, (b) steady-state population and (c) coherences in the VETS model at $\gamma_d = 0$. Parameters are the same as in Fig. 3.6.

3.8 Cooling current in the 4lQAR. (a)-(d) Solution of the Redfield equation with an increasing decoherence rate between the intermediate states. (e) When $\gamma_d$ is sufficiently strong, we retrieve the secular behaviour.

3.9 COP of the 4lQAR for $\gamma_d = 0$ and $\gamma_d/\gamma = 100$ (overlapping). Parameters are the same as in Fig. 3.8. The dashed line corresponds to the Carnot bound for a cooling machine, $\eta_C = \frac{\beta_h - \beta_w}{\beta_c - \beta_h}$, which equals 1.7 in our parameters.

3.10 (a) COP vs. cooling power for the 4lQAR at $\gamma_d = 0$ while increasing $g$ from $10^{-3}$ to 0.4 as we move inward. The black dashed line corresponds to the secular limit at vanishing $g$, showing an endoreversible operation. To generate these plots, the frequency $\theta_c$ was varied within the cooling window. (b) Maximum cooling current and (c) COP at that value, optimized at every point with respect to $\theta_c$. Parameters are the same as in Fig. 3.8.

3.11 Schemes of nanoscale energy conversion devices that can be captured with our generic models. (a) The VETS model can be realized by a conducting junction with two degenerate electronic states. (b) The 3lQAR may correspond to a non-degenerate electronic junction, with the work bath responsible for internal transitions. (c) The 4lQAR can represent a photovoltaic cell. Heat absorbed from the work reservoir is used to transfer carriers—thus energy—from the cold metal to the hot metal. The red, blue and orange arrows represent energy exchange processes with the hot, cold and work heat baths. The effect of the decoherence bath is omitted for simplicity, but it can be further included.

3.12 Model diagrams of the VETS described in 3.2, when the upper states are degenerate, near-degenerate and non-degenerate (zero electronic coupling, $g$, small $g$, and large $g$). Going across the rows, are representations of the model in various bases: the energy basis, so-called secular basis and the site basis (basis which considers the excited states as coupled). In the centre square, (2b), $\Delta$, $\gamma_h$ and $\gamma_c$ are complex system and system-bath coupling factors, and $\omega$ is a real energy splitting.

3.13 Same as 3.12, except with only positive terms in $\hat{S}_{h,c}$, which gives rise to a different site basis and overall behaviour. After degeneracy is broken, the secular basis and energy basis become identical (there are no steady-state energy basis coherences in the non-degenerate model).

3.14 Current calculated for panel (1a) of Fig. 3.13, for $g = 0$. The ratio of current calculated with the full Redfield equation (with coherences) to the current calculated with a secularised master equation (without coherences) in the Class 2 VETS, as a function of temperature bias and excitation gap, $\theta = \omega_{2,1}$, $\bar{T} = 1$, $\omega_c = 50$, $\gamma_{L,R} = 0.001$.

3.15 4lQAR identical to the one studied in Sec. 3.3, considering the energy basis, secular basis and site basis at zero, small and large $g$.

3.16 Same as 3.15, except with only positive terms in $\hat{S}_c$, which gives rise to a different site basis and overall behaviour. After perfect degeneracy is broken, the secular basis and energy basis become identical (there are no steady-state energy basis coherences in the non-degenerate model).
3.17 Model for an energy transfer system constructed by addition of two degenerate spins, each coupled to a hot and cold bath. We display the energy basis and secular basis when the noise is correlated (cooperative) vs uncorrelated (independent). The $1, 2$ labels in $\Gamma^{(1,2)}_\alpha$ correspond to which of two sets of hot and cold baths are mediating the transitions. In the cooperative case, one hot bath and one cold bath mediate all the transitions.

4.1 Scheme of the NESB nanojunction, while illustrating with curvy arrows the counting process with the phase factors decorating the system-bath interaction, see Eqs. (4.6)-(4.18). The expansive arrows display the direction of the net heat flow in steady-state. (a) Counting system-bath heat exchange only at the left contact. (b) Counting heat exchange in a symmetrical manner. Model parameters include $\Delta$ as the spin spacing in the energy basis. The baths are characterized by spectral functions $g_\alpha(\omega)$ and an inverse temperature $\beta_\alpha$.

4.2 (a)-(b) Real and imaginary parts of the cumulant generating function for the $L$ bath in the dephasing model, as a function of time. Parameters are $\omega_c = 50$, $T_L = T_R = 5$, $\gamma = 0.01$, $\xi = 0.01$.

4.3 Representative examples of the imaginary (a)-(b) and real (c) components of the generating function for heat exchange in the NESB model. Panel (b) displays the imaginary part of the cumulant generating function as it reaches steady-state. Results in panel (c) are not fully converged, and should be considered qualitative. Parameters are $\Delta = 1$, $\omega_c = 10$, $\bar{T} = 5$, $T_L - T_R = 0.05$, $\gamma = 10^{-3}$, $\delta t = 0.3$, $\Delta k = 5$.

4.4 (a) Steady-state heat current in the NESB model as a function of the dimensionless system-bath coupling parameter $\gamma$ with $\Delta k = 7$ and different time steps $\delta t$. Results are compared to NIBA simulations. (b) Weak coupling results are compared to the Redfield QME and the Majorana Green’s function approaches. (c)-(d) Exemplifying convergence of results at $\gamma = 0.1$ as a function of (c) $\Delta k$ while fixing the time step and (d) $\delta t$ for a fixed memory time. Parameters are $\Delta = 1$, $\omega_c = 50$, $\bar{T} = 5$, $T_L - T_R = 0.5$.

4.5 (a) Steady-state heat current in the NESB model as a function of temperature difference $T_L - T_R$. iFCSPI simulations are compared to Redfield and Majorana-GF approaches. (b)-(c) Convergence is achieved for both small and large temperature bias as illustrated upon varying (b) the memory range $\Delta k$ with a fixed $\delta t = 0.07$, and the (c) time step $\delta t$ with a fixed $\Delta k = 7$. The arrow in panel (b) points to the direction of converging results. Parameters are $\Delta = 1$, $\gamma = 0.1$, $\omega_c = 50$, $\bar{T} = 5$.

4.6 (a) Steady-state heat current as a function of the tunnelling element $\Delta$ in the weak system-bath coupling regime. We present three curves for the iFCSPI with different time steps $\delta t$. iFCSPI results are compared to Redfield QME (full), Majorana-GF (dashed-dotted), and NIBA (dashed) results. The latter is known to fail in the large $\Delta$ regime. (b) Demonstration of convergence behaviour: series of results from $\Delta k = 1 - 6$ for $\delta t = 0.05$. The arrow points to the direction of increasing $\Delta k$. The case $\Delta k = 7$, which is presented in panel (a) is highlighted in filled circles. Parameters are $\gamma = 0.01$, $\omega_c = 50$, $\bar{T} = 5$, $T_L - T_R = 0.5$.
A.1 Electrical conductance vs. inter-site tunnelling \( v \). In the coherent tunnelling limit \( G \propto \frac{1}{v^2} \). In the hopping regime \( G \propto v^2 \). Parameters used are \( \epsilon_B = 0.5, v = 0.05, \gamma_{\nu} = 0.2, \Delta \mu = 0.01 \text{ eV} \).

A.2 Electrical conductance as a function of the hybridization energy, \( \gamma_L = \gamma_R \). When \( \gamma_d = 0 \) we resolve tunnelling conductance for \( N = 3, G \propto \gamma_L \gamma_R (\triangle) \) and ballistic motion for \( N = 7 \) when \( \gamma_{\nu} \ll \epsilon_B (\circ) \). The conductance dependency on \( \gamma_{\nu} \) diminishes upon increasing dephasing strength. We used \( T = 300 \text{ K}, \epsilon_B = 0.5, v = 0.05, \Delta \mu = 0.01 \text{ eV}, \) dephasing probe simulations.

F.1 Error Analysis: An asymmetric counting of energy exchange in the NESB model leads to nonzero heat current at zero temperature difference. We display a fixed-memory analysis of the nonphysical current by reducing the time step as in Figure 4.4. Inset: linear fit demonstrating the behaviour of the spurious current at \( \delta t \to 0 \). Parameters are \( \Delta = 1, T_L = T_R = 5, \gamma_{L,R} = 0.01, \omega_c = 50 \).

F.2 Error Analysis: (a) Nonzero heat current at zero temperature difference when \( \gamma_L \neq \gamma_R \). The counting field is applied symmetrically to the \( L \) and \( R \) baths, which are coupled asymmetrically to the spin system. (b)-(c) Linear fit of the spurious current, demonstrating its behaviour as \( \delta t \to 0 \). Parameters are \( \Delta = 1, T_L = T_R = 5, \gamma_{avg} = 0.01, \omega_c = 50 \).
Introduction

Technology miniaturisation has reached what must be nearly the smallest possible dimension, the single molecule (or single-atom) limit. By shrinking devices to this scale, we hope to achieve improvements in selectivity, sensitivity, customisability, power and efficiency, just to name a few relevant features. When building real or theoretical nanodevices (machines that operate on nanometer or smaller length scales), we do not always even know in advance what kinds of improvements we can hope for; even after decades of work, basic exploration remains a key part of today’s research programs. As a corollary to this, and very exciting from a basic science perspective, the nanoscale is a terrific playground for the exploration of fundamental questions, in particular relating to quantum dynamics and statistical physics. In this thesis, we focus in particular on devices that conduct or block electrical or heat current, or interconvert heat and work.

Molecular junctions are constructed by stringing up a molecule like a wire between two or more metallic leads. Once the ends are connected, one can apply a temperature or voltage bias via the leads, and induce charges to migrate from one to another, via the molecule. One may then study its characteristics as e.g. a switch, a resistor or a sensor. A common approach to constructing a molecular junction is via a scanning tunnelling microscope, where molecules are deposited on a surface, and prodded by the tip of a very sharp needle in order to make chemical contact, before being retracted, tautening the wire. While perhaps not a practical approach for mass production of nanodevices, this experimental setup allows us to study the behaviour of single molecules in a relatively controlled manner. One may ask, what makes such molecular electronic devices attractive? Organic molecules have two advantages in this space: (i) Through synthetic organic chemistry techniques, we have a high degree of control on the structure and therefore properties of the molecules, and (ii) the space of potential designs and resulting properties of organic molecules is almost unfathomably diverse. By exploring this chemical space, we hope to discover new and useful properties, and leverage them into useful devices.

Quantum heat machines, rather than acting as conduits for the motion of charges, instead exchange energy with their surroundings, often converting some energy input into a useful output, as in a heat engine or refrigerator. In theory, such machines could be constructed out of any quantum system allowing transitions between its discrete energy states, such as single or small groups of atoms, ions, or spins. Due to the difficulty of interacting with matter on this scale, and setting up the correct interactions with multiple energy reservoirs, experimental realisations of such devices are so far limited, though theoretical investigation has been energetic [4, 5, 6, 7, 8, 9]. Again we can ask, why the fuss about such tiny energy conversion devices? We have again the allure of miniaturisation, and understanding the thermodynamic and operational principles of nanoscopic devices is critical if we want to build and utilize them [10, 11, 12, 13, 14]. Perhaps even more alluring are the as yet unknown properties of such systems. Using thermodynamics, one can for many systems make confident assertions about the
limits of power and efficiency which a macroscale device can achieve; this is not yet true for devices on the quantum scale, obeying Schroedinger’s, rather than Newton’s equations. This leads directly to the fundamental question: how do the laws of thermodynamics translate from steam engines to single atoms? Analysing quantum heat machines using the appropriate theories, we can begin to answer this.

The theoretical thrust of this thesis is the exploration of the mechanistic instrumentality of different physical effects in nanodevice operation. Concordant with this is, we develop and discuss theoretical methods in the context of their ability or inability to capture such effects. The Landauer theoretical formalism is central to the study of transport in molecular junctions. It carries the two advantages of being very simple to use and understand, as well as capturing exactly the coherent-elastic motion of charge carriers in a noninteracting system [15]. Thus, for molecular junctions that allow charges predominantly to cross via a coherent tunnelling mechanism, such as those with short molecular bridges, or with some metallic character, Landauer theory frequently gives the current with good accuracy. This does not give the full picture however, since molecules vibrate and interact with their surroundings, both of which contribute to incoherent charge transport effects including charge hopping and disorder. Such incoherent effects are completely omitted from the Landauer formula, which is a serious problem for longer molecular wires, particularly at higher temperatures or when submerged in a solvent, where they may over-dominate the coherent tunnelling and so determine the current.

Electron-nuclei interactions are central to the operation of molecular electronic systems [16]. Atomic motion in molecules and their surroundings opens up new channels for electronic conduction and ultimately, can result in the emergence of ohmic conduction [17, 18]. Energy exchange between conducting electrons and nuclei can locally heat the junction [19, 20, 21, 22, 23], as was demonstrated experimentally in Refs. [24, 25, 26], and drive vibrational instabilities [27, 28, 29, 30, 31], even resulting in a rupture of the molecular bridge [32]. These complex many-body effects can be captured within seemingly simple models: The Anderson-Holstein model describes molecular junctions with a single electronic site coupled to a dominant vibrational mode [33]. In donor-acceptor junctions, phonon emission and absorption processes facilitate charge transfer between two molecular electronic sites (or orbitals) [27, 28, 29, 34, 30, 35, 36, 37]. Tight-binding models with several electronic sites and multiple vibrational modes have been employed to describe charge transfer in extended molecules, linear organic molecules [33], and DNA [38].

To address this shortcoming in the Landauer approach, in Part I of this thesis we will implement, characterise and apply the Landauer-Büttiker probe technique to problems of conduction and device operation in molecular junctions [39, 40, 41]. This probe technique phenomenologically incorporates incoherent effects, giving rise to an electron hopping mechanism, among other environmental effects. With it, we accurately predict the electrical conductance in long, conjugated molecular wires, and further, predict and explain the functionality of ds-DNA nanowires and molecular tunnelling diodes.

In the heat transfer literature, quantum master equations of various types are the most common tools of the theoretical trade [42, 43]. Such master equations take on many flavours, each tailored to a particular situation, e.g. fast or slow equilibration of bath modes, wide or narrow spacing of subsystem energy levels, strong or weak coupling between the subsystem and baths. In the weak system-bath coupling limit, with a fast bath, the tool of choice is generally a Redfield-type master equation, which can be secularized into a Lindblad form via decoupling of populations and coherences in the energy basis. Though many past and ongoing studies have sought to push our understanding of device operation and thermodynamic principles into the strongly interacting and non-Markovian limits, interesting questions remain in the Redfield regime.
The question of equivalence, and indeed supremacy of quantum over classical processes is intensely interesting. Can one construct a quantum device with properties superior to those achievable in a classical one, and further, what makes a quantum device “quantum” [44, 45]? An area of focus has been the role of quantum coherences, and particularly their potentially beneficial impacts on device performance [10, 11, 46, 47, 12]. Part II of this thesis opens with a general study on the phenomenon of noise-induced coherence in autonomous quantum thermal devices, and their impacts on the power and efficiency of quantum absorption refrigerators. We will study a model in which the “quantum” role of coherence is to deactivate the machine, while its non-coherent counterpart runs smoothly [48]. To reconcile this with previously observed cases of coherence boosting device power output, we posit a new picture through which to analyse device operation which consolidates and clarifies our understanding of the role of noise-induced coherences.

Beyond the Redfield regime, there are serious ongoing discussions in the literature on the role of strong system-bath coupling, non-Markovian bath, time-dependent driving, and other difficult-to-calculate effects on the operation of quantum heat machines [49, 50, 51, 52, 53, 54, 55, 56]. Each of these may introduce new physical properties and mechanisms, which may or may not further distinguish the operational characteristics of quantum devices from those of classical. To further enable studies in these difficult parameter regimes, we introduce in Chapter 4 a new method for computing the full-counting statistics of heat transfer, to yield not just energy current, but also its cumulants. This iterative full-counting statistics path integral is numerically exact, and when employed appropriately with an efficient algorithm, should deliver accurate results for any parameter regime, thereby enabling studies of otherwise difficult or complex devices.
Part I

Chapters 1 & 2: Charge Transport with Büttiker Probes
Part I Introduction

With the advent of tools for constructing and characterizing nanostructures such as the scanning tunnelling microscope and the atomic force microscope, a vast playground was opened for researchers in a variety of fields to study new types of microscopic systems. Within this nanoscale realm lies the potential for new types of machines and devices; an undiscovered country of possibilities for technological applications as well as opportunities to enhance our basic understanding of the world.

In this first part of the thesis, we consider the application of Büttiker probes to electronic conduction through organic molecules. The Landauer scattering formalism for such “molecular wires” has proven successful in studies of such systems, being quite attractive due to its low computational cost and relative simplicity, but the method is incomplete; it does not incorporate incoherent charge transport effects originating from the molecule itself or the surrounding environment. Such effects can be critically important, particularly in cases where the charge carriers must travel a long distance, and therefore call for theoretical attention.

We open in Chapter 1 with a detailed study of a method that rectifies this key shortcoming of the Landauer formalism in a phenomenological manner, the Landauer-Büttiker probe (LBP) technique, including simulations of physically relevant systems. Beginning from a uniform linear system (a wire), we explore the various mechanisms of charge transport through the molecular junction, and their dependence on environmental interactions, as phenomenologically introduced by Büttiker probes. Detailed information on the implementation and behaviour of the LBP are given, and we validate our protocol by comparison with experiments on long, conjugated molecular wires. Chapter 1 wraps up with an application to a more complex system - a double ladder model of ds-DNA, wherein recent experiments have identified an intriguing new behaviour, potentially mixing so-called coherent and incoherent effects. We use the LBP to attack this problem and explain its behaviour in terms of a combination of transport mechanisms, enabled by environmental effects.

Following our success in developing, characterizing and utilizing the LBP in Chapter 1, we extend the technique in Chapter 2 to the high voltage bias regime, where dissipation of energy to the environment is expected to become relevant. We implement a new protocol for this regime, and examine the role of elastic and inelastic incoherent scattering on the charge transport characteristics of a 1D wire. The LBP is then applied to the problem of single-molecule diodes, the most basic functional component of an organic circuit. While many types of diodes or rectifiers have been proposed, modelling of their behaviour is typically limited to the bare Landauer technique; we rectify this by introducing environmental effects via the LBP, and uncovering their role in device operation. We explore several types of diodes, and find that environmental interactions may play a critical role, generally suppressing though sometimes creating current rectification.
Chapter 1

The Landauer-Büttiker Probe Technique: Behaviour and Applications

1.1 Introduction

Understanding of charge transport mechanisms in single-molecule junctions is essential for the realization of molecular electronic devices, as well as for elucidating many processes in chemistry, biology, and condensed phase physics. Examples include charge transfer in DNA [57, 58], a process which plays a crucial role in mutagenesis and carcinogenesis, electron transfer reactions [59, 60, 43], and electron correlation effects at the nanoscale, such as in quantum dots and molecular junctions [15, 18, 17].

Experiments probing electron transfer (ET) rates in donor-acceptor DNA molecules [61, 62, 63, 64], self-assembled monolayers and single-molecule wires [65, 66, 67, 68, 69, 70, 71, 1, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82] have demonstrated the central role of at least three limiting transport mechanisms: phase-coherent off-resonance tunnelling (superexchange), coherent resonant (ballistic) tunnelling, and incoherent hopping [43, 18]. The tunnelling mechanism relies on the coherent motion of charges through molecules, and it dominates when decohering interactions are minimal. Deep tunnelling conduction decreases exponentially with distance, becoming ineffective in long molecules. In contrast, resonant tunnelling is insensitive to molecular length, with a thermal activation profile distinct from that of other thermally-assisted processes such as hopping [83]. Ballistic motion is often difficult to realize in real molecules due to static disorder and dynamic fluctuations, therefore, long-range electron transfer is typically dominated by incoherent hopping processes, where electrons (or holes) fully localise on molecular sites, and hop between them in an incoherent manner. Such a multi-step hopping conduction is characterized by a linear enhancement of resistance with molecular length. Furthermore, in molecular wires bridging two voltage-biased electrodes, “field emission” (Fowler-Nordheim tunnelling) behaviour develops when the applied voltage bias transforms the tunnelling barrier from a rectangular form into a triangular shape [1, 75].

In an effort to explain experimental results, and moreover, predict molecular electronic functionality, a plethora of theoretical and computational methodologies have been developed, aiming to explore the role
of environmental effects (internal molecular motion or the surrounding matrix) on molecular conduction. These tools can be roughly grouped into two classes: (i) microscopic-physical modelings which are valuable for small systems, and (ii) phenomenological descriptions, compromising the completeness and exactness of the model to enable large-scale calculations.

The first type of approaches corresponds to models in which molecular vibrations, and other many-body interactions such as electron-electron repulsion are explicitly included in the model Hamiltonian. The dynamics and steady-state properties of the system can then be analyzed by a variety of treatments. A non-exhaustive list, focusing on vibrational effects in molecular conduction, includes density operator approaches [84, 85], Green’s function tools [33] and path integral simulations [86, 31, 87]. Since the vibrational degrees of freedom and/or electron-electron interactions are explicitly incorporated in such treatments, simulations are restricted to minimal models with a single molecular electronic state, or a pair of states. The Anderson-Holstein model takes into account a single electronic level and a particular vibration. Other common modelings consider only two molecular orbitals, the HOMO and LUMO, as decisive for electronic conduction [33]. It should be mentioned that recently developed approaches which combine time-dependent density functional theory for open quantum systems with the principles of the nonequilibrium Green’s function method [88, 89, 90] offer an efficient route for studying dissipative electron transport in large-realistic systems, to describe e.g. electron transfer across graphene monolayers [88, 89].

Complementing minimal-microscopic approaches, it is beneficial to establish effective-phenomenological methodologies for electronic conduction with a more favourable scaling with molecular size. The Lindblad formalism, Redfield theory, and other kinetic equations, are examples of such approaches [42, 43]. In these treatments the interaction of electrons with environmental degrees of freedom is incorporated into the dynamics via decoherence and dissipation rates which are introduced into the equations of motion for the reduced density matrix. Variants of such projection operator techniques have been employed extensively in the literature to model electron, proton, phonon, and exciton dynamics in condensed phases [43, 60]. In donor-bridge-acceptor electron transfer (DBA-ET) processes, such methods have proven useful for describing, in a unified manner, both the tunneling and the incoherent-hopping regime [91, 92, 93, 94, 95, 96, 97, 98, 99, 100]. More recent works rigorously examined the consistency of these effective treatments for describing steady-state characteristics [101, 102, 103], and applied kinetic approaches to predict electronic functionality [104, 105].

A distinct phenomenological route to implement decoherence and inelastic effects was introduced by Büttiker in Refs. [39, 106]. In this “Landauer-Büttiker probe” (LBP) approach the noninteracting Hamiltonian is augmented by probe terminals in which electrons lose their phase memory and exchange energy with probes’ degrees of freedom. This technique, so far mostly employed in mesoscopic physics (also referred to as D’Amato-Pastawski model in certain implementations [40]), is particularly appealing: It allows one to model phase breaking processes, e.g. in quantum dots, while using the Landauer nonequilibrium Green’s function (NEGF) formalism [15, 18, 17, 107], which omits interactions. Recently, it was used e.g. to study heat to work conversion efficiency in thermoelectric devices [108, 109, 110] and magnetotransport in quantum dot systems [111, 112]. Beyond electronic conduction, the LBP technique has been adopted to explore heat transport and thermal rectification in linear chains [113, 114, 115, 116, 117, 118, 119] and two-dimensional constrictions [120].

The LBP method has proven itself predictive in studies of charge and heat transport in mesoscopic physics. Can it appropriately describe environmental effects on electronic conduction in molecular junc-
tions? Recent works examined this question: It was demonstrated in Refs. [41, 121] that the technique can indeed yield the tunnelling-to-hopping transition in conjugated molecular wires under the application of dephasing probes. The technique has been further applied in Ref. [122] to explore the role of decoherence on quantum interference in molecular conduction, and in Ref. [123] to examine the connection between charge transfer kinetics and steady-state currents. While these works proved that the LBP method can provide physically-correct transport characteristics in molecular electronic configurations, a careful exploration of its predictions as a function of length, temperature, dephasing, applied voltage bias, and bridge energetics is still missing. Our objective here is to employ the LBP technique and examine whether it can yield results consistent with our comprehensive knowledge of environmental-assisted electron transfer effects in molecular electronic junctions. Particularly, the technique should depict the turnover in transport, from tunnelling to hopping, with increasing molecular size, temperature, and dephasing rates.

Another objective of this chapter is to develop an approximate analytic expression for hopping conduction in molecular junctions. Several works have undertaken this task in a donor-bridge-acceptor configurations to construct the electron transfer rate, a related quantity [94, 98, 99, 96, 97, 124, 125]. However, few theoretical studies considered this problem in a metal-molecule-metal setup [95, 126, 127, 128, 79], which differs fundamentally from the DBA-ET situation: While in the latter case the initial condition places all electrons in the donor state with a given energy, in a metal-molecule-metal experiment many electronic states in the metals contribute, and electrons, with a thermal distribution of energies, determine the electronic conductance.

Simulations presented in this work confirm that the LBP method can properly emulate experimentally-observed characteristics of molecular electronic conduction in wires with a tunable “dephasing strength” parameter, characterizing the strength of electron-environment interactions. Based on our simulations we suggest an analytic expression which describes hopping conduction in molecular wires. The Landauer-NEGF technique is nowadays the leading method in modelling the operation of phase-coherent molecular electronic devices [15, 18, 17, 107, 129]. Particularly, recent measurements of molecular thermopower (see for example Refs. [130, 131]) and heat dissipation in nanojunctions [132] were explained using this method. By establishing here the appropriateness of the LBP treatment in molecular electronic problems we advocate for the natural generalization of the quantum chemistry Landauer-NEGF technique to incorporate environmental-assisted effects by including LBPs, as demonstrated in Ref. [41, 121, 133, 134, 135, 136, 137, 138, 139]. As we show in Chapter 2, such studies can be performed far from equilibrium.

This Chapter is organized as follows. In Sec. 1.2 we present the wire model and the probe technique. Sec. 1.3 summarizes transport mechanisms in molecular junctions. In Sec. 1.4 we present mechanistically illustrative numerical simulations under low applied voltage. Based on observations, we construct an analytic expression for bath-assisted molecular electronic conduction. In Sec. 1.5 we apply our computational method and compare findings to experimental results for transport in long conjugated molecules, showing good agreement under a single tunable parameter. Sec. 1.6 considers the interesting case of a ds-DNA junction where coherent and incoherent currents have comparable magnitudes, and how one can characterize the functioning of a device in this regime, focusing particularly on DNA nanowires. We conclude in Sec. 1.7. Discussion of the impact and applications of probes under large applied bias is quite involved, and therefore occupies Chapter 2 in its entirety.

In this work we interchangeably refer to the molecular system as a “molecular wire”, “molecular
junction”, or “molecular bridge”. Identifying the system as a “wire” emphasizes that molecules under consideration include repeating units, and that they are capable of transferring charges over long distances. The term “junction” highlights the geometry: the molecule is placed between two metal electrodes, distinguishing it from the DBA situation. “Bridge” describes the structure assumed: We study situations in which molecular orbitals relevant for transport lie above the Fermi energies of the two electrodes. Molecular electronic degrees of freedom are coupled to environmental coordinates (here, mimicked by probes). The environment may correspond to internal molecular vibrations or solvent degrees of freedom (we exclude the metals’ electrons from this definition). We collectively refer to these nuclear coordinates as a “thermal bath”, “environment”, or “surrounding”, assumed in this work to be maintained at the temperature of the metals (see Ref. [138] for a study of thermoelectricity in a nonequilibrium thermal environment).

1.2 Model and Method

1.2.1 Model Hamiltonian

We consider a molecule bridging metal electrodes, with the total Hamiltonian

\[ \hat{H} = \hat{H}_M + \hat{H}_L + \hat{H}_R + \hat{H}_T + \hat{V}_P. \]  \hspace{1cm} (1.1)

It comprises the molecular wire \( \hat{H}_M \), two electrodes \( \hat{H}_L \) and \( \hat{H}_R \), and a coupling Hamiltonian \( \hat{H}_T \) allowing charge transfer between the two leads and the wire. We further introduce (in a phenomenological manner) dephasing and inelastic effects for electrons on the molecule. This is achieved by attaching local reservoirs \( (\hat{H}_P) \) to each site in the wire via coupling Hamiltonian \( \hat{V}_P \), see Fig. 1.1. The molecular wire includes \( N \) single-level sites of energy \( \epsilon_n \),

\[ \hat{H}_M = \sum_{n=1}^{N} \epsilon_n \hat{c}_n^\dagger \hat{c}_n + \sum_{n=1}^{N-1} v_{n,n+1} \hat{c}_n^\dagger \hat{c}_{n+1} + \text{h.c.} \]  \hspace{1cm} (1.2)

Here, \( \hat{c}_n^\dagger (\hat{c}_n) \) are fermionic creation (annihilation) operators of electrons on each site in the wire, the parameters \( v_{n,n+1} \) are the inter-site tunnelling energies. In Sec. 1.3-1.5 which follow, we consider molecules made of identical building blocks, thus we introduce the short notation \( \epsilon_B = \epsilon_n \) and \( v = v_{n,n+1} \).

In general, any tight-binding geometry is possible, and indeed in Sec. 1.6 we address a detailed double-ladder model

The metal electrodes are modeled as a Fermi sea of noninteracting electrons,

\[ \hat{H}_\nu = \sum_k \epsilon_{\nu,k} \hat{a}_{\nu,k}^\dagger \hat{a}_{\nu,k}, \quad \nu = L, R. \]  \hspace{1cm} (1.3)

\( \hat{a}_{\nu,k}^\dagger (\hat{a}_{\nu,k}) \) are fermionic creation (annihilation) operators of electrons with momentum \( k \) in the \( \nu \) lead.

Electrons can tunnel from the \( L \) (\( R \)) metal to site 1 (\( N \)),

\[ \hat{H}_T = \sum_k g_{L,k} \hat{a}_{L,k}^\dagger \hat{c}_1 + \sum_k g_{R,k} \hat{a}_{R,k}^\dagger \hat{c}_N + \text{h.c.} \]  \hspace{1cm} (1.4)

In the absence of the probes, this Hamiltonian dictates phase-coherent electron dynamics, reflected e.g.,
Figure 1.1: (a) A molecular wire with $N$ electronic sites (inter-site tunnelling $v$ and bridge height $\epsilon_B$) coupled to a thermal environment, represented by the shaded region surrounding the electronic states. The thermal bath, including molecular and external vibrational degrees of freedom, is characterized by its temperature $T$, spectral density function with a cutoff frequency $\Omega$ and electron-vibration coupling strength $\gamma_d$. (b) In this work we introduce the environment in a phenomenological manner by using the probe technique, attaching fictitious metal terminals to electronic sites. The figure illustrates voltage probes, characterized by their temperature and chemical potentials which are determined such that there is zero net charge current to each probe.

by a tunnelling behaviour [43]. We now include $N$ probes, additional metal electrodes

$$\hat{H}_P = \sum_{n=1}^{N} \sum_{k} \epsilon_{n,k} \hat{a}_{n,k}^\dagger \hat{a}_{n,k}.$$  \hspace{1cm} (1.5)

The $n$th probe can exchange particles with the $n$th site of the molecular wire,

$$\hat{V}_P = \sum_{n=1}^{N} \sum_{k} g_{n,k} \hat{a}_{n,k}^\dagger \hat{c}_n + h.c.$$  \hspace{1cm} (1.6)

Here $\hat{a}_{n,k}^\dagger$ ($\hat{a}_{n,k}$) are fermionic creation (annihilation) operators for an electron in the $n = 1, 2, ..., N$ probe with momentum $k$, $g_{n,k}$ are the tunnelling energies from the $n$th molecular site into the $n$th probe. To eliminate charge leakage processes from the molecular wire into the probes we enforce certain conditions on conduction. In Sec. 1.2.2 we describe in detail two such constraints, the “dephasing probe” and the “voltage probe”.
1.2.2 Büttiker probes

The Landauer approach provides an exact description of phase coherent quantum transport [15]. Given its simplicity, it is appealing to use it beyond the coherent limit. Indeed, as was shown in Refs. [39, 106, 40], one can implement elastic and inelastic scattering of electrons with other degrees of freedom, possibly phonons, photons, and other electrons, by introducing additional terminals (probes) into the model system. The key point here is that the parameters of these terminals, essentially their local charge distributions, should be set in a self-consistently such that there is no net (average) particle current between the physical system of interest and the probes.

The probe technique can be implemented under different self-consistent conditions, allowing us to craft electron scattering processes: purely elastic dephasing effects are implemented via the “dephasing probe”, while dissipative-inelastic effects are introduced through the “voltage probe”. Further, dissipationless inelastic scattering processes can be admitted by requiring the net average fluxes of particles and heat between the probe terminal and the system to vanish, termed as the “temperature-voltage probe”. The various probes can be implemented in the linear response bias regime, as well as far from equilibrium [111, 134, 138].

We employ $\nu$ to identify the $L$ and $R$ (physical) metal electrodes to which the molecule is connected. We count the probe terminals with the index $n$ and use $\alpha$ to identify all leads, the two metal electrodes $\nu = L, R$ and the $n = 1, 2, ..., N$ probes.

Since the model Hamiltonian does not include interactions, its charge transfer characteristics can be described with the Landauer-Büttiker formalism [15]. The total current leaving the $L$ contact is given by

$$I_L = \frac{e}{2\pi \hbar} \sum_{\alpha} \int_{-\infty}^{\infty} T_{L,\alpha}(\epsilon) [f_L(\epsilon) - f_\alpha(\epsilon)] d\epsilon. \quad (1.7)$$

This expression should be multiplied by a factor of 2 to account for the spin degree of freedom. Since magnetic effects are absent, $T_{\alpha',\alpha}(\epsilon) = T_{\alpha,\alpha'}(\epsilon)$. $f_\nu(\epsilon) = \left[e^{\beta(\epsilon - \mu_\nu)} + 1\right]^{-1}$ are the Fermi functions in the physical electrodes, given in terms of the inverse temperature $k_B T = \beta^{-1}$ and chemical potentials $\mu_\nu$.

The functions $f_n(\epsilon)$ are to be determined from the probe condition.

The electrical conductance is defined as the ratio of charge current to applied voltage, $\Delta V = (\mu_L - \mu_R)/e$,

$$G = I_L/\Delta V. \quad (1.8)$$

This definition does not necessarily assume low voltages. One often further defines a linear response electrical conductance requiring the applied bias to be the smallest energy scale in the system, $|e\Delta V| < 1/\beta, D, \gamma_\nu, e_B, v, \gamma_d$, with $\gamma_\nu$ and $\gamma_d$ defined after Eq. (1.14) and $D$ as the bandwidth of the metal leads, the largest energy scale in the problem. In our simulations we principally work under the low-bias condition, and for simplicity calculate the conductance from Eq. (1.8).

In direct analogy to Eq. (1.7), the net current between the $n$th probe and the system can be written as

$$I_n = \frac{e}{2\pi \hbar} \sum_{\alpha} \int_{-\infty}^{\infty} T_{n,\alpha}(\epsilon) [f_n(\epsilon) - f_\alpha(\epsilon)] d\epsilon. \quad (1.9)$$
The transmission functions in Eqs. (1.7) and (1.9) are obtained from the \((N \times N)\) Green’s function and the hybridization matrices [43],

\[
\mathcal{T}_{\alpha,\alpha'}(\epsilon) = \text{Tr}[\hat{\Gamma}_\alpha(\epsilon)\hat{G}^{\alpha'}(\epsilon)] = \text{Tr}[\hat{\Gamma}_\alpha(\epsilon)\hat{G}^{\alpha'}(\epsilon)\hat{G}_\alpha(\epsilon)\hat{G}^{\alpha'}(\epsilon)],
\]

where the trace is performed over the \(N\) states of the molecule. The general form of the retarded Green’s function is given as

\[
\hat{G}_\alpha(\epsilon) = \left[\hat{I}_\epsilon - \hat{H}_M + i\hat{\Gamma}/2\right]^{-1},
\]

with \(\hat{\Gamma}(\epsilon) = [\hat{\Gamma}(\epsilon)]^1\), the total hybridization matrix, \(\hat{\Gamma} = \hat{\Gamma}_L + \hat{\Gamma}_R + \sum_{j=1}^{N} \hat{\Gamma}_j\), and \(\hat{H}_M\) the Hamiltonian of the \(N\)-state molecular system. For the case of a 1-dimensional, nearest-neighbor coupled wire, the retarded Green’s function is the inverse of a tridiagonal matrix, \(\hat{A} = [\hat{A}\dagger]^{-1}\), with the matrix elements

\[
\hat{A}_{n,n}(\epsilon) = \epsilon - \epsilon_B + i\frac{\gamma_L(\epsilon)\delta_{n,1} + \gamma_R(\epsilon)\delta_{n,N} + \gamma_n(\epsilon)}{2},
\]

\[
\hat{A}_{n,n \pm 1}(\epsilon) = -v.
\]

For the model under study, the hybridization matrices have a single nonzero value as follows,

\[
[\hat{\Gamma}_n(\epsilon)]_{n,n} = \gamma_n(\epsilon),
[\hat{\Gamma}_L(\epsilon)]_{1,1} = \gamma_L(\epsilon),\quad [\hat{\Gamma}_R(\epsilon)]_{N,N} = \gamma_R(\epsilon),
\]

with energies

\[
\gamma_\alpha(\epsilon) = 2\pi \sum_k |g_{\alpha,k}|^2 \delta(\epsilon - \epsilon_{\alpha,k}).
\]

We work in the wide-band limit, unless otherwise stated, and take \(\gamma_\alpha\) as energy independent parameters. In this work unless explicitly stated to be otherwise (short section in Chapter 2), we assume that all sites in the wire are similarly affected by the probes, thus we use a single parameter to identify the probe-molecule hybridization energy, \(\gamma_d = \gamma_n\). We also define the harmonic mean \(\gamma = \frac{1}{2} \gamma_L\gamma_R/(\gamma_L + \gamma_R)\) as a measure for the molecule-metal coupling.

We now describe the dephasing probe and the voltage probe conditions. In the linear response regime the two probes act similarly on the molecule, and our results in this Chapter are essentially indifferent to the choice of probe.

**Dephasing Probe.** Incoherent - but elastic - scattering processes are implemented via the dephasing probe condition, where we demand charge and resolved energy conservation: Each probe is required not only to conserve the particle number in the junction, but furthermore, it cannot contribute nor dissipate energy to electrons, at any energy. Mathematically, this is expressed by requiring the resolved current at each probe, the integrand in Eq. (1.9), to nullify,

\[
I_n(\epsilon) = 0, \quad \forall n
\]
Explicitly, using Eq. (1.9), these $N$ conditions can be organized as

$$\hat{M}(\epsilon)\hat{f}(\epsilon) = \hat{v}(\epsilon),$$

(1.16)

with $\hat{f}(\epsilon)$ the vector of unknown probe functions $f_n(\epsilon)$,

$$\hat{v}_n(\epsilon) = T_{n,L}(\epsilon)f_L(\epsilon) + T_{n,R}(\epsilon)f_R(\epsilon),$$

(1.17)

the constant-known terms, and

$$\hat{M}(\epsilon) = \begin{bmatrix}
\sum_\alpha T_{1,\alpha}(\epsilon) & -T_{1,2}(\epsilon) & -T_{1,3}(\epsilon) & -T_{1,4}(\epsilon) & \ldots \\
-T_{2,1}(\epsilon) & \sum_\alpha T_{2,\alpha}(\epsilon) & -T_{2,3}(\epsilon) & -T_{2,4}(\epsilon) & \ldots \\
-T_{3,1}(\epsilon) & -T_{3,2}(\epsilon) & \sum_\alpha T_{3,\alpha}(\epsilon) & -T_{3,4}(\epsilon) & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots
\end{bmatrix}$$

This set of $N$ linear equations for the distributions of each probe $f_n(\epsilon)$ is solved by a matrix inversion at every energy $\epsilon$ within the band (which is taken as broad). In numerical simulations we used an energy grid with spacing $\delta\epsilon \sim 10^{-5} - 10^{-4}$ eV, smaller than the smallest relevant energy scale, and bandwidth $\sim 20$ eV, greater than the largest molecular energy scale.

At this point we should clarify the action of the dephasing probe, since the term “dephasing” carries different meanings for different communities. In the language of molecular orbitals $|M\rangle$, eigenstates of $\hat{H}_M$, dephasing probes scatter electrons between orbitals: The dephasing probe absorbs an electron from orbital $|M\rangle$ and injects it incoherently elsewhere, while conserving energy. To demonstrate this, we define the molecular eigenstates by the fermionic creation operator $\hat{d}^\dagger_m$, $\hat{H}_M = \sum_m E_m \hat{d}^\dagger_m \hat{d}_m$, then formally expand the local-site operators, $\hat{v}_n = \sum_m \lambda_{n,m} \hat{d}_m$. In the energy basis the $N$ probes are coupled to the $N$ molecular orbitals, $\hat{V}_P = \sum_{n,m} \lambda_{n,m} g_{n,k} \hat{d}^\dagger_n \hat{d}_m + h.c.$, providing a mechanism for (environmentally-mediated) transitions between molecular electronic states. The energy resolved current to the $n$th probe is given by

$$I_{n,k} = i \left\langle \sum_m \left( g_{n,k}^* \lambda_{n,m} \hat{d}^\dagger_m \hat{d}_{n,k} - g_{n,k} \lambda_{n,m} \hat{d}^\dagger_n \hat{d}_m \right) \right\rangle$$

Since under the dephasing probe we demand that $I_{n,k} = 0$, this expression reveals that the $n$th probe takes electrons of energy $\epsilon_k$ e.g. from the $m$th orbital and disperses them into the other orbitals. For example, If we consider a single probe and two molecular orbitals, $m_1$ and $m_2$, the dephasing probe condition translates to the conservation law $I_{m_1 \rightarrow \text{probe}}(\epsilon) = I_{\text{probe} \rightarrow m_2}(\epsilon)$, i.e., the net energy flow to the probe is zero, but it exchanges electrons between orbitals. This type of elastic process is different from phase-coherent elastic scattering from impurities or the boundaries, accounted for in the original Landauer formula. The dephasing probe thus opens up new incoherent-elastic channels for conduction, beyond coherent motion.

**Voltage Probe.** Local inelastic-dissipative effects can be introduced into the wire by demanding that the net total particle current flowing between each probe and the system, Eq. (1.9), vanishes,

$$I_n = 0.$$  

(1.18)

Out-of-equilibrium, these $N$ equations can be solved numerically, as was done in phononic models [119].
Analytic results for $\mu_n$ can be reached in linear response [108],

$$
\mu_n \sum_{\alpha} \int_{-\infty}^{\infty} \left( -\frac{\partial f_{eq}}{\partial \epsilon} \right) T_{n,\alpha}(\epsilon) d\epsilon - \mu_n' \sum_{n'} \int_{-\infty}^{\infty} \left( -\frac{\partial f_{eq}}{\partial \epsilon} \right) T_{n,n'}(\epsilon) d\epsilon
$$

$$
= \int_{-\infty}^{\infty} d\epsilon \left( -\frac{\partial f_{eq}}{\partial \epsilon} \right) \left[ T_{n,L}(\epsilon) \mu_L + T_{n,R}(\epsilon) \mu_R \right].
$$

We can further simplify Eq. (1.19) at low enough temperatures, $1/\beta < \gamma/v$. In this limit, the transmission function is assumed to be flat in the vicinity of the Fermi energy, in a region where the Fermi function suffers significant changes, $\frac{\partial f_{eq}}{\partial \epsilon} \sim -\delta(\epsilon - \epsilon_F)$.

At low applied bias, dephasing and voltage probes behave nearly indistinguishably. This can be justified by noting that in linear response and at low enough temperatures the voltage probe can support energy exchange processes only within a small energy interval, $\mu_n - \mu_F$, effectively stopping dissipation and leading it to perform similarly to the dephasing probe (see Fig. 1.8). This point is expounded upon in Chapter 2 of this work; for the remainder of this Chapter, we consider a low voltage bias, and thus voltage and dephasing probes should be generally interchangeable.

Below we refer to the hybridization energy $\gamma_d$ between molecular sites and the probes (voltage or dephasing type) as “dephasing strength”. As explained above, $\gamma_d/\hbar$ does not correspond to a “pure dephasing” rate. This situation is similar to that reached with the perturbative (system-bath weak coupling) Redfield equation [95]: Bath-assisted dynamics are admitted to the model by adding dephasing operators, acting locally on different sites of the wire. In the energy basis of the molecule these local bath operators give rise to bath-induced transitions between molecular orbitals [94]. As a result of the probe condition, the current leaving the $L$ contact is identical to the current reaching the $R$ terminal, $I_L = -I_R$.

### 1.2.3 Structured environment

The interaction of electrons with molecular vibrations is explicitly described by the following model

$$
\hat{H} = \hat{H}_M + \hat{H}_L + \hat{H}_R + \hat{H}_T + \hat{H}_{ph} + \hat{H}_{e-ph}.
$$

The molecular wire and the electrodes are the same as in Eqs. (1.2)-(1.4). The bosonic (phonon) environment and its coupling to electrons is given by

$$
\hat{H}_{ph} = \sum_{q,n} \omega_{q,n} \hat{b}^{\dagger}_{q,n} \hat{b}_{q,n},
$$

$$
\hat{H}_{e-ph} = \sum_{q,n} h_{q,n} (\hat{b}^\dagger_{q,n} + \hat{b}_{q,n}) \hat{c}^\dagger_n \hat{c}_n.
$$

Here $\hat{b}^{\dagger}_{q,n}$ ($\hat{b}_{q,n}$) stands for a bosonic creation (annihilation) operator responsible for exciting a mode of frequency $q$, coupled to the electron number operator $\hat{c}^\dagger_n \hat{c}_n$. The environment and its coupling energies $h_{q,n}$ provide the “spectral density” function $J_n(\omega) = \sum_q |h_{q,n}|^2 \delta(\omega - \omega_{q,n})$, possibly comprising a broad (low frequency) contribution, as well as discrete high frequency vibrational modes. It was illustrated in many studies that structured environments support involved dynamics in the subsystem; essentially, the back action of the bath on the system drives “non-Markovian” dynamics [42].

To model such effects within the LBP technique we may adopt energy-dependent probe relaxation
rates, defined in Eq. (1.14). Specifically, we use in 1.4.5 the Debye-Drude function (though we are in general not limited),

$$\gamma_d(\epsilon) = 2\tilde{\gamma}_d \frac{\Omega|\epsilon|}{\epsilon^2 + \Omega^2},$$

(1.21)

which reaches the maximum value $\tilde{\gamma}_d$ at the cutoff frequency, $\gamma_d(\epsilon = \Omega) = \tilde{\gamma}_d$. Electrons arriving at the $n$th electronic site with energy $|\epsilon| \lesssim \Omega$ are likely to exchange energy with the probes’ degrees of freedom. In contrast, electrons will not scatter to the probe terminals if $|\epsilon| \gg \Omega$, instead coherently cross the junction. This behaviour corresponds to the expected effects of electron-phonon interactions.

### 1.3 Transport Mechanisms

In this section we summarize mechanisms of electrical conductance of molecular wires in (i) the coherent limit, when $\gamma_d = 0$, see Fig. 1.2(a), and (ii) assisted by the environment with $\gamma_d \neq 0$, see Fig. 1.2(b).

#### 1.3.1 Coherent electrons: Ballistic motion and tunnelling

In the absence of the probes, $\gamma_d = 0$, the current obeys the standard Landauer expression,

$$I_L = \frac{e}{2\pi\hbar} \int_{-\infty}^{\infty} d\epsilon T_{L,R}(\epsilon)[f_L(\epsilon) - f_R(\epsilon)].$$

(1.22)

Pronounced temperature dependence of transport characteristics is typically attributed to the hopping mechanism, but the current can also strongly depend on temperature in coherent tunnelling due to the Fermi functions in this expression. We illustrate this next. We consider the contribution of a single-dominant narrow resonance,

$$T_{L,R}(\epsilon) \sim \gamma A(\epsilon_B) \delta(\epsilon - \epsilon_B).$$

(1.23)

Here $A$ as a dimensionless prefactor. We highlight its dependence on the bridge energetics, but it may further depend on other molecular parameters, inter-site tunnelling $v$, hybridization to the electrodes $\gamma_\nu$ and molecular length $N$. The prefactor $\gamma$, the harmonic average of $\gamma_L$ and $\gamma_R$, has been included here as the resonance width. Using this narrow-resonance form, Eq. (1.22) reduces to

$$I_L = \frac{e}{2\pi\hbar} \gamma A(\epsilon_B)[f_L(\epsilon_B) - f_R(\epsilon_B)]$$

$$= \frac{e}{2\pi\hbar} \gamma A(\epsilon_B)e^{\beta\epsilon_B}[e^{-\beta\mu_R} - e^{-\beta\mu_L}]f_L(\epsilon_B)f_R(\epsilon_B).$$

(1.24)

In the linear response limit, $\beta\Delta\mu < 1$, we expand the functions to the lowest non-trivial order in voltage,

$$G = G_0 \gamma A(\epsilon_B)e^{\beta\epsilon_B}$$

$$\xrightarrow{\beta\epsilon_B \gg 1} G_0 \gamma A(\epsilon_B)e^{-\beta\epsilon_B}.$$
The combination $\beta e^{-\beta \epsilon_B}$ suppresses the tunnelling conductance at both low and high temperatures, providing a temperature dependence distinctively different from standard Arrhenius behaviour. Here $G_0 = e^2/2\pi\hbar$; we left out the factor of $\times 2$ coming from the spin degree of freedom.

Going back to Eq. (1.24), we now consider a finite bias situation, $\beta \Delta\mu > 1$. In this case we maintain only the larger factor $e^{\beta \Delta\mu}$ in the numerator of Eq. (1.24), for $\Delta\mu > 0$, and again take the limit $\beta \epsilon_B \gg 1$. We now reach an Arrhenius activation form for the conductance [77],

$$ G = G_0 \gamma A(\epsilon_B) e^{-\beta(\epsilon_B - |e\Delta V|/2)}. \tag{1.26} $$

Eqs. (1.25)-(1.26) describe contribution to conductance from thermally excited electrons, populating energies in resonance with a narrow molecular orbital of energy $\epsilon_B$. These electrons cross the molecule in a ballistic manner as dephasing and inelastic terms are missing from these formulae.

Next, we broaden the resonance (1.23). This allows electrons at the Fermi energy to cross the bridge, off-resonance. We assume (i) that the applied bias is small to expand $f_\nu(\epsilon) \sim f_{eq}(\epsilon) - \frac{\partial f_{eq}}{\partial \epsilon}(\mu_\nu - \epsilon_F)$, and (ii) that the transmission function is almost flat (constant) close to the Fermi energy. We then reach the following, well-known, result

$$ I_L = \Delta\mu \frac{e}{2\pi\hbar} T_{L,R}(\epsilon_F) \int_{-\infty}^{\infty} \frac{-\partial f_{eq}(\epsilon)}{\partial \epsilon} d\epsilon $$

$$ = \Delta\mu \frac{e}{2\pi\hbar} T_{L,R}(\epsilon_F). \tag{1.27} $$

The conductance is proportional to the transmission evaluated at the Fermi energy, and it does not depend on temperature,

$$ G = G_0 T_{L,R}(\epsilon_F). \tag{1.28} $$

In the “deep tunnelling” regime when the barrier height is large, $\epsilon_B > v, \gamma_\nu$, the transmission function can be simplified into the “superexchange” expression [43]

$$ T_{L,R}(\epsilon_F) \approx \frac{\gamma_L \gamma_R v^2}{[(\epsilon_B - \epsilon_F)^2 + (\gamma_L/2)^2][(\epsilon_B - \epsilon_F)^2 + (\gamma_R/2)^2]} \left( \frac{v}{\epsilon_B - \epsilon_F} \right)^{2(N-2)} $$

$$ \frac{\epsilon_B > \gamma_\nu}{v^2} \frac{\gamma_L \gamma_R}{v^2} \left( \frac{v}{\epsilon_B - \epsilon_F} \right)^{2N} $$

$$ = \frac{\gamma_L \gamma_R}{v^2} e^{-aN} \left( \frac{\epsilon_B}{\epsilon_B - \epsilon_F} \right)^{2N}. \tag{1.29} $$

Recall that we set energies relative to the Fermi energy ($\epsilon_F = 0$). Eq. (1.29) indicates that the conductance decays exponentially with molecular size, $L \equiv aN$, with $a$ as a unit length. Identifying the tunnelling decay constant by $\kappa \equiv \frac{2}{a} \ln \left| \frac{\epsilon_B}{\epsilon_F} \right|$ (often denoted by $\beta$ in the literature, here reserved for the inverse temperature), we arrive at the familiar form

$$ G \sim G_0 e^{-\kappa L}. \tag{1.30} $$

Fig. 1.2(a) depicts the ballistic [Eqs. (1.25)-(1.26)] and tunnelling [Eq. (1.29)] contributions to the current.
1.3.2 Bath-assisted transport

Calculations based on perturbative master equations suggest that long-range electrical conduction may be captured by a rational function [95], corresponding to experimental observations of long-range ohmic-like conduction in molecular wires [61, 62, 63, 65, 66, 67, 70, 71, 1, 72, 73]. In Sec. 1.4 we present detailed simulations using the LBP technique, and based on observations, we construct the following form for the hopping (H) conduction,

$$G_H \sim G_0 A(T) \frac{v^2}{\epsilon_B^2} \frac{\gamma_d^2}{N + l}.$$  (1.31)

It is valid when the bridge is high $\epsilon_B \gg v, \gamma_d, \Delta \mu$, as well as $\epsilon_B > \gamma$, and in the range $15 < \beta \epsilon_B < 30$. This corresponds to the “deep tunnelling” regime, with $\epsilon_B = 0.5$ eV and temperatures in the range ±150 K around room temperature. As before, $N$ stands for the number of repeating units in the wire, $\gamma_d$ is the dephasing strength, $v$ the inter-site tunnelling, $\epsilon_B$ the bridge energy relative to the Fermi energy, $A(T)$ a dimensionless prefactor which depends on temperature, possibly in a form weaker than the “bare” Arrhenius factor, e.g., $A(T) \sim \beta e^{-\beta E_A}$, with an activation energy $E_A$, linearly proportional to $\epsilon_B$. The parameter $l$ is introduced to accommodate the tunnelling-to-hopping transition point, see for example Fig. 1.3.

Similarly to environmentally assisted DBA-ET rates, Eq. (1.31) describes an ohmic conduction, it depends on $v^2$, and as expected, grows with $\gamma_d$. However, an exact correspondence to ET rates is missing [93, 94, 96, 97, 124, 125, 98, 99]. While these two quantities, DBA-ET rate and the electrical conductance (examined here) are obviously related, their properties are fundamentally different in some ways: DNA-ET processes involve electron localisation on the donor and acceptor sites whereas in a molecular wire setup electrons are transferred through the bridge between metal electrodes. Thus,
the hybridization energy of the bridge to the metals and the thermal occupation factor of electrons in the bulk largely determine the electrical conductance. Furthermore, in DBA situations the Franck-Condon factor, taking into account the energy difference between donor and acceptor states and the solvent-induced reorganization energy, dictates the transmission rate, while it is missing from molecular electronic conduction [126, 127]. Theoretical studies have predicted a linear relationship between DBA-ET rates and the conductance (for molecules with high barriers), but experiments indicate that these two quantities are not simply linearly correlated [140], possibly due to differences in bath-induced decoherence rates and bridge energetics [123].

Fig. 1.2(b) schematically depicts the probe-assisted hopping conduction, Eq. (1.31). While in DBA-ET situations electrons can populate the bridge only if thermally excited, in the junction setup the molecular orbitals are broadened due to their hybridization to the metals [Lorentzian lineshapes in Fig 1.2(b)], and this broadening allows electron to occupy molecular states without thermal activation.

We further argue that at low temperatures, equation (1.31) should be generalized to

$$G_D = G_0 \sum_{m=2,3}^{N} \left( \frac{v_{m-1}}{\epsilon_B} \right)^2 \tilde{F}_m(\gamma_L, \gamma_R, \gamma_d, T).$$  

(1.32)

interpolating between the coherent result (1.29) using $\tilde{F}_N = \gamma_L \gamma_R$ and $F_{m<N} = 0$ and the hopping limit (1.31) when $F_2 \sim A(T)\gamma_d^2/(N+l) \gg F_{m>2}$.

1.4 Results: Tunnelling to Hopping Conduction

We describe here the LBP numerical simulations of molecular electronic conduction (mostly under the dephasing probe), with the goal to construct an approximate closed-form expression for the hopping conduction, as reported in Eq. (1.31). We focus on a uniform-symmetric system, $\epsilon_B = \epsilon_n = 0.5 - 1$ eV, $v_{n,n+1} = v = 0.05 - 0.3$ eV and $\gamma_L = \gamma_R = 0.2 - 1$ eV. The temperature of the $L$ and $R$ leads, as well as the probes, is taken within the range $T = 150 - 400$ K, fixed across the junction. In this section we restrict simulations to the low voltage regime, $\Delta \mu = 10^{-4} - 0.01$ eV. The voltage shifts the position of the Fermi energy at the contacts, $\mu_L = \mu_F + e\Delta V/2$, $\mu_R = \mu_F - e\Delta V/2$, but given the small bias, bridge energies are left alone. The dephasing strength $\gamma_d$ (probe hybridization) is taken uniform along the chain. We provide it in units of eV; when divided by $\hbar$ it translates to a rate constant.

The net current flowing under an applied bias $\Delta \mu$ is calculated in three steps: (i) We construct the matrices $\tilde{G}$ and $\tilde{\Gamma}_\alpha$, then the transmission coefficient between every two terminals $T_{\alpha,\alpha'}(\epsilon)$ from Eq. (1.10). (ii) We include environmental effects e.g. with dephasing probes. This is achieved by calculating (numerically) the functions $f_\alpha(\epsilon)$ using the probe condition Eq. (1.15). (iii) We evaluate the net-total current from the $L$ electrode via Eq. (1.7). As mentioned above, the probe conditions ensure that the current leaving the $L$ metal is identical to the current arriving at the right electrode, $I \equiv I_L = -I_R$. For dephasing probe, moreover, $I(\epsilon) = I_L(\epsilon) = -I_R(\epsilon)$.

1.4.1 Length dependence

The behaviour of the conductance with increasing molecular length is displayed in Fig. 1.3 under a range of dephasing energies, $\gamma_d = 0 - 100$ meV. In the absence of dephasing the conductance decays exponentially with molecular length for $N \sim 1 - 5$, in agreement with Eq. (1.29), but beyond that it
Figure 1.3: Electrical conductance as a function of molecular length \( N \) at \( T = 300 \) K using different dephasing strengths, \( \gamma_d = 0, 1, 10 \) and \( 100 \) meV, as indicated in the figure caption, (dephasing probe condition). (a) A semi-logarithmic plot demonstrates that \( G \) decays exponentially with length in short chains at weak dephasing. (b)-(e) An inverse algebraic behaviour (1.31), \( G^{-1} \propto N \), is established for long chains at large enough dephasing. Dominating transport mechanisms are marked in panel (a).

is fixed (and small), independent of size. This residual component emerges due to incoming electrons of energy \( \epsilon_B \) (occupying the tail of the Fermi function), which are crossing the junction ballistically. In contrast, at finite dephasing strengths and beyond \( N \sim 5 \) the tunnelling behaviour is overpowered by a hopping-ohmic contribution \( G^{-1} \propto N \). Fig. 1.3 establishes two central results for hopping conduction: at finite dephasing strength long-range electron transfer follows an ohmic form, and that \( G \propto \gamma_d^2 \) in this region.

1.4.2 Thermal activation

The onset of an Arrhenius behaviour at high enough temperatures is considered a central characteristic of hopping dynamics in donor-bridge-acceptor electron transfer processes. However, Eq. (1.26) reveals that in metal-molecule-metal geometries a thermally activated conduction can take place even in the coherent regime, supporting ballistic-resonant behaviour. In fact, electrons which are thermally activated in the metal are more likely to cross the junction ballistically rather than in an ohmic fashion.
Figure 1.4: Temperature dependence of the electrical conductance for (a) \( N = 4 \) site wire and (b) \( N = 10 \) site wire, demonstrating tunnelling behaviour at low temperatures, ballistic-resonant activated conduction at high temperatures, and hopping behaviour when \( \gamma_d \neq 0 \), at low-intermediate temperatures. Parameters are \( \epsilon_B = 0.5 \), \( v = 0.05 \), and \( \gamma_L = \gamma_R = 0.2 \), \( \Delta \mu = 0.001 \) eV, dephasing probe condition.

Figure 1.5: Activation energy \( E_A \), as resolved from Arrhenius plots as in Fig. 1.4, plotted against the bridge energy \( \epsilon_B \), demonstrating a linear relationship. Parameters are indicated in Fig. 1.4.

Figure 1.4 displays this behaviour. First, focus on the case of \( \gamma_d = 0 \) (red line). At very low temperatures the conductance does not depend on temperature at all (tunnelling contribution). At high temperatures, an Arrhenius behaviour is observed, with an activation energy \( E_A \), indicating ballistic conduction at zero dephasing. Fig. 1.5 demonstrates that the activation energy \( E_A \), the slope in the Arrhenius regime, \( \log G \propto -\beta \), linearly follows the bridge height \( \epsilon_B \).

At finite dephasing strength the situation is rather involved. Let us first focus on the low temperature regime of Fig. 1.4. While the temperature dependence is rather weak, it is clear that \( G \) is increasing as \( G \propto \gamma_d^2 \). This indicates on an activation-less dephasing assisted conductance, see Eq. (1.31). At high temperatures and for long wires (see for example \( N = 10, T^{-1} = 0.03 \) K\(^{-1}\)) the conductance shows an activated form, but it does not depend on \( \gamma_d \), for \( \gamma_d = 1 - 10 \) meV. This again points to a ballistic motion; the dominant role of temperature is to enhance the population of electrons in resonance with the bridge, with the ballistic component dominating hopping contribution. Thermally-activated hopping
conduction (1.31) further shows up, but only when the dephasing strength is high and the bridge is short, see \( N = 4, \ T^{-1} = 0.02 \ \text{K}^{-1} \) and \( \gamma_d = 100 \ \text{meV} \).

To summarize, unlike DBA-ET rates, activated conductance in junctions does not expose transport mechanisms: At low temperatures, a seemingly activation-less conductance may reflect either deep-tunnelling or dephasing-assisted conduction of deep electrons. Similarly, activated transport at high temperatures may correspond to both ballistic and ohmic components.

### 1.4.3 Environmental interaction strength

![Figure 1.6: Kramers-like behaviour of the electrical conductance with dephasing strength (dephasing probe). Parameters are indicated within the figure.](image)

The role of dephasing strength \( \gamma_d \) on the conductance is explored in Fig. 1.6, and we observe a characteristic “Kramers-like” turnover behaviour \[141\]. At low dephasing the conductance increases with \( \gamma_d \) as it opens up a new route for electrons to cross the bridge, by hopping between sites. At large dephasing strengths \( \gamma_d/\epsilon_B \gtrsim 2 \) the conductance drops approximately as \( \gamma_d^{-1} \). In a classical language one attributes this decay to the impediment of electrons at strong friction, resulting in an overdamped dynamics. This Kramers-like turnover behaviour was demonstrated in other studies of electron transfer \[93, 94, 98, 99\]. Investigations based on Redfield \[94\] and Lindblad equations \[99\] even provided a very similar value for the turnover point. Related trends were also observed in recent explorations of environmental-assisted quantum energy transport in light-harvesting biomolecules \[142\].

Note that in the Kramers’ theory the barrier crossing rate first increases linearly with friction strength, then decreases as the inverse of friction. Here, we observe a more intricate behaviour: The LBP conductance increases linearly with dephasing in short chains, \( G \propto \gamma_d \), but in long chains the enhancement follows \( G \propto \gamma_d^2 \), in the weak-dephasing regime.

The quadratic dependence \( G \propto \gamma_d^2 \) is a direct result of the phenomenological-probe modelling of bath-assisted electron scatterings. Unlike a genuine electron-phonon scattering process, in which an electron is scattered \textit{between} different electronic states assisted by a phonon, the probes \textit{absorb} an
electron and emit it (possibly) at a different molecular state, to be re-absorbed by another probe. This probe-molecule-probe transfer process of electrons results in the $\gamma_d^2$ functional form, in analogy with the $\gamma_L \times \gamma_R$ term in Eq. (1.29). In short chains, the $L$ and $R$ metals-to-probes scattering is significant, more than multiple probe-molecule-probe electron scatterings, to construct the prefactor $\gamma \cdot \gamma_d$. While the quadratic dependence is not necessarily physical, it is yet encouraging to find that the Kramers-like turnover is well reproduced here, in a seemingly correct value.

1.4.4 Junction energetics

To further expose the dependence of the hopping conductance on the junction’s energy parameters, we study the behaviour of $G$ with $\epsilon_B$ (set relative to the Fermi energy), inter-site tunnelling $v$, and the hybridization energy $\gamma_{L,R}$. As before, we restrict parameters to the regime $\epsilon_B > v, \gamma_{L,R}$.

![Figure 1.7: Conductance as a function of the bridge energy $\epsilon_B$. $v = 0.05$, $\gamma_{L,R} = 0.2$, $\gamma_d = 10^{-3}$ (dephasing probe) and $\Delta \mu = 0.01$ eV.](image)

In Fig. 1.7 we display the conductance as a function of $\epsilon_B$ for $N = 8$ and $N = 12$ under nonzero dephasing and reveal a crossover from $G \sim e^{-\beta \epsilon_B}$ to $G \sim \frac{1}{\epsilon_B}$, corresponding to the transition between a ballistic behaviour (no length dependence) dominating at small $\epsilon_B$, to off-resonance dephasing-induced hopping conduction.

We now analyse more carefully the dependence of the conductance on temperature and bridge energy. We recall that two limiting mechanisms prevail in the absence of dephasing effects: deep tunnelling conduction and ballistic transmission. Ballistic motion dominates in long wires, and it carries the factor $\exp(-\beta \epsilon_B)$, see Eqs. (1.25)-(1.26), reflecting the thermal occupation of electrons in the metal at the bridge energy $\epsilon_B$. Since it is non-dissipative, the ballistic component does not decay with distance, see Fig. 1.3. Dephasing-assisted conductance has a non-trivial temperature dependence due to the contribution of many electrons in the metal. In Fig. 1.8(a) we find that at low temperatures the conductance is missing an Arrhenius activation factor, $G(\epsilon_B = 0.4)/G(\epsilon_B = 0.8) \sim \left(\frac{0.8}{0.4}\right)^4 = 16$, while a different behaviour takes place at high temperatures $T = 350$ K, as demonstrated in panel (b). Here, in
Figure 1.8: Analysis of bath-assisted conduction, $\gamma_d = 1$ meV. (a) At low temperatures $T = 150$ K and for high bridges an activation-less transport takes place. (b) At high temperatures $T = 350$ K the conductance is enhanced by a thermal factor. Panels (a1)-(a4) and (b1)-(b4) expose the ohmic-like behaviour in long wires, $v = 0.05$, $\gamma_{L,R} = 0.2$, $\Delta \mu = 0.01$ eV, dephasing probe condition (full symbols), voltage probe (empty symbols).

conjunction with an ohmic-like decay, (focus on the red and black lines) $G(\epsilon_B = 0.4)/G(\epsilon_B = 0.8) \sim 10^5$, reflecting an activated-thermally enhanced conductance. We confirm in panels (b1)-(b3) that an ohmic-like behaviour develops with $1/G \propto N$.

We also compare in Fig. 1.8 the operation of the dephasing and voltage probes. We find that at this low bias limit ($\Delta \mu = 10$ meV) transport characteristics are almost identical under either probes: the tunnelling-to-hopping crossover takes place at a similar molecular bridge size, and the values for the conductances are close. The two probes show some deviations only when the bridge height is taken relatively low $\epsilon_B = 0.2$ eV, with the dephasing probe yielding lower values for conductance (larger resistance per site) in the hopping regime.

1.4.5 Structured environment results

We implement a structured environment by using energy-dependent dephasing energies with the Debye-Drude form, Eq. (1.21), see Fig. 1.9. As expected, we find that the conductance in the hopping regime is reduced due to the non-Markovianity of the bath, while the tunnelling and ballistic regimes are unaffected. The effect is clearly observed at low temperatures, but it is significantly mitigated at higher temperatures, when the dominant mechanism is ballistic conduction.
Chapter 1. The Landauer-Büttiker Probe Technique: Behaviour and Applications

Figure 1.9: Electrical conductance as a function of length using structured (Debye-Drude form, Eq. 1.21) and unstructured ($\gamma_d$ is a constant) environments at high and low temperatures. At low temperatures the conductance is sensitive to the cutoff frequency $\Omega = 0.1$ eV. We used $v = 0.05$, $\epsilon_B = 0.5$, $\gamma_{L,R} = 0.2$, $\Delta\mu = 0.01$ eV and $\gamma_d = 1, 10$ meV as indicated, dephasing probe condition. For unstructured environments we used $\gamma_d = 1, 10$ meV; independent of energy.

1.5 Comparison to Experiments: ONI wires

In this Section we examine experimental results using the LBP method, to demonstrate the utility of the technique. Ref. [1] reported the resistance and current-voltage characteristics of conjugated oligonaphthalenefluoreneimine (ONI) molecular wires of different lengths, up to 10 nm with 10 repeating units, measured using conducting-probe atomic force (CP-AFM) microscopy. Based on the length-dependent and temperature-dependent resistance behaviour, it was argued that short wires conduct via a coherent-tunnelling transport mechanism, while around 4 nm a transition in transport behaviour, from tunnelling to thermally-activated hopping, took place. Below, we use the data reported in Ref. [1] and extract relevant parameters for our model. We then demonstrate in Figs. 1.10-1.11 that by tweaking the dephasing rate and the temperature we can reasonably reproduce experimental results of transport in ONI wires, further providing some insights.

It should be emphasized that values for resistance reported in Ref. [1] correspond to a monolayer with $M \sim 100$; $M$ is an estimate for the number of molecules under the measuring tip [1]. If we assume a linear scaling of the conductance, $G(M) \sim MG(1)$, the resistance should obey $R(M) \sim M^{-1}R(1)$. Certainly, this is an approximation which is not always justified; the conductance of a single-isolated wire $G(1)$ may significantly deviate from the monolayer conductance scaled-down, $G(M)/M$, due to cooperative effects, inter-wire couplings and substrate-mediated coupling. These effects may increase or decrease the conductance per wire [143, 144, 145, 146, 147]. A careful study of such effects with the LBP method is of interest. Here instead we use a naive-linear scaling approximation: We take resistance values reported in Figs. 6 and 8 of Ref. [1] and multiply them by $M = 100$; see the symbols (+) in Figs. 1.10 and 1.11. Below we explain which parameters in our modelling are affected by this simplified
Figure 1.10: Analysis of experimental results. We extracted data for the resistance of an ONI monolayer with \( M \sim 100 \) from Fig. 6 of Ref. [1], and multiplied it by \( M = 100 \) to approximate resistance per molecule. Top: a single ONI wire. (a)-(b) Experimental data (+) [1] as a function of molecular length, compared to probe-method simulations with \( \gamma_d = 0, 0.2, 0.5 \) meV, top to bottom (dotted lines with empty squares) assuming (a1)-(a2) \( T = 300 \) K and (b1)-(b2) \( T = 280 \) K. Panels (a1)-(b1) illustrate the tunnelling region for \( N = 1 - 4 \), panels (a2)-(b2) uncover the ohmic behaviour for \( N > 5 \). Dephasing-probe simulations were performed with \( \epsilon_B = 0.8 \) eV, \( v = 0.22 \) eV, \( \gamma_{L,R}=0.018 \) eV, applied voltage \( \Delta \mu = 0.01 \) eV and dephasing strengths in the range \( \gamma_d = 0 - 1 \) meV.

To uncover model parameters from Ref. [1], \( \epsilon_B, v, \gamma_{L,R}, \) and \( \gamma_d \), we first determine the unit length of the ONI wires to be \( a \sim 1 \) nm. We then obtain our parameters by following three steps:

(a) Bridge energetics. In the tunnelling regime \( N = 1 - 3, G \sim e^{-\kappa Na}, \) with \( \kappa = 2.5 \) nm\(^{-1} \) [1]. Using the relation \( \kappa \equiv \frac{2}{a} \ln \left| \frac{eB}{v} \right| \) [see Eq. (1.29)], we resolve the ratio \( \epsilon_B/v = 3.4 \). To obtain the bridge height \( \epsilon_B \) and inter-site energies, separately, we note that the activation energy in ONI wires was approximated by \( E_A \sim 0.55 \) eV from an Arrhenius plot [1]. Furthermore, in Fig. 1.4 we found that while the activation energy linearly follows the bridge height, the slope deviates from unity, \( \epsilon_B \sim 1.4E_A \) for \( \gamma_d \sim 5 \) meV. We thus select the value \( \epsilon_B = 0.8 \) eV, and immediately receive \( v = 0.22 \) eV. Note that these estimates are not affected by the scaling employed. Note also that the ballistic conductance is very sensitive to temperature near room temperature, and therefore is also very sensitive to the bridge height/activation energy. Even when using our “corrected” \( \epsilon_B = 0.8 \) value for bridge energy, we still observe excess ballistic conductance near room temperature, and can thus only match experimental results at a lower, “effective
Figure 1.11: Analysis of experimental results for the temperature dependence of conductance in ONI wires. Experimental data (+) [1] for $N = 7$ is compared to simulations with $\gamma_d = 0, 0.2, 0.4$ meV (empty squares, top to bottom). For reference, we also show the $N = 3$ case (o) in which the resistance is independent of dephasing in the range $\gamma_d \sim 0 - 5$ meV (consistent with the experiment). Other parameters are the same as in Fig. 1.10.

We try to reproduce this data using the parameters resolved in the discussion above, but find out that while at room temperatures and above, the experimental data is reasonably captured by our simulations with $\gamma_d \sim 3 - 4$ meV, at lower temperatures the experiment is reproduced with $\gamma_d = 0$ meV. A possible explanation for this behaviour is that the dephasing rate in fact depends on temperature, $\gamma_d(T)$, and its value should be taken small $\gamma_d \ll 1$ meV at low temperatures, $T = 240$ K, while at room temperature it reaches values identified above.
Our analysis is based on the linear scaling assumption. It was demonstrated in Ref. [143] that this holds only beyond a certain molecular-island size of a few tens of molecules. Scaling the experimental results of Ref. [1] by $M \neq 100$ would alter our estimate for $\gamma_\nu$ and $\gamma_d$: recall that $G \propto \gamma_L \gamma_R$ in the tunnelling regime and $G \propto \gamma_d^2$ in the hopping limit, see Sec. 1.4. As a limiting case, if reported values in Ref. [1] were to correspond to a single molecule rather than to $M \sim 100$ molecules, our simulations would fit the data with the same values for the bridge energetics, $\epsilon_B = 0.8$ eV, $v = 0.22$, but with (factor of 10 larger) $\gamma_L = \gamma_R = 0.18$ eV and $\gamma_d \sim 2$ meV. These values should serve as an upper estimate for dephasing strength.

Concluding our observations, the probe technique under weak dephasing as a tweaking parameter can capture the turnover behaviour between superexchange and hopping regimes in molecular wires, given the correct system parameters as inputs. We also see from Fig. 1.10(a2), as well as in Fig. 1.11, that in order to match the experiment across all temperatures and lengths, the tuning parameter $\gamma_d$ must depend on temperature, and that one should take into account corrections to the bridge height as it relates to the activation energy.

1.6 Mixed Coherent/Incoherent Transport in ds-DNA

Coherent tunnelling and multi-step hopping transport mechanisms have been extensively examined in conjugated molecular wires, see e.g. Refs. [70, 1], and in biological molecules [148, 149, 150, 63]. For example, in single DNA molecules, these mechanisms were revealed by studying a variety of sequences [151, 152, 62, 153, 154, 155]. In $(GC)_n$ sequences, site-to-site hopping is the dominant transport mechanism, where each purine base serves as a hopping site for holes [153, 154]. In contrast, GC-rich sequences with mediating $(A:T)_m$ blocks support superexchange with the conductance decreasing exponentially with $m$, and the AT block acting as a tunnelling barrier. Here, A, G, C and T are the adenine, guanine, cytosine and thymine bases, respectively.

Motivated by the challenge to uncover the role of quantum coherent effects in biological activity [13], charge transfer via intermediate tunnelling-hopping conduction has recently received theoretical and experimental attention [156]. Particularly, in DNA molecules, an intermediate coherent-incoherent (ICI) situation is expected to be promoted if partial delocalisation of charges beyond a single G base could be managed. Indeed, recent measurements of charge transport in double-stranded DNA molecules suspended between electrodes have revealed an interesting ICI transport regime [2, 157]: In an alternating $(GC)_n$ sequence the resistance increased linearly with length, consistent with the picture of incoherent charge hopping between the G sites. In contrast, sequences of two segments of G bases, $G_nC_n$, showed linear enhancement with $n$ dressed by periodic oscillation, suggesting that charges were partially delocalised within stacked GC segments [2].

Prior theoretical work on charge transport characteristics in DNA has been done using rate equations [148, 158, 63] and the Landauer approach [159]. Researchers have attempted to capture more complex solvent, backbone and counterion effects using phenomenological approaches, [160, 161, 162], QM/MM methods [163, 164, 165, 166, 167], stochastic Schrödinger equations [168], Green’s function approaches [169], quantum rate equations [170], and semiclassical approximations [171]. We use the Landauer-Buttiker probe technique explained above, which captures coherent effects and incorporates phenomenologically the effect on a solvent/phonon environment, at minimal computational cost.

It should be mentioned that transport calculations on double-stranded DNA including phenomenologically-
introduced decoherence effects via the LBP framework were previously reported in Ref. [162]. Our
calculations below similarly employ the LBP technique, yet unlike Ref. [162], we do not rely on the
D’Amato-Pastawski effective transmission formula [40], which is limited to the low temperature off-
resonance regime. This generalization (or more accurately, use of the original LBP equations), allows us
to analyse metal-molecule-metal structures with the Fermi energy positioned in resonance (within \( k_B T \))
with molecular electronic states.

1.6.1 Molecular system: Stacked and alternating GC-DNA

Following Ref. [2], we focus on two representative DNA sequences: alternating-G sequences 5’-A(CG)\(_n\)T-3’,
denoted by ‘A’, and stacked-G sequences, 5’-AC\(_n\)G\(_n\)T-3’, identified by ‘S’, with \( n = 2 − 9 \). The
DNA molecules are double-stranded and self-complementary, so as the complementary sequences of
the alternating (stacked) G sequences similarly includes alternating (stacked) G strands.

![Diagram of stacked and alternating DNA sequences](image.png)

Figure 1.12: Example of stacked and alternating DNA sequences investigated in this work. (a)-(b) and
(c)-(d) are the ladder and simplified 1D models for alternating and stacked sequences, respectively. See
Appendix B for site energies and tunnelling matrix elements.

Since each purine base serves as a hopping site for a hole, the alternating system is expected to support
a localised hopping conduction. In contrast, conduction in stacked sequences may rely on partial hole
delocalisation. Figure 1.12 exemplifies the A and S structures for \( n = 3 \). We present in (a) and (c) the
ds-DNA models used in this section, detailed parameters are given in Appendix B. In (b) and (d) we show simplified 1D models that retain the essential features, namely either consistent site-site coupling for the alternating sequence and a weaker coupling separating in the center for the stacked sequence.

We model A and S sequences by a tight-binding ladder-model Hamiltonian, see e.g. Ref. [169, 172, 173, 174, 160]. The ladder Hamiltonian describes the topology of a ds-DNA molecule which is \( n \) base-pairs long, with each site representing a particular base. We assume that charge transport takes place along the base-pair stacking, ignoring the backbone.

\[
\hat{H}_M = \sum_{j=1}^{n} \sum_{s=1,2} \epsilon_{j,s} \hat{c}^\dagger_{j,s} \hat{c}_{j,s} + \sum_{s\neq s' = 1,2} t_{j,ss'} \hat{c}^\dagger_{j,s} \hat{c}_{j,s'} + \sum_{s,s'=1,2} t_{j,j+1,ss'} (\hat{c}^\dagger_{j,s} \hat{c}_{j+1,s'} + h.c.).
\]  

The index \( s = 1, 2 \) identifies the strand. \( \hat{c}^\dagger_{j,s} \) creates a hole on strand \( s \) at the \( j \)th site with the on-site energy \( \epsilon_{j,s} \). \( t_{j,ss'} \) and \( t_{j,j+1,ss'} \) are the electronic matrix elements between nearest neighbouring bases. This model mimics the topology of the ds-DNA molecule; helical effects are effectively included in the renormalized electronic parameters.

We use the parametrization of Ref. [175], which is calculated at the DFT level, and distinguishes between backbone orientations (5’ and 3’). In this parametrization, on-site energies vary depending on the identity of neighbouring sites. Following Ref. [160], we simplify this description and assign a single value (averaged) for on-site energies for each base, see Table I. The electronic matrix elements were taken directly from Ref. [175], tables are included in Appendix B.

| \( \epsilon_G \) | \( \epsilon_A \) | \( \epsilon_C \) | \( \epsilon_T \) | \( t_{G||C} \) | \( t_{A||T} \) |
|----------------|-----------|-----------|-----------|--------------|--------------|
| 8.178          | 8.631     | 9.722     | 9.464     | -0.055       | -0.047       |

Given the molecular Hamiltonian, we calculate transport characteristics of the metal-molecule-metal junction using the LBP method as described in Sec. 1.2.1. We connect the DNA molecule to metal leads as sketched in Fig. 1.12, and take into account environmental effects (structural motion, solvent, counterions) by attaching local probes to each site. Following experiments [2, 168], our simulations explicitly include the A:T base pairs at the two ends. Therefore, in e.g. 5'-A(CG)\(_n\)T-3' junctions, we have \( N = 4n + 4 \) molecular electronic sites within the tight-binding ladder model.

Beyond the molecular electronic structure of the ds-DNA, three additional parameters should be provided as inputs to the LBP equations: The position of the Fermi energy \( \epsilon_F \) relative to the molecular states, the strength of metal-molecule hybridization \( \gamma_{L,R} \), and an appropriate value for \( \gamma_d \). In principle, we could use a range of values for \( \gamma_d \), to capture the susceptibility of different bases and sites along the DNA molecule to environmental interactions. Here, for simplicity, we use a single value for \( \gamma_d \), identical for all bases and sites. While one could carefully optimize these three parameters, \( \epsilon_F \), \( \gamma_{L,R} \) and \( \gamma_d \), to reproduce experimental results [2, 168], our goal here is to develop a general understanding of transport characteristics as supported by the two sequences. Thus, we select reasonable values and study the transport behaviour with several representative examples. We do not attempt careful fitting to experimental results.
1.6.2 ds-DNA results

Figure 1.13: Ladder model. Resistance of (a) alternating (GC)$_n$ and (b) stacked G$_n$C$_n$ sequences, see Fig. 1.12 for the ladder model. Panel (c) overlays A and S simulations along with experimental results from Ref. [2]. Simulations were performed at room temperature, with $\gamma_d = 0.01$, 0.03 and 0.05 eV, $\gamma_{L,R} = 0.05$ eV.

Figure 1.14: Ladder model. Resistance of (a) alternating (GC)$_n$ and (b) stacked G$_n$C$_n$ sequences, panel (c) overlays A and S results. Parameters are the same as in Fig. 1.13, but we take $\gamma_{L,R} = 1$ eV.

Figure 1.13 displays LBP calculations for the A and S sequences as depicted in Fig. 1.12. We set $\epsilon_F = \epsilon_G$, and use $\gamma_{L,R} = 0.05$ eV and $\gamma_d=0.0-0.05$ eV. These parameters excellently reproduce transport characteristics in the alternating sequence: We recover experimental values [2] for the overall resistance, as well as the resistance per site (slope), see panel (a), receiving $\sim 0.5$ MOhm per unit length for $\gamma_d = 0.03$ eV. Based on the linear increase of resistance with $n$, we argue that in alternating sequences charge transport proceed via a site-to-site hopping conduction. Note that $\gamma_d$ in the range 5-50 meV is comparable to electronic matrix elements in DNA structures, see Appendix B. Also, we confirmed that we can reproduce qualitatively the tunnelling-to-hopping crossover in conductance when implanting an (AT)$_m$ block within a GC rich sequence, as observed in Refs. [153, 154], see Ref. [137].

Our simulations of stacked sequences in Fig. 1.13 only qualitatively agree with measurements [2]: We observe an even-odd trend in resistance, yet note on a very small slope with respect to length. This result should be contrasted by experiments demonstrating that S and A sequences support similar resistances per site [2]. We argue that in alternating sequences hopping contribution dominates, while in S sequences the ballistic contribution initially controls charge transfer. In-line with our expectations, stacked structures support coherent-delocalised conduction, turning into ohmic behaviour for long enough
Figure 1.15: Energy spectrum for alternating (a1)-(a2) and stacked (s1)-(s2) ladder models, with $N = 4n + 4$ electronic states. Panels (a2) and (s2) zoom over the low-energy range. The dashed line marks the Fermi energy, and we set $\epsilon_F = \epsilon_G = 0$.

We display in Fig. 1.15 the electronic eigenenergies of A and S sequences with $n = 3 - 7$ units. Recall that we place the Fermi energy at $\epsilon_F = \epsilon_G = 0$, and the energies of the other three bases are set relative to this value. We find that both A and S sequences support four bands, deriving from the different bases. When we zoom-in on the energy levels close to the Fermi energy (lower panels) we find that in A sequences the G band separates into two sub-bands, with the Fermi energy placed within the gap (order of $k_BT$). To contrast, in S sequences, the G band (panel s2) does not develop a significant gap. Furthermore, in stacked structures with $n = 3, 5, 7, ...$ the Fermi energy touches a molecular resonance, while for $n = 4, 6, ...$ the Fermi energy is slightly offset from the Fermi energy. The energy level structure immediately suggests that in A sequences ohmic-hopping conduction should dominate: charges are injected into the first G site from the metal across a nonzero energy barrier, and hopping between G sites is thermally activated according to the low barrier ($< 0.1$ eV) between G states [94]. In contrast, the S system supports a metallic-like structure for the G band. Charge injected from the metal is immediately delocalised over the system, and transport through the molecule is partially ballistic given the metallic band structure, missing gaps.

We repeated the simulations of Fig. 1.13 while employing parametrization from Ref. [176] (not shown). In this set, electronic coupling between bases were generated from QM/MD simulations, by averaging couplings over the MD trajectory. We found that these parameters [176] generated similar results as in Fig. 1.13, with the even-odd contrast in stacked sequences moderately amplified.

In Fig. 1.14 we perform simulations with strong metal-molecule hybridization, $\gamma_{L,R} = 1$ eV. In comparison to Fig. 1.13 we find that the resistance of A sequences is almost independent of the contact energy, in support of the hopping model. In contrast, the resistance of the S sequence is significantly reduced at stronger hybridization. Also, the even-odd effect almost disappears. This is because the ballistic resistance (which is responsible for the even-odd effect) is very small at large $\gamma$, and the overall resistance is dominated by the hopping contribution, which is linear with $n$. 
The observed deviations from experiment could result from several simplifying assumptions: (i) We assumed that the electronic structures of the two families, A and S, are identical and static. However, studies show that these sequences may organize differently: with ‘structure A’ and ‘structure B’ for stacked and alternating sequences, respectively [177, 178]. A more accurate estimate of the resistance properties may then be retrieved by first generating electronic parameters specific to each sequence. Also, one should modify $\gamma_d$ between A and S sequences, to capture the specific characteristics (i.e. flexibility) of each structure. (ii) We assumed that environmental effects are uncorrelated and act identically on all bases. This assumption could be addressed by extracting $\gamma^k_d$, for each base $k$, from quantum mechanics/molecular mechanics simulations, to characterize electronic (spatial and temporal) fluctuations by simple analytic correlation functions [168].

In our simulations of double-stranded DNA using a ladder Hamiltonian, we assigned the parameters $\gamma_d$, $\gamma_{L,R}$ and $\epsilon_F$ so as to generate robust and physically meaningful results. The Fermi energy $\epsilon_F$ was taken to be near the site energy of G bases, which are believed to constitute the primary charge transfer pathway for both hopping and ballistic current. $\gamma_d$ and $\gamma_{L,R}$ were taken within the range of values comparable to molecular parameters. $\gamma_d$ in particular is of the same order as the G-G electronic coupling for stacked sequences (see Appendix B), which allows incoherent hopping and coherent even-odd effects to co-mingle, providing insight into ICI behaviour. Our results were also quite robust to fluctuations of $\gamma_{L,R}$ within reasonable limits.

The steady-state electronic density matrix of the molecule contains information on the stationary population (diagonal elements) and surviving coherences between sites (off-diagonal terms). The density matrix can be readily calculated within the LBP method [179]

$$\rho_{j,k} = \frac{1}{2\pi} \sum \int_{-\infty}^{\infty} de \tilde{G}_r^{\alpha}(\epsilon) \tilde{\Gamma}_\alpha \tilde{G}^{\alpha}(\epsilon)|_{j,k} f_\alpha(\epsilon),$$

(1.34)

with the probe distribution functions as received from the probe condition.

Figure 1.16: Density matrix map of the ladder model for (a) alternating and (b) stacked sequences. Parameters are $\gamma_{L,R} = 0.05$ eV, $\gamma_d = 0.03$ eV, room temperature, $\epsilon_F = \epsilon_G$.

In support of transport calculations, we display in Fig. 1.16 maps of the density matrix in alternating (GC)$_5$ (left) and stacked G$_5$C$_5$ (right) sequences. The enumeration begins at the left contact, and we
organize the bases as follows, 
\[(s = 1, j) \rightarrow |2j - 1\rangle, \ (s = 2, j) \rightarrow |2j\rangle, \ j = 1, 2, ..., \] with \(s\) as the DNA strand (1 is the strand coupled to the left electrode, and 2 to the right, see Fig. 1.12), and \(j\) as the base pair index. The colour map reveals the following features: 

(i) Population is high (red) on the G sites (recall that we set \(e_F = e_G\)).

(ii) In both A and S sequences neighbouring G bases maintain coherence (yellow squares).

(iii) In S sequences, coherences survive even between G’s that are placed further apart. In fact, delocalisation is preserved even across segments. For example, the first G (state |3\rangle) maintains its coherence with the last G (state |22\rangle), which is placed on the other segment.

We further analysed the density matrix of stacked sequences of different lengths \((n = 3 - 6)\). In all cases the density matrix displays extended coherences between G sites. We do not however observe clear even-odd signatures (between e.g. \(n = 5\) and \(n = 6\)).

### 1.7 Conclusions

We demonstrated that the Landauer-Büttiker probe technique can be used to simulate electronic conduction in molecular junctions under the influence of a thermal environment. This LBP approach can be incorporated with little effort into the commonly used Landauer-NEGF formalism, to phenomenologically introduce bath-assisted site-to-site hopping conduction.

Our simulations revealed different transport mechanisms: In the absence of dephasing effects we identified deep-tunnelling conduction in short wires and ballistic transport at high temperatures, a result of resonant transmission. Under finite dephasing, hopping conduction was the dominant transport mechanism in longer wires, showing temperature dependence which was generally weaker than the Arrhenius activation factor in the explored range of parameters.

Principal observations are: 

(i) Length-dependence investigations of molecular conduction indicate a tunnelling-to hopping turnover, while temperature dependence may appear similar in both regimes. 

(ii) Kramers-like turnover behaviour manifests itself under the LBP method. Weak dephasing effects promote hopping conduction, but dephasing becomes detrimental to transport when \(\gamma_d \gtrsim \epsilon_B\).  

(iii) Structured environments can be implemented within the LBP method, by using energy-dependent dephasing coefficients. (iv) A closed-form expression for the hopping conduction was constructed, Eq. (1.31), within stated parameters. (v) The LBP method provided a semi-quantitative match for length dependent resistance in ONI wires reproducing the tunnelling to hopping crossover, as well as the resistance’s temperature dependence- as long as we allow the dephasing strength to become temperature dependent. (vi) We found that so-called alternating DNA chains conduct primarily via site-to-site incoherent hopping, while in stacked sequences there is also an oscillating ballistic contribution, owing to the delocalisation of molecular orbitals along adjacent G bases, and that these oscillations are related to the parity of stacked segments via the molecular band structure. This finding was possible due to the LBPs ability to model a mixture of coherent and incoherent effects.

Büttiker’s probes offer an easily implemented means to introduce dephasing and inelastic effects into molecular electronic applications, yet, obviously they do not absolutely correctly emulate physical process e.g., electron-vibration interaction. While overall the LBP approach ensures the conservation of current across the molecule, one should remember that the probes are modelled as metal electrodes, collections of Fermi sea electrons which themselves participate in the transport process. Essentially, the quadratic dependence of the hopping conductance on the probe hybridization \((G_H \propto \gamma_d^2)\) reflects probe-molecule-probe electron scatterings, with an incoming electron from probe \(n\) arriving at the molecule, leaving
it to probe $n'$; complementary processes ensure conservation of charge and energy, as necessary. In contrast, microscopic modelling of electron-vibration interactions should yield to lowest order a hopping conductance linear in the dephasing rate, possibly modifying Eq. (1.31), $\gamma_d^2 \rightarrow \gamma_d/\beta$. Thus, while the probes reproduce the hopping-ohmic nature of bath-assisted conduction, the predicted dephasing and temperature dependence should be taken with caution.

Mapping Böttiker probes to real molecular degrees of freedom is non-trivial. Since the LBP is not derived as an approximation for a phononic environment, with an electron self-energy arising from interactions with molecular vibrations, but rather as a purely fermionic system, where the self-energy arises from interaction with the probes, the correspondence between the two is not obvious. One promising avenue would be to compare our simulations to projection-operator approaches and first-principles techniques [31]. Of particular interest would be the so-called electron-phonon dephasing approach, which models incoherent elastic scattering similar to the dephasing probe, but via a microscopically derived model [180]. A recent work compared the two approaches in ds-DNA models similar to those studied in Section 1.6 [181], though a more in-depth study would be required to establish thorough physical correspondence.

The relationship between $\gamma_d$ and the magnitude of environmental/incoherent effects in real molecules should be investigated. An experimental correspondence would inform the correct usage of the LBP for real systems and build confidence in its usefulness. The most common avenues for experiments to address such interactions are observations of the tunnelling-hopping crossover, and the thermal activation characteristics. In terms of unimolecular experiments, there is a great wealth of literature on photoinduced charge transport [182, 183, 184], while in the molecular junction literature monolayers are more common [70]. It is tempting to draw on the former to inform the latter, since length and temperature dependence are generally expected to follow similar trends in both. It is known, however, that the correspondence between electron transfer rates and molecular conduction is non-trivial [123, 126], and further that current scaling from a single molecule to a monolayer may not be strictly linear [143].

Constraining ourselves for now to junction-type setups, we propose two experimental protocols which should give good information on the magnitude and role of electron-environment interactions, and help build a connection to the probe dephasing parameter, $\gamma_d$. First, we propose a series of conductance measurements on a repeating, conjugated molecular wire, which can be chemically modified in such a way that minimally affects frontier orbital energetics (and therefore the tunnelling behaviour), but may significantly change the vibrational/structural characteristics.

For just one example of the type of morphology we are proposing, consider substituted oligothiophenes, such as the ubiquitous poly(3-hexylthiophene) (P3HT), part of the thiophene family of molecules which have been extensively studied in molecular junction conductance experiments [185, 186, 187]. Thiophenes of this type typically consist of relatively planar thiophene rings, with substituent, often alkyl, side chains branching off each ring, and are known to realize an extremely rich bulk morphology [188]. These molecules realise both our criteria: we can test length dependence via increasing the number of thiophenes, and we can tune the molecular vibrational/rotational behaviour by changing the character of the side chains. The key factors to consider when changing the side-chains are the relevant vibrational frequencies and accompanying electron-phonon couplings. One could modulate these by changing the length of alkyl substituents, or by other chemical modification, so long as it does not strongly impact the frontier orbital energetics and conjugation. It is reasonable to suppose that such oligothiophenes, realizing different structural dynamics may demonstrate different tunnelling-hopping crossovers and thermal
activation behaviour as a result of changing electron-vibration interaction strength, which we can map to the dephasing parameter used in the LBP.

A further point that one could consider as an opportunity or a complication is the tendency for oligo(3-alkylthiophene)s to cooperatively interact and orient relative to one another, again depending on the nature of their side-chains, and the manner of their deposition. In a sparse monolayer this may have no significant impact, but at a certain density we expect that cooperative effects may become significant. This may increase the difficulty of measuring single-molecule conductance, but also opens a potentially interesting avenue into study of cooperative effects.

A second and perhaps more direct route to tuning the system-environment interaction is to perform a standard molecular wire conductance experiment in an electrolyte solvent, and study the change in conductance as the molecular length and ionic strength are modulated. A similar experiment was carried out examining the interplay of length, voltage and pH on polypeptide systems [189], though where they examine the effect of protonation, we are interested strictly in the electrostatic interactions between solvent electrolytes and polar moieties on the molecular wire. They further restrained themselves to the tunnelling regime, whereas we are interested in the tunnelling-hopping crossover. We expect that the impact of a more strongly interacting solvent environment will manifest in the conductance characteristics, which we can model via the LBP to gain further insight into e.g. realistic values of $\gamma_d$ in different types of systems. A caveat of this approach is that the presence of a strong electrolyte may impact more than the molecular subsystem; it has been shown for certain oligothiophenes that an electrolyte solvent and asymmetrical leads geometry may generate a significant rectification in the current via an electrostatic effect [190]. By operating at a low voltage bias, one should be able to mitigate this phenomenon. Further, one should carefully design the subsystem molecule such that increasing ionic strength does not ionize the wire itself, or otherwise grossly impact its energetics.

In Chapter 2, we extend the LBP to the large voltage-bias regime, explain its behaviour, and examine several device applications. One can further extend this approach to develop a voltage-temperature probe, and apply it to problems of thermoelectric transport [139, 104, 191], which we do not discuss here.
Chapter 2

Dissipative High Bias Conduction and Device Operation

2.1 Introduction

A central advantage of the Landauer-Büttiker probe (LBP) technique is the ability to craft different types of incoherent scattering processes according to certain conditions. These conditions manifest in the “dephasing” and “voltage” probes, which respectively allow only elastic or inelastic-dissipative scattering [111, 133]. In older studies and in the previous Chapter, the LBP technique was demonstrated to be a useful means to phenomenologically describe low-bias incoherent effects in mesoscopic conductors [40, 192, 193, 194, 195, 196, 197, 198, 199] and molecular junctions [41, 121, 200, 122, 123, 133, 201]. These simulations indicate that the LBP technique can reproduce several key features in molecular electronic conduction: a “Kramers-like” turnover of conductance as a function of the system-environment coupling strength, onset of a thermally activated conductance at finite temperature, and a transition from tunnelling to ohmic conduction with increasing the molecular size [133]. It was also shown in Chapter 1 that the LBP method can semi-quantitatively reproduce experimental conductance results for long, conjugated oligomers and double stranded DNA.

The implementation of the inelastic LBP (termed “voltage” probe) to electron and heat transport problems in mesoscopic, nano, and molecular systems has been typically limited to linear response applications given fundamental and computational challenges. Only recently, the utility of the voltage probe to high bias problems has been established: The mathematical uniqueness of the solution was proven in Ref. [202], and simulations demonstrating nonlinear charge and energy functionality with a facile convergence were reported in Refs. [119, 120, 203, 204, 111, 134, 135, 138]. The first goal of this Chapter is to simulate environmentally assisted charge transfer in molecular junctions under large applied voltage biases, and examine novel effects materializing in this regime due to incoherent inelastic scattering processes. Such inelastic effects are assumed to develop from the interaction of electrons with e.g. intra and inter molecular vibrational degrees of freedom, mimicked here using voltage probes.

Our second goal is to explore the role of inelastic effects on the operation of minimal nanodevices (namely, diodes) far-from equilibrium. One of the simplest building blocks in ordinary semiconductor circuitry, essential for realizing molecular-based electronics, is the rectifier (diode). In fact, the Aviram-Ratner proposal for an organic molecular rectifier gave early impetus to the field of molecular electronics
in 1974 [205]. Since then, molecular rectifiers have been fabricated from thin films, self-assembled monolayers (SAMs) [206, 207, 208, 209, 210], and single molecules [211, 16, 212]. However, in general reported rectification ratios were rather low. Only recently have SAMs [213, 214, 215, 216] and single molecule junctions [217, 190] provided robust molecular rectifiers with high conductance, and rectification ratios of two and even three orders of magnitude.

What is the mechanism of electron current rectification in molecular junctions? The literature includes several constructions based on molecules with an asymmetric backbone, different molecule-metal linkers at the two ends, or electrodes of different materials [218]. Fundamentally, from the principles of quantum transport, it is apparent that coherent conduction of noninteracting electrons, as described in scattering theory by the Landauer formula, cannot materialize rectification when energy levels are fixed, independent of applied bias [17]. Two necessary conditions should be simultaneously met for achieving the diode effect: many body interactions should play a role, and a spatial asymmetry should be built into the junction, see e.g. Refs. [219, 220], exemplifying charge and heat rectification. Many-body effects, however, may be included at the level of mean-field, by assuming a screening interaction which creates a voltage drop across the molecular bridge [218, 43]. In particular, theoretical and computational investigations of tunnelling diodes employ molecules that are asymmetrically coupled to the electrodes. Using model calculations or first-principle simulations, it is assumed or demonstrated that the junction develops an asymmetric potential profile under bias in the forward and backward direction, see e.g. Refs. [221, 222, 217, 223]. This in turn results in asymmetric IV characteristics. The development of a voltage drop inside the molecule, however, can be only justified when many body effects (essentially electron-electron interactions) play a role in the junction. Asymmetry and many body interactions are necessary but insufficient conditions for demonstrating the diode effect. In some models only specific types of spatial asymmetry resulted in the diode effect, see e.g. [224, 225].

In this Chapter, we begin with a discussion of the general characteristics and behaviour of a molecular wire under high bias and in contact with voltage probes. We then explore the role of voltage probes in an experimentally relevant tunnelling diode setup, and finally explore a novel diode effect driven by an environmental asymmetry, that is, by the interaction with the probes.

2.2 Voltage Probe Far From Equilibrium

The methods adopted in Chapter 1 of this thesis are identically employed here, except for the introduction of a far-from-equilibrium voltage probe technique we describe presently.

Incoherent inelastic-dissipative effects can be introduced by requiring the net total particle current flowing between each probe and the system, Eq. (1.9), to vanish,

\[ I_n = 0, \quad n = 1, 2, \ldots, N. \]  

(2.1)

As in Chapter 1, we force the probe distribution functions to take the form of Fermi functions, \( f_n(\epsilon) = \left[ e^{\beta(\epsilon - \mu_n)} + 1 \right]^{-1} \), and we search for the set \( \mu_n \) which fulfils Eq. (2.1). In the linear response regime this condition translates to a set of \( N \) linear equations which can be solved formally-analytically to give the chemical potential \( \mu_n \) of the probes. In this limit, energy exchange with the environment (probes) is small, and effectively, the voltage probe acts similarly to a dephasing probe [133, 135]. Far from equilibrium, voltage probes *inelastically* scatter electrons between molecular orbitals, absorbing
electrons, then injecting them with a range of energies determined by the distribution function within each probe.

Outside the limits of linear response we need to solve Eq. (2.1) without any approximations. This equation constitutes a set of $N$ nonlinear equations, thus an exact analytic solution is in general not forthcoming. We address this problem by retraction to a fully numerical procedure. We employ the Newton-Raphson method to find the unique set of roots for the $N$ probes’ chemical potentials $\mu_n$ [202, 111, 134, 135]. For example, the 3-probe case iterates according to

\[
\begin{bmatrix}
\mu_1^{k+1} \\
\mu_2^{k+1} \\
\mu_3^{k+1}
\end{bmatrix}
= \begin{bmatrix}
\mu_1^k \\
\mu_2^k \\
\mu_3^k
\end{bmatrix}
- \begin{bmatrix}
\frac{\partial I_1}{\partial \mu_1} & \frac{\partial I_1}{\partial \mu_2} & \frac{\partial I_1}{\partial \mu_3} \\
\frac{\partial I_2}{\partial \mu_1} & \frac{\partial I_2}{\partial \mu_2} & \frac{\partial I_2}{\partial \mu_3} \\
\frac{\partial I_3}{\partial \mu_1} & \frac{\partial I_3}{\partial \mu_2} & \frac{\partial I_3}{\partial \mu_3}
\end{bmatrix}^{-1}
\begin{bmatrix}
I_1 \\
I_2 \\
I_3
\end{bmatrix}_k
\]

(2.2)

Here, $\mu_n^k$ denotes the potential profile in the $n$th probe after the $k$th iteration, beginning from a certain-physical initial guess. The method converges regularly for a wide range of parameters, usually requiring tens to hundreds of iterations, with certain conditions requiring specialized guesses. Convergence is confirmed by checking that $\mu_n^k$ remains fixed over several iterations, and that the leakage current to each probe is small ($|I_n|/|I_L| < 10^{-5}$). Using either (dephasing, voltage) probe condition the current leaving the $L$ contact should be identical to the current reaching the $R$ terminal, $I_L = -I_R$. However, the energy resolution, that is, the distribution in the energies of electrons arriving at the right contact, is quite different, as we demonstrate below.

### 2.3 Finite Bias Simulations

We adopt an identical model system to what was examined in Section 1.4, specifically a uniform 1D molecular wire with probes locally attached at each site, with a single addition: the flat bridge of molecular sites will deform under bias. As was discussed in several works [226, 227, 228, 229], in the weak metal-molecule coupling limit the applied voltage typically drops only at the metal-molecule contacts (symmetrically or asymmetrically), thus the barrier maintains its equilibrium form. In contrast, at intermediate-strong molecule-metal coupling the applied bias largely drops across the molecule. Assuming a linear drop, the molecular barrier transforms from a rectangular to a trapezoidal shape, then to a triangular form when the bias exceeds the barrier height. To model this behaviour, we perform our finite-bias simulations assuming a linear ramp potential profile,

\[
\epsilon_n = \epsilon_B + \frac{\Delta \mu}{2} - \frac{\Delta \mu(n-1)}{N-1},
\]

(2.3)

which corresponds to a barrier being symmetrically reshaped from a rectangular into a triangular form by the applied voltage. The 1st and $N$th sites are pinned at a height $\epsilon_B$ from the electrodes’ Fermi energies $\mu_L$ and $\mu_R$, respectively. The remainder of the wire sites follows a linearly decreasing profile.

#### 2.3.1 Current-voltage characteristics

The linear response behaviour of the 1D bridge model was explained in Chapter 1. In the absence of probes, coherent electrons either ballistically conduct (in resonance situations), or via the tunnelling
Figure 2.1: (a) I-V characteristics with a linearly deformed bridge [Eq. (2.3)] with N=6 sites of height $\epsilon_B = 0.5$. Other parameters are intra-site coupling $v = 0.05$, leads coupling $\gamma_{L,R} = 0.2$, dephasing strength $\gamma_d=0, 0.001, 0.01, 0.1$ eV (organized bottom to top at low voltage), with dephasing probe (dashed) and voltage probe (full), and temperature for leads and probes $T = 298$ K. The dotted line at $\Delta \mu = 0.5$ eV marks the value beyond which molecular resonances appear within the bias window. Beyond $\Delta \mu = 1.0$ eV, more than half of the sites of the bridge are situated within the bias window. Zoom over (a2) $\gamma_d = 100$ meV, (a3) $\gamma_d = 1$ meV.

mechanism (when $\epsilon_B > \gamma_v, v, T$ ). It was shown that the significant contribution of the probes has been to support a hopping conductance beyond tunnelling, satisfying (in the high-barrier regime)

$$G_H \sim G_0 A(T) \frac{v^2}{\epsilon_B} \frac{\gamma_d^2}{N + l}.$$  \hspace{1cm} (2.4)

Here $G_0 = e^2/2\pi\hbar$ is the quantum of electrical conductance per spin, $A(T)$ is a dimensionless temperature-dependent prefactor (typically weaker than an Arrhenius factor), $N$ is the number of sites on the chain, and $l$ a parameter characterizing the crossover from tunnelling to hopping.

In the low bias limit, dephasing and voltage probes similarly affect electronic conductance [133, 135]. In contrast, Fig. 2.1 shows that far from equilibrium the two probes arrange for very different behaviour due to energy exchange processes which are allowed under the voltage probe condition, but prohibited by the dephasing probe. We note several important features in different regimes of the bias voltage, identified by regions R1, R2 and R3:

(R1) In the low-bias region R1, $\Delta \mu \ll \epsilon_B, k_B T$, conduction is off-resonant in the sense that all molecular orbitals (and thus transmission resonances) are placed outside the bias window. In this region, the two probes (full and dashed lines) similarly act on the junction. The effect of the environment is to promote an incoherent hopping conduction, monotonically enhancing the current with $\gamma_d$ in this range of parameters [133]. The current increases with voltage since molecular levels are being gradually tuned down, to shrink the energy gap $\epsilon_B$ between the bridge and the chemical potentials of the metals.
(R2) At high bias, once molecular electronic states move into the bias window, the two probes begin to manifest distinct effects. Within our parameters, the bridge is tilted into a resonance condition once $\epsilon_6 \leq \mu_L$, satisfied here when $\Delta\mu \geq 0.5$ eV. More molecular states are pushed into the bias window as we continue to increase the bias. Eventually, when $\Delta\mu = 1$ eV, three molecular electronic sites (out of six) already satisfy the resonance condition. We identify the region beyond that, $\Delta\mu > 1$ eV, as the “deep resonant regime” R3.

As we highlight in panels (a2) and (a3), in the R2 region the probes act similarly around $\Delta\mu \sim 0.5$ eV. As we approach region R3, significant deviations start to show up particularly at low dephasing strengths $\gamma_d = 1, 10$ meV. It is interesting to note that the probes more similarly act at higher dephasing strength. This appears to be the case due to the fact that at high dephasing strength the incoherent current is very large relative to the direct L-R tunnelling, and extreme level broadening due to $\gamma_d$ dictates performance.

(R3) In the high bias region $\Delta\mu \gtrsim 1.0$ eV, the dephasing probe suppresses the resonant current, in some cases even below the coherent limit, while the voltage probe generally supports increasingly high currents (negative differential conductance may show up, but the overall trend is the growth of current with voltage). This result is one of the main observations of this chapter: Under large bias, elastic decoherence effects degrade the current in uniform bridges, but energy exchange processes facilitate conduction. The explanation for this behaviour is straightforward: The bridge energetics shift significantly under large biases assuming the profile (2.3), or a similar deformation. When energy exchange processes are allowed, electrons cross the junction while dissipating energy within each site, resonantly following the molecular electronic energy profile, to yield high currents. In contrast, since the dephasing probe condition does not allow energy exchange, at high bias electrons need to cross a junction with highly dispersed energy states—elastically. This scenario leads to low currents. Thus, the same potential profile can be beneficial for conduction if electrons can “slide down”, while leaving excess energy behind, or disadvantageous, when only elastic processes are permitted.

For the dephasing probe, the precise value of voltage where the turnover behaviour takes place depends on the model assumed for the potential profile. However, the overall crossover behaviour is robust to the details of the potential drop, as long as levels are monotonically shifting away from equilibrium in response to bias.

We also note that even-odd effects appear $I-V$ characteristics, particularly when $\gamma_d = 0$ (not shown here): When $N$ is odd, the molecular site at the center of the bridge, $n = (N + 1)/2$, precisely overlaps with the Fermi energy of the left lead at high bias, resulting in a large coherent contribution relative to the even-$N$ setup. The addition of probes works to attenuate this via peak broadening and the addition of the hopping current which does not depend on parity. A similar effect was found in physical wires, such as the ds-DNA discussed in Chapter 1.

We emphasize that the decay of the current with bias with dephasing probes, as observed in Fig. 2.1, stems from the dispersion of molecular energies in the high-bias regime. At equilibrium, the molecular-backbone (bridge) analysed here includes identical sites; under bias, Eq. (2.3) dictates level separation. In contrast, if we were to begin with an energetically asymmetric junction, e.g., a two-site molecule with $\epsilon_1 < \epsilon_2$, levels would shift toward each other when $\mu_L > \mu_R$ [again, assuming (2.3)], and the two probes (voltage, dephasing) would then similarly affect the current, enhancing it through the hopping contribution [134].

Can experiments reflect the significant deviation between probes in region R3 as reported in Fig.
2.1? Inspecting the literature we note that in relevant setups measurements are typically reported up to $\sim 1$ V, covering regions R1 and R2. Specifically, $I-V$ characteristics of conjugated multi-unit linear wires generally exhibit an enhancement of current with voltage, more consistent with the voltage probe results. For example, the OPI and ONI self-assembled monolayers of Refs. [70, 1] and OPE wires in Ref. [74] were measured with bias up to 1.5 V demonstrating a current monotonically increasing with bias, with an estimated barrier height $0.3 - 0.7$ eV. These values are in line with parameters assumed in our simulations. Similar results were reported in ultra-thin CuPc (Copper Phthalocyanine) heterojunctions [82]. Energy dissipation is expected to take place in these systems, consistent with the behaviour of the voltage probe. According to our simulations, beyond 1.5 V (not reported in these experiments), the majority of electronic levels are placed within the bias window and inelastic effects become highly influential. In this case, unless energy dissipation from the conducting system to the environment is highly effective, significant heating will take place, leading to junction’s instabilities and eventually to rupture.

The transition from “direct tunnelling” to “field emission transport” can be revealed from a Fowler-Nordheim (FN) plot, looking at $\log(I/V^2)$ as a function of $1/V$, to extract the barrier height from the minima of this plot. Within our parameters, this analysis is relevant in the region $\Delta \mu < 1$ eV—where the two probes similarly act. Thus, a typical FN plot (as reported e.g. in Refs. [70, 1]) does not visibly reveal signatures of inelastic effects.

2.3.2 Inside the probes

![Figure 2.2](image)

Figure 2.2: Magnitude of energy-resolved currents at the left and right contacts, calculated as the integrand of Eq. (1.7), and an analogous current at the right side. The voltage probe (top) permits energy dissipation, therefore the energy-resolved current leaving the left-high bias-lead (dark purple) is not the same as that arriving at the right low-bias lead (pink). The dephasing probe (bottom) does not allow dissipation, and the left and right energy-resolved currents are identical. Parameters are the same as in Fig. 2.1, $\gamma_d = 10$ meV. (a) and (d): Low voltage with off-resonant conduction. (b) and (e): Low-intermediate voltage with off-resonant conduction, and (c) and (f): High-bias simulations with resonant transmission.

When voltage probes are attached to the molecular bridge, dissipation takes place stepwise at each site; the probes absorb electrons at a certain energy, and re-inject them, typically at lower energies.
Dephasing probes, in contrast, conserve energy. This fundamental distinction is illustrated in Fig. 2.2 where we compare (absolute value) energy-resolved currents at the left and right contacts, the integrand of Eq. (1.7), and the analogous one at the right end.

Panels (a) and (d) display the behaviour at low bias, $\Delta \mu = 10$ meV, using voltage and dephasing probes, respectively. The voltage probe condition shows little separation between $|I_L(\epsilon)|$ and $|I_R(\epsilon)|$, and thus close to zero dissipation. The dephasing and voltage probes here act nearly identically, and produce almost equivalent resolved currents. As we increase the bias to 200 meV in panels (b) and (e), we start to see peak separation in resolved currents under the voltage probe, and the voltage and dephasing probe resolved currents are now distinguishable. However, in this regime both probes still produce very similar total currents, since critically, individual molecular resonances have not yet entered the bias window. At high bias, $\sim 1$ eV, voltage probe dissipation has become large, with $|I_L(\epsilon)|$ and $|I_R(\epsilon)|$ not overlapping at all in panel (c). We can also identify several distinct peaks corresponding to molecular resonances. The dephasing probe in panel (f) shows a much sparser picture, with a single, very weak resonance in the resolved current. This produces the result shown in Fig. 2.1, where the voltage probe current continues to increase in this regime, diverging from the collapsing dephasing probe current.

Summing up, the dephasing probe, since it demands elastic collisions, cannot take advantage of multiple molecular resonances, whereas the voltage probe allows electrons to dissipate energy to the environment and be re-injected at different energies in a given chain, dramatically increasing the current.

Figure 2.3: Potential profile within voltage probes along the chain for $\gamma_d = 10$ meV in the R1, R2, R3 regions for (a), (b), (c), respectively. Parameters are the same as in Fig. 2.1.

We further analyse the operation of the voltage probe in different bias regimes by plotting in Fig. 2.3 the self-consistently calculated chemical potential $\mu_n$ within each probe along the chain. Recall that the probes’ electron distributions follow the form of a Fermi function with a fixed temperature $T$. In the case of the linearly deformed bridge as used here, the probes’ potential profile is close to being linear at high bias. The reason is that molecular resonances separate as the bias increases, and the probes follow this dispersion. In the case of a flat molecular bridge (un-deformed by applied bias), it can be shown that the internal profile at high bias becomes highly nonlinear, with probes’ internal potentials clustering near dominant molecular resonances.
2.4 Tunnelling Diodes under Environmental Effects

We now turn to the examination of the robustness of tunnelling diodes against environmental effects, when electrons on the junction suffer from decoherence, inelastic effects, and energy dissipation due to their interaction with an “environment”, consisting of degrees of freedom such as intramolecular vibrations, solvent, and other electrons. Naturally, since the rectification mechanism in tunnelling diodes, depicted in Fig. 2.4(a)-(c), relies on the sharp contrast between resonant transmission and deep tunnelling, rectification ratios should deteriorate when incoherent processes play a role.

Tunnelling diodes were investigated for example in Ref. [3], where a DFT + NEGF approach was employed for the study of coherent transport in a three-fragment 1,2-bis(4-(phenylethynyl)phenyl), showing a rectification ratio of $R \sim 1000$. A similar approach (with a different backbone) was adopted in Ref. [230], manifesting $R \sim 100$. These studies and similar proposals employ the Landauer formula for coherent conduction, with the additional assumption of level shift under bias.

2.4.1 Model

Here we are concerned with single molecule rectifiers made of three fragments, e.g., donor-$\sigma$-acceptor junctions. While in their original proposal Aviram and Ratner assumed vibrationally-assisted intramolecular electron transfer [205], a related diode can be realized based on quantum tunnelling, as presented in Figure 2.4.

![Figure 2.4: Illustration of the examined tunnelling diode. Displayed are levels (a) at zero bias, (b) forward bias, providing a resonant situation beneficial for conductance, and (c) under reverse bias when levels are shifted away from each other resulting in small tunnelling currents.](image)

We focus on recent proposals for highly rectifying tunnelling diodes built from three-fragment molecular backbones such as 1,2-bis(4-(phenylethynyl)phenyl)ethane junctions [3], see Fig. 2.5. This asymmetric molecule includes conjugated groups at each end of the junction and a weak tunnelling link in the form of a saturated carbon bridge, breaking conjugation. $IV$ characteristics of this system, as calculated with a DFT + NEGF approach, were excellently matched with the two-site (HOMO and HOMO-1) model Hamiltonian

$$\hat{H} = \begin{bmatrix} \epsilon_1 + \frac{1}{2}\alpha eV & v \\ v & \epsilon_2 - \frac{1}{2}\alpha eV \end{bmatrix},$$

with $\epsilon_{1,2}$ as the conjugated groups’ site energies at zero bias, $v$ a small tunnelling energy between the units, and $\alpha$ a phenomenological parameter which describes the fraction of the voltage drop within the molecule, the response to the screening interaction. At zero bias, $\epsilon_1 = 0$ and $\epsilon_2 < 0$. Under forward
bias defined as $V > 0$, a resonance situation can be met once $\epsilon_1 + \frac{1}{2} \alpha eV \approx \epsilon_2 - \frac{1}{2} \alpha eV$, with the shifted levels buried within the bias window, resulting in high currents. Under the reversed operation only tunnelling currents contribute in coherent scenarios, see Fig. 2.4. Coherent transport can be described by the Landauer formalism [17]. We construct the metal-molecule hybridization matrices with coupling strengths $\gamma_{L,R}$,

$$\hat{\Gamma}_L = \gamma_L \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad \hat{\Gamma}_R = \gamma_R \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}. \quad (2.5)$$

In Fig. 2.5 we display the $IV$ characteristics and the corresponding rectification ratio

$$R(V) \equiv \frac{|I(V > 0)|}{|I(V < 0)|} \quad (2.6)$$

for the 1,2-bis(4-(phenylethynyl)phenyl)ethane molecule, reproducing rectification ratios up to $R \sim 1000$ in the coherent limit, as discussed in Ref. [3].

We now assess the role of a thermal environment on this predicted excellent rectifying behaviour. The coupling of electrons to other degrees of freedom, e.g., internal molecular vibrations, solvent, other electrons, causes phase decoherence of transmitted electrons, inelastic scattering processes, and energy relaxation. A detailed and accurate description of many-body processes in molecular conduction is a challenging task [33]. Fortunately, the LBP is able to capture such effects phenomenologically at a very low cost. We implement the probe technique here by coupling the two molecular sites to independent metals (probes), identified by '1' and '2'. These metals can exchange electrons with the junction, and their properties are determined self-consistently as usual to introduce relevant thermal effects. In direct analogy with Eq. (2.5), we construct the molecule-probes hybridization matrices as

$$\hat{\Gamma}_1 = \gamma_d \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad \hat{\Gamma}_2 = \gamma_d \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}, \quad (2.7)$$

The energy scale $\gamma_d$ corresponds to the effective interaction of electrons with intra-molecular and inter-molecular vibrational modes. $\gamma_d$ parallels with damping rates introduced in quantum master equation approaches (Redfield, Lindblad) [43], to similarly contain in a common manner electron-phonon interaction effects.

2.4.2 Two-state diodes

The diode functionality is demonstrated in Fig. 2.5(a)-(c). Inelastic-environmental effects deteriorate the device operation, as expected, yet the junction rectifies substantially even when $\gamma_d$ is order of the tunnelling energy $v$. When inelastic effects are strong, $\gamma_d \gg v$, the junction supports only $R \sim 50$. Naturally, these values reduce when $\epsilon_2$ is placed closer to the Fermi energy, when the gap $\epsilon_1 - \epsilon_2$ is reduced, and when $\gamma_{L,R}$ takes larger values, as was demonstrated in Ref. [3]. The effect of the temperature is mild (not shown); for $\gamma_d = 0 - 100$ meV rectification ratios reduce by $\sim 5\%$ when increasing the temperature from 10 to 500 K. Only at higher temperatures, on the order of 0.1 eV, does the temperature significantly affect the diode function.

To understand the decline in the diode operation under environmental effects we display in Fig. 2.6 the energy resolved currents at the two terminals, $I_L(\epsilon)$ and $I_R(\epsilon)$. These currents are calculated from


Figure 2.5: Tunnelling diodes under inelastic effects with parameters corresponding to the 1,2-bis(4-(phenylethynyl)phenyl)ethane molecule (top panel), serving as the backbone of the diode. (a) IV characteristics of the junction, (b) rectification ratio $R$, and (c) level diagram showing the chemical potentials $\mu_{L,R}$ at the two leads (dashed lines) and the eigenenergies of $\hat{H}$, Eq. (2.5) (full lines). Parameters here and throughout this subsection correspond to a two-state model of the molecule (top panel) with $\epsilon_1 = 0$, $\epsilon_2 = -0.329$, $v = 0.0109$, $\gamma_{L,R} = 0.03$, all in units of eV, and $\alpha = 0.55$ [3], $T = 298$ K. $\gamma_d = 0, 0.01, 0.1, 0.3$ eV.

The integrand in Eq. (1.7) and the corresponding equation for the right terminal. We find that at small biases (0.05 V) the resolved current arranges a single peak located close to the Fermi energy, Fig. 2.6(a). The role of the environment is to broaden this peak, and to slightly enhance the current due to the contribution of inelastic terms. The behaviour of the resolved currents at the voltage 0.6 V is displayed in Fig. 2.6(b). This voltage arranges a resonance configuration most beneficial for conductance, see Fig. 2.4(b). When $\gamma_d = 0$, a single-large contribution to the current shows up (clipped here for clarity), located around $\epsilon = -0.165$ eV, corresponding to the energy of the two molecular sites. When we allow energy exchange with the environment, electrons with energies reaching $\mu_R = 0.3$ eV contribute, see $|I_R(\epsilon)|$. These electrons dissipate their energy on the junction, and are re-emitted at the other terminal with lower energies, down to $\mu_L = -0.3$ eV, see the behaviour of $|I_L(\epsilon)|$. Under the reversed bias $-0.6$ V, corresponding to the configuration of Fig. 2.4(c), an analogous behaviour takes place, see Fig. 2.6(c).

We further present in Figs. 2.6(b)-(c) the resolved current under the dephasing probe condition, when decoherence effects take place without relaxation. In this case, energy conservation is enforced and electrons on the junction do not absorb/dissipate energy from/to the thermal bath, thus $|I_L(\epsilon)| = |I_R(\epsilon)|$. 
Figure 2.6: Energy resolved currents in the coherent limit $\gamma_d = 0$ (black) and under inelastic effects $\gamma_d = 0.05$ eV. In the latter case $|I_L(\epsilon)| \neq |I_R(\epsilon)|$, i.e., the current profile of electrons entering the junction is different from the one leaving it. The three panels follow the configurations of Fig. 2.4: (a) Low bias, when inelastic effects play a little role. (b) At peak voltage $\sim 0.6$ V the two states are in resonance, $\epsilon_1 + \alpha eV/2 \sim \epsilon_2 - \alpha eV/2 = -0.165$ eV. (c) At large negative voltages $-0.6$ V, $\epsilon_1 + \alpha eV/2=0.165$ eV and $\epsilon_2 - \alpha eV/2 = -0.49$ eV. In panels (b)-(c) we further depict the resolved current under the dephasing probe condition when energy relaxation is not allowed (dashed line). Parameters are the same as in Fig. 2.5.

The effect of the environment is to broaden the coherent current profile, again disturbing the operation of the diode. Interestingly, the microscopic differences between the two probes as reflected in Fig. 2.6 do not translate to the macroscopic operation of the device in the present model, and the total-integrated currents under either probes are almost identical. This observation however is not general, and deviations between probes (emulating different microscopic processes) may clearly affect functionality, particularly in multi-site chains as was shown in Sec. 2.3.1.

The departure from the strict tunnelling picture limits the operation of the junction as a diode since the contrast between resonant transmission and tunnelling no longer stringently holds with inelastic electrons contributing to the current. Note that $\gamma_{L,R}$, the coupling of the molecule to the metals, corresponds to levels’ broadening, and affects the diode in a parallel manner as the tunnelling current becomes over-dominated by ballistic electrons. This effect is presented in Fig. 2.7(a)-(c), displaying contour plots (log scale) of rectification ratios as a function of $\gamma_{L,R}$ and applied voltage bias at different values for $\gamma_d$.

In Fig. 2.8 we further present the rectification ratio at peak voltage, $R(V_p)$, as a function of $\gamma_d$. Weakly hybridized junctions operate better as tunnelling diodes, yet they support lower currents and are more susceptible to inelastic effects. The case $\gamma_{L,R} = 1$ meV shows a distinct decay trend as compared to other values. In this case the hybridization energy is the smallest energy scale in the problem and while at $\gamma_d = 0$ the junction excellently rectifies, this function more rapidly deteriorates when environmental effects participate. In contrast, when the levels are largely broadened with $\gamma_{L,R} = 0.1$ eV, the junction still rectifies well with $R \sim 100$ in the coherent limit, and it is resistant to the environment as long as $\gamma_d \lesssim 0.1$ eV.

### 2.4.3 Four-state diodes

The rectifying behaviour of a tunnelling diode could be enhanced significantly if we manage to attenuate the tunnelling current under reverse bias, while keeping intact the resonant current in the forward
Figure 2.7: Map of rectification ratios as a function of applied bias and metal-molecule hybridization (starting at values $\gamma_{L,R} = 1$ meV). (a) Coherent limit, (b) $\gamma_d = 10$ meV, and (c) $\gamma_d = 100$ meV. Parameters are the same as in Fig. 2.5.

direction. We recall that in an $N$-site molecular chain the tunnelling conductance decays exponentially with distance, while the resonant-coherent current is independent of chain length [43] (leaving aside decoherence and dissipation effects). We therefore suggest a generalisation of the two-state tunnelling diode of Fig. 2.4 to include four molecular states, two sites within each conjugated unit, see Fig. 2.9. In the energy representation, each conjugated unit includes two closely spaced orbitals (at zero bias) instead of a single level. This principle was employed in Ref. [216] to experimentally realize highly rectifying junctions, albeit employing only one conjugated unit and a long saturated tail. The Hamiltonian of the four-site molecule takes the form

$$\hat{H} = \begin{bmatrix} \hat{H}_1 & \hat{V}_{12} \\ \hat{V}_{21} & \hat{H}_2 \end{bmatrix},$$

with $\hat{H}_{1,2}$ describing the conjugated units and $\hat{V}_{12}$ and $\hat{V}_{21}$ comprising the tunnelling terms through the $\sigma$ bridge,

$$\hat{H}_1 = \begin{pmatrix} \epsilon_1 + \alpha eV/2 & v_1 \\ v_1 & \epsilon_1 + \alpha eV/2 \end{pmatrix}; \quad \hat{V}_{12} = \begin{pmatrix} 0 & 0 \\ v & 0 \end{pmatrix} ;$$

$$\hat{H}_2 = \begin{pmatrix} \epsilon_2 - \alpha eV/2 & v_2 \\ v_2 & \epsilon_2 - \alpha eV/2 \end{pmatrix}; \quad \hat{V}_{21} = \begin{pmatrix} 0 & v \\ 0 & 0 \end{pmatrix} .$$
The two orbitals within each conjugated unit are made close in energy; $v_{1,2}$ determines departure from degeneracy.

To make a meaningful comparison to the two-site junction, we employ here the same parameters as in Fig. 2.5. The IV characteristic of the model is displayed in Fig. 2.9, demonstrating a very large rectification ratio in the coherent limit, but a strong decline in operation under environmental effects. The four-site design thus offers an improved diode functionality, yet a greater sensitivity to thermal effects since (i) a minuscule tunnelling current is more easily outplayed by inelastic processes and (ii) the forward resonant current is more fragile in a longer bridge.

### 2.5 Environmentally Induced Diodes

The common “tunnelling diode”, examined in Section 2.4, relies on the dramatic contrast between deep tunnelling conductance and ballistic transport. In these systems, rectification arises e.g. out of an energetic asymmetry in the bridge - sensitive to the bias polarity - with decoherence and inelastic effects shown to be destructive to performance.

Here, in contrast, we focus on a different mechanism for the diode effect, originating solely from the interaction of electrons with the environment. Such inelastic effects are assumed to develop from the interaction of electrons with e.g. intra and inter molecular vibrational degrees of freedom, mimicked here using voltage probes. This environmentally-induced diode (EID) effect is relatively weak in our modelling, but may provide insight into anomalous rectification in systems which are expected to be symmetric coherent conductors. To isolate the effect, we maintain the energies of molecular states fixed under bias. Obviously, in real systems various effects may play together to yield an asymmetric current.

We present below two types of EIDs. In both cases a spatial asymmetry is included, but the current is symmetric (no rectification) in the Landauer coherent limit and under dephasing probes; rectification appears only when incoherent inelastic effects are allowed. In type 1 EIDs, the molecule is asymmetrically...
Chapter 2. Dissipative High Bias Conduction and Device Operation

Figure 2.9: Top: Scheme of a four-site diode in the site representation (left), and energy representation within each conjugated moiety (right). Bottom: Operation of the junction as a diode (a) IV characteristics, (b) rectification ratio, and (c) level diagram with (dashed lines) chemical potentials and (full lines) the four eigenenergies of the molecule. Parameters are $\epsilon_1 = 0$, $\epsilon_2 = -0.329$, $v = 0.0109$, $\gamma_{L,R} = 0.03$ eV, and $\alpha = 0.55$ as in Fig. 2.5, as well as $v_1 = v_2 = 0.03$ eV for the tunnelling energy within each conjugated unit. The temperature is set at $T = 298$ K and $\gamma_d$ was varied as indicated in the figure.

hybridized to the leads, see Fig. 2.10. Type 2 EIDs are structurally uniform, but the coupling strength to the environment varies asymmetrically along the molecule, see Fig. 2.11.

2.5.1 Rectification via asymmetric metal-molecule coupling

We consider a junction with a symmetric molecular backbone but dissimilar couplings to the electrodes, $\gamma_L \neq \gamma_R$. Assuming the bridge energies do not shift under bias, in the fully coherent Landauer picture this setup leads to identical values for the forward and reversed currents and thus zero rectification. We now include identical probes along the wire. Rectification is missing if we use dephasing probes, see Sec. 2.5.3. However, once we allow inelastic effects (voltage probes), we find that the magnitude of the current is higher from the strongly coupled contact to the weak one, than in the reverse direction, see Fig. 2.10.

The effect can be correlated with the behaviour of the potential profile within probes. As we point out below in Sec. 2.5.3, close to equilibrium the probe potential profile satisfies $\mu_n^+ + \mu_n^- \sim \mu_L + \mu_R$. 
with little rectification showing up. Note that according to our conventions \( \mu_L + \mu_R = 0 \), marked by a dotted line in Fig. 2.10(b) and \( \mu_n^\pm \) is the probes’ profile under a forward (+) and backward (−) polarity. Inspecting Fig. 2.10(b), at high bias this mirror symmetry is obviously violated, \( \mu_n^+ + \mu_n^- > 0 \), manifested by the diode effect.

Fig. 2.10(a) displays a crossover behaviour for rectification: In short chains and at low \( \gamma_d \), dissipationless tunnelling dominates transport. Rectification gradually increases with growing \( \gamma_d \) once inelastic conduction becomes substantial. However, at high enough \( \gamma_d \) peak broadening makes forward and backward currents similar, dampening rectification. As expected, the diode effect grows with applied voltage bias, as dissipation effects become more substantial. However, to be consistent with the assumption of fixed bridge energetics irrespective of \( \Delta \mu \), we limit our simulations here to relatively low biases.

### 2.5.2 Rectification with spatially asymmetric molecule-bath interactions

Fig. 2.11 illustrates a second type of an EID: The molecular electronic structure is symmetric, but its coupling to the thermal environment varies monotonically along the wire. Such a modulation could reflect intrinsic molecular-structural asymmetries. Alternatively, it could develop when using two distinct contacts which induce different local environments on different parts of the molecule [190]. Fig. 2.11(a) displays the rectification behaviour as a function of \( \gamma_d \). Similarly to EID-type 1, we observe an enhancement of the diode effect with voltage and a crossover behaviour with \( \gamma_d \). The diode effect reflects itself (weakly) in the asymmetric response of the molecule to inelastic scattering induced by the environment, see Fig. 2.11(b). Consistently with Sec. 2.5.3, in linear response situations \( \mu_n^+ + \mu_n^- \sim 0 \),
Figure 2.11: Type 2 EID. Top: Schematic representation of the diode. The electronic structure is spatially symmetric and $\gamma_L = \gamma_R$, but coupling strength to the surrounding environment assumes a certain profile, represented by the colour gradient of the bath, $\gamma_1 > \gamma_2 > \gamma_3$, with the integer standing for the site index left to right. (a) Rectification ratio as a function of coupling to the environment. Parameters are the same as in Fig. 2.10, with $\gamma_1 = 2\gamma_d$, $\gamma_2 = \gamma_d$, $\gamma_3 = \gamma_d/2$. (b) Potential profile within the probes, demonstrating the development of an asymmetry in the junction’s response to applied bias under inelastic effects at peak value $\gamma_d = 0.4$ eV.

missing rectification, while at finite bias $\mu^+_n + \mu^-_n > 0$, materializing the effect.

We note that the current is higher when $\gamma_d$ is reduced in the same direction of bias drop: $\Delta \mu = \mu_L - \mu_R > 0$ and $\gamma_1 > \gamma_2 > \gamma_3$, than the opposite setup. This can be rationalized as follows. When $\Delta \mu > 0$, high-energy electrons ejected from the $L$ metal can immediately relax energy on site 1, to physically populate electronic levels. In the reversed direction, electrons enter the junction to a site weakly interacting with the bath, thus they minimally dissipate their energy. As a result, electrons cross the junction less effectively, in an off-resonant manner.

2.5.3 Absence of rectification with dephasing probes

The EIDs described above operate due to the participation of inelastic electron scattering in the transport process, implemented with voltage probes. We prove next that dephasing probes cannot materialize rectification in these type of models. An important working assumption in our derivation, consistent with the discussion in Secs. 2.5.1-2.5.2, is that molecular levels do not shift under bias. In what follows, currents and probes’ distributions under forward bias ($\mu_L > \mu_R$) are identified by a plus sign; reversed-bias measures are recorded by a negative sign.

Ignoring physical coefficients, under a forward bias the energy-resolved current leaving the $L$ contact is obtained from Eq. (1.7),

$$I^+_L(\epsilon) = T_{L,R}(\epsilon)[f_L(\epsilon) - f_R(\epsilon)] + \sum_n T_{L,n}(\epsilon)[f_L(\epsilon) - f^+_n(\epsilon)],$$

(2.8)
with \( f^+_n(\epsilon) \) the distribution functions of dephasing probes at each site. These functions are determined from the following \( N \) equations

\[
I^+_n(\epsilon) = T_{L,n}(\epsilon)[f_L(\epsilon) - f^+_n(\epsilon)] + T_{R,n}(\epsilon)[f_R(\epsilon) - f^+_n(\epsilon)] + \sum_{n'} T_{n',n}(\epsilon)[f^+_{n'}(\epsilon) - f^+_n(\epsilon)] = 0, \quad (2.9)
\]

see Eq. (1.9). We now reverse the bias voltage. The particle current leaving the \( L \) contact (now negative) is given by Eq. (2.8), only switching \( \mu_L \) by \( \mu_R \), thus \( f_L(\epsilon) \) by \( f_R(\epsilon) \),

\[
I^-_L(\epsilon) = T_{L,R}(\epsilon)[f_R(\epsilon) - f_L(\epsilon)] + \sum_n T_{L,n}(\epsilon)[f_R(\epsilon) - f^-_n(\epsilon)]. \quad (2.10)
\]

Note that in general \( f^-_n(\epsilon) \neq f^+_n(\epsilon) \), with \( f^-_n(\epsilon) \) satisfying the following equations, analogous to Eq. (2.9),

\[
I^-_n(\epsilon) = T_{L,n}(\epsilon)[f_R(\epsilon) - f^-_n(\epsilon)] + T_{R,n}(\epsilon)[f_L(\epsilon) - f^-_n(\epsilon)] + \sum_{n'} T_{n',n}(\epsilon)[f^-_{n'}(\epsilon) - f^-_n(\epsilon)] = 0, \quad (2.11)
\]

The diode effect corresponds to \( \Delta I = I^+_L + I^-_L \neq 0 \), a nonzero contribution under bias reversal. Explicitly, adding up Eqs. (2.8) and (2.10) we get

\[
\Delta I(\epsilon) = \sum_n T_{L,n}(\epsilon)[f_L(\epsilon) + f_R(\epsilon) - f^+_n(\epsilon) - f^-_n(\epsilon)]. \quad (2.12)
\]

To prove that rectification is missing, \( \Delta I(\epsilon) = 0 \ \forall \ \epsilon \), we follow a procedure similar to that employed in Ref. [116]. The sum of Eqs. (2.9) and (2.11), for every probe \( n \), is given by

\[
[T_{L,n}(\epsilon) + T_{R,n}(\epsilon)][f_L(\epsilon) + f_R(\epsilon) - f^+_n(\epsilon) - f^-_n(\epsilon)] = -\sum_{n'} T_{n',n}(\epsilon)[f^+_{n'}(\epsilon) + f^-_{n'}(\epsilon) - f^+_n(\epsilon) - f^-_n(\epsilon)]. \quad (2.13)
\]

Eq. (2.13) constitutes a set of \( N \) linear equations (which should be solved at every value \( \epsilon \)). The \( N \) unknowns are the combinations \( [f^+_n(\epsilon) + f^-_n(\epsilon)] \), and the inhomogeneous terms are proportional to the nonzero distributions \( [f_L(\epsilon) + f_R(\epsilon)] \). Inspecting Eq. (2.13), we immediately infer the solution, which is unique,

\[
f^+_n(\epsilon) + f^-_n(\epsilon) = f_L(\epsilon) + f_R(\epsilon), \ \forall n \quad (2.14)
\]

We substitute this solution into Eq. (2.12) and receive \( \Delta I = 0 \). This concludes our derivation that a diode effect is missing under dephasing probes.

We emphasize that the proof holds for an arbitrary molecular structure, with probes possibly inter-
acting at different strengths at different sites. The basic assumptions involved are: (i) The molecular electronic structure stays intact under bias reversal, i.e. mean field effects such as level shift under bias are not included. (ii) Only elastic (yet incoherent) scatterings are allowed via dephasing probes.

How does the proof detailed above fail in the case of voltage probes? Essentially, expressions (2.8)-(2.13) are valid—after integration over energy. The analogue of equation (2.13) however becomes non-linear in the case of voltage probes, and rather difficult to solve. This is because for voltage probes we demand that the functions \( f_n^\pm(\epsilon) \) take the form of Fermi functions, thus we need to solve the equations (2.13) for the internal variables \( \mu_n^\pm \). In this case, Eq. (2.14) is not necessarily satisfied, and the junction can rectify current. At small bias, we perform Taylor expansions for \( f_n^\pm \) near equilibrium. In linear response, the probes’ potentials satisfy the symmetry relation \( \mu_n^+ + \mu_n^- \sim \mu_L + \mu_R = 0 \), and rectification is absent. The violation of the mirror symmetry \( \mu_n^+ + \mu_n^- \neq 0 \) can therefore be associated with the onset of rectification, as demonstrated in Figs. 2.10-2.11.

Classical [231] and quantum-mechanical based [220, 232] simulations of charge and heat rectification in nanoscale conductors have shown that two conditions are necessary for the diode effect to set in: The junction should be spatially asymmetric, and many-body effects should participate in conduction. The probe method incorporates phenomenologically many-body electron-phonon effects. The proof above furthermore points out that many-body effects relevant for inducing rectification should involve energy exchange processes.

Here, in contrast, we identified two types of diodes which operate only due to the interaction of electrons with their thermal environment. We further provided a rigorous proof that dephasing probes cannot support charge-current rectification without additional effects, e.g., mean-field level-shift under bias.

### 2.6 Conclusions

We established the applicability of the Landauer-Büttiker probe formalism to molecular electronic transport systems under high biases, completing the picture started in Chapter 1. The present analysis contributes fundamental understanding of the role played by incoherent elastic and inelastic scattering of electrons in high-bias transport junctions and provides practical-operational directions for designing functionality.

The voltage probe, admitting energy exchange and dissipation processes, is more relevant to many molecular electronic situations than the dephasing probe, yet the latter is easier to implement and suitable for low voltage setups. Our work illustrated that in high bias applications the two probes may act distinctively, to yield fundamentally different \( I-V \) characteristics and function. One of our main observations was that under large bias, when molecular electronic levels are dispersed from each other (yet placed within the bias window), elastic decoherence effects degrade the current with bias, while energy exchange processes facilitate conduction.

We further pushed the method to the study of molecular diodes, and their operation under environmental effects, i.e. beyond a strictly coherent picture of electronic motion. We analysed the operation of molecular tunnelling diodes comprising conjugated-saturated-conjugated segments under environmental effects inducing decoherence and energy relaxation. Specifically, we employed a two-site molecular junction with parameters corresponding to the 1,2-bis(4-(phenylethynyl)phenyl)ethane junction [3]. This system operates as a diode since (i) an asymmetry is built into the molecular backbone, and (ii) an
internal potential drop develops within the molecule in response to applied bias. For these reasons, we expect our findings are fully general to constructions with different backbones or system energetics, provided they follow these design principles. The contrast between resonant and tunnelling conductances is the key to the optimization of the diode, with rectification ratios reaching three orders of magnitude in coherent situations. The diode performs well under environmental effects as long as $\gamma_d \lesssim v$, providing $R \sim 100 - 500$. The decline in the operation of the diode under thermal effects ensues from the contribution of incoherent electrons, playing down the contrast between resonant transmission and tunnelling conductance. We further proposed the design of an improved rectifier, suggesting a chemical backbone supporting two closely spaced orbitals within each conjugated unit. This structure provides $R \sim 10^5$ within our parameters when $\gamma_d = 0$, though this type of diode shows a greater susceptibility to environmental effects and is likely more complicated to construct.

An inelastic vibration-assisted diode obeying a similar principle of level alignment was investigated in Refs. [30, 31], with a weak, phonon-assisted hopping energy instead of the direct tunnelling $v$. Despite the different conduction mechanism (resonant vs. hopping), this setup produced IV characteristics closely resembling the curve in Fig. 2.5.

Finally, we discovered and characterized a new type of molecular diode, wherein rectification is driven by the environmental interactions. In general, and indeed as we found, designs for molecular diodes are based largely on the assumption of pure coherent motion, with dephasing-incoherent effects degrading performance. Here, in contrast, we identified two types of diodes which operate only due to the interaction of electrons with their thermal environment.

In summary, the phenomenological LBP technique for simulating incoherent effects in electronic conduction is effective for applications in molecular transport junctions. Our work illustrates that: (i) At high bias, dephasing and voltage probes may predict significantly different $I$-$V$ curves, and (ii) Experimental results on linear chains, showing the enhancement of current with voltage at high voltage $\Delta \mu \gg \epsilon_B$, are more consistently described with the (more difficult to implement) voltage probe, evincing the important role of inelastic effects in transport. (iii) Environmental effects degrade the performance of tunnelling diodes which operate by exploiting the difference between resonant and deep tunnelling conduction regimes. (iv) Incoherent-inelastic effects combined with structural asymmetry may yield small rectification.
Part I Summary

In this first Part of the thesis, we applied the Landauer Büttiker probe technique to problems of charge transport in nanoscale junctions. In Chapter 1, we demonstrated the applicability of the technique to real molecular wires, while exploring the phenomenological behaviour induced by the probes. Specifically, we showed that the probe faithfully recovers several of the key incoherent effects one would expect from a real vibrational/solvent environment, and can be used to accurately model experimental results, at very low cost. We further showed where the phenomenology does not fully agree with our prior conception of the role of the environment, particularly in the scaling with temperature and system-environment coupling.

In Chapter 2 we were able to create a consistent far-from-equilibrium framework for the probe technique, and by delving deeply into the behaviour of the probes, we elucidated the roles of elastic and inelastic scattering in high-bias conduction. With a high-bias method in hand, we were able to explore relevant device applications, and learn about the general behaviours of molecular diodes in the presence of an environment; we found that generally this effect is deleterious, though under certain circumstances the environment can generate a diode effect where none was present in the coherent limit.

Overall we find the LBP to be a useful technique for studies of conduction at the nanoscale. It is computationally cheap and conceptually simple, it reproduces many of the desired features of physical environmental interactions, and it is highly general in its scope of potential applications. We maintain the position from our first works on this subject [133], that the LBP should be added to the general toolbox of theoreticians and experimentalists, who often rely heavily on the bare Landauer approach. We have even generated a free to use, publicly available version of our code, capable of simulating the current as well as the thermopower using the LBP [233, 138]. Use of this code, or addition of probes to an existing program is straightforward and highly accessible, and provides useful, sometimes crucial physical insights.
Part II

Chapters 3 & 4: Quantum Thermal Transport
Part II Introduction

Where Part I focused on charge transport, and its applications in nanoelectronic devices, Part II considers heat transport, and its applications to energy conversion devices. There are two obvious reasons why we should be interested in problems of energy conversion at the nanoscale: (i) we wish to build and understand new types of miniaturized devices, and (ii) they are a fantastic model, like the steam engine in the eighteenth and nineteenth centuries, for studies of the thermodynamic properties of quantum systems. To both of these ends, we begin this part of the thesis with a study of heat transport in quantum heat machines (QHMs), and particularly the role of quantum coherence in their operation [4].

In recent years, a major question in the study of QHMs has been the impact of persistent, energy basis coherence in their nonequilibrium behaviour, and operational characteristics such as power output and conversion efficiency. It is important to note that “coherence” in Part II carries a different meaning than in Part I. In the context of charge transport in molecular junctions, coherence is associated heavily with the quantum tunnelling mechanism, captured so well by the Landauer approach. We say that charge transport is coherent if it occurs largely via a tunnelling mechanism. In Part II we very specifically define coherences as the off-diagonal elements of the reduced density matrix, in the system energy basis, with particular focus on any such elements which survive to the nonequilibrium steady-state. The preponderance of attention has focused on systems wherein such coherences can boost performance, beyond so-called “classical” or secular limits [10, 46]. In Chapter 3, we propose a model wherein noise-induced coherence fully suppresses the power output of the device, and analyse it piece-by-piece, to understand the mechanics of this behaviour. Going beyond a single model, we propose an inexpensive and intuitive method for unambiguously analysing the role of coherence in QHMs, and apply it to several basic QHM building blocks to illustrate common effects. We also discuss the role of common approximations from the literature, such as in the the secular or local Lindblad approaches, and their application within the parameter regimes in question.

In Chapter 4, we introduce a new, numerically exact protocol for computing the heat transfer and related statistics through an open system, bilinearly coupled to bosonic heat baths. This new method, the iterative full-counting statistics path integral (iFCSPI) is based on the famed iterative quasi-adiabatic path integral (iQuAPI) algorithm, and is very simple to incorporate in an existing iQuAPI code. When applied to a minimal model system we find that our new method agrees well with existing methods in their regimes of validity, but, like many path integral approaches, can be difficult to converge, notably in the long-memory (non-Markovian) and strong system-bath coupling limits. We discuss in detail the technical/analytical aspects, including the sources of certain errors introduced by Trotter splitting of the propagators, and further derive the exact form of the generating function for the heat in the “dephasing” model.
Chapter 3

Coherence in Quantum Thermal Devices

3.1 Introduction

Nanoscale classical and quantum heat machines (QHMs) can be constructed out of a few ions [234], atomic-like systems such as natural defects in diamond [235], and even one atom [236], to convert input energy into mechanical, optical, electrical, or thermal work. By utilizing non-classical resources, quantum heat machines may even perform beyond the Carnot limit [237]. Paired with exciting real-world applications, QHMs present a rich playground to investigate fundamental questions at the intersection of thermodynamics and quantum dynamics [238, 239, 240, 4, 235, 241, 242].

Of obvious importance in the study of QHMs are questions over the thermodynamic consistency of the employed open quantum systems methodologies. Projection operator methods are ubiquitous in this area [42, 43], often relying on a perturbative expansion in the system-bath coupling energy, a Markovian (fast-bath) approximation, and the neglect of coherences in the working system through the application of the so-called secular approximation. Indeed, it has been shown that certain popular quantum master equation approaches, such as the local-basis Lindblad method, may not respect the laws of thermodynamics, e.g. allowing the heat current to flow against the temperature gradient [243, 244, 245, 246, 247]. This issue is vexing enough without considering that it is not generally easy nor necessarily possible to prove that a certain approximate approach respects thermodynamic laws.

Studies of coherence and decoherence in condensed phases are ubiquitous in the open quantum systems literature. Relevant to our work are the extensive discussions around the role of quantum coherences in energy transfer [13, 14, 248] and in the operation of QHMs [9, 10, 11, 12, 249, 250, 46, 251, 252, 253, 44, 254, 255]. For a recent review from a resource theory perspective, see Ref. [256]. Questions around the role of coherences in QHMs and the thermodynamic consistency of methods are in fact intimately linked. For example, global secular quantum master equation approaches, such as the Gorini-Kossakowski-Lindblad-Sudarshan (GKLS, frequently simply “Lindblad”) equation [257, 42], neglect the effect of coherences on device operation. Local secular quantum master equations can re-include some of the effects of coherence, via a change of basis, coming at the cost of strict thermodynamic consistency [245, 247, 246]. On the other hand, nonsecular quantum master equations of the Redfield type [43] cannot in general be guaranteed to provide fully positive populations due to issues concerning
initial system-bath correlations \([258, 259, 260]\), and in general are cumbersome to treat analytically. The Redfield equation may further be exercised in a local-site basis, resulting in an improper long-time (equilibrium) state for the system \([261, 94, 262]\).

In this Chapter, we address the interplay of bath-induced coherence and decoherence processes in an analytically tractable model for a quantum absorption refrigerator (QAR) \([5]\), and further attempt to draw general conclusions on the operational role of coherences in device operation. We emphasize that we are considering device operation only in the weak system-bath coupling limit. Performance of strongly-coupled (system-bath) devices is a pursuit of a significant importance, but due to methodological constraints, is difficult to access. In Chapter 4, we present a new method which may allow one to access this strong-coupling regime.

A QAR is a continuous-cycle, non-driven (or autonomous) heat machine. It extracts heat from a cold reservoir and dumps it to a hot reservoir, assisted by heat absorbed from a so-called work reservoir. The simplest version of such a device, the three-level quantum absorption refrigerator (3lQAR) \([263]\), has been explored in great detail in the weak system-bath coupling limit. Its operating characteristics, such as power and efficiency, are easy to derive when employing Markovian quantum master equations, see e.g. Refs. \([264, 265]\). Internal system coherences disappear in the 3lQAR in the steady-state limit, and the cooling performance can approach the Carnot bound. The basic model and its extensions were recently discussed e.g. in Refs. \([266, 267, 268]\). Recent studies on QARs looked at physical realizations \([8]\), the impact of internal leaks and dissipation \([269]\), and the roles of topology \([270]\), internal couplings \([251]\), noise-induced coherence \([44]\), radiation-induced coherence \([271]\), and strong system-bath coupling effects \([272]\). Other questions of interest include the cooling performance of the QAR at maximum power \([273, 274, 265]\), and the behaviour of its current fluctuations \([275]\).

Here, in order to probe the role of steady-state coherences in the operation of QARs, we model a four-level quantum absorption refrigerator (4lQAR); in our design, the four-level working fluid is coupled to three thermal reservoirs (work, hot and cold), as well as an additional, purely decohering bath. The role of this additional bath is similar to that which has been played by the dipole cross-couplings in previous studies \([44, 276, 277]\). It allows us to observe the smooth transition from zero to maximal coherence, with the added benefit that we can estimate the robustness of the device coherence to environmental effects. This minimal model allows us to interrogate the roles of internal coupling strength, coherence and decoherence in the device operation. Furthermore, using the 4lQAR model we identify and diagnose the shortcomings of secular master equations in the context of QHMs.

To help us understand the operation of the 4lQAR, we analyse two simpler, three-level model systems: the V energy transfer system (VETS) and the 3lQAR. The VETS, a generalization of the well-studied V-system \([278, 276, 279, 277, 254]\), describes energy exchange between two thermal reservoirs. It gives us insight on methodological issues and the role of coherence in the transport behaviour. The 3lQAR forms the basic template for a QAR, which we use to examine the behaviour of the more compound 4lQAR.

There has been an active study into coherence effects in QHMs, see for example \([9, 10, 11, 12, 249, 250, 46, 251, 252, 253, 44, 254, 271]\). Here, we provide a rigorous and thorough analysis of the problem within a model system, by studying the interplay between a wide range of internal system couplings and decoherence effects, which largely determine the device performance. Our examination is grounded in a microscopic quantum mechanical equations of motion derived without heuristics. Discussions of methodological aptitude of secular master equations have largely focused on problems of energy transport
and especially recently, on the local vs. global issue rather than the secular vs. nonsecular problem [262, 247, 246]. In our discussion below we address these questions in the context of both energy transfer and heat to work conversion, and further develop and utilize a numerical technique which will assist us in understanding the role of coherence in quantum heat machines more generally.

Briefly, the central observations of this Chapter are: (i) The presence of steady-state coherences in the 4lQAR model degrade the cooling current, but not the efficiency, which in fact is largely unaffected by internal coherences. (ii) The cooling performance of the model can be explained based on the behaviour of its building blocks (the VETS and 3lQAR), allowing us to identify key mechanisms in compound models. (iii) The popular secular approximation provides nonphysical predictions for energy transfer and cooling when applied outside its regime of applicability. While this observation is not overly surprising, it emphasizes the importance of a judicious application of open quantum system techniques in the area of quantum thermodynamics. (iv) Through numerical studies in a so-called “secular basis”, we can understand the effects of system coherences from a more easily interpreted, purely “classical” kinetic lens.

3.2 Models

The total Hamiltonian of an open quantum system coupled to multiple (counted by \( \alpha \)) reservoirs includes a system Hamiltonian \( \hat{H}_S \), thermal reservoirs \( \hat{H}_\alpha \), and system-bath coupling terms

\[
\hat{H} = \hat{H}_S + \sum_\alpha \hat{H}_\alpha + \sum_\alpha \hat{S}_\alpha \otimes \hat{B}_\alpha.
\]  

(3.1)

For simplicity, the reservoirs are assumed to comprise collections of independent harmonic oscillators with creation operator \( \hat{b}_{q,\alpha}^\dagger \) of mode \( q \) with frequency \( \omega_{q,\alpha} \) in the \( \alpha \) bath,

\[
\hat{H}_\alpha = \sum_q \hbar \omega_{q,\alpha} \hat{b}_{q,\alpha}^\dagger \hat{b}_{q,\alpha}.
\]  

(3.2)

The bath operator \( \hat{B}_\alpha \) describes displacements of bath oscillators from equilibrium,

\[
\hat{B}_\alpha = \sum_q \lambda_{q,\alpha} \left( \hat{b}_{q,\alpha}^\dagger + \hat{b}_{q,\alpha} \right).
\]  

(3.3)

\( \hat{S}_\alpha \) is a system operator, which is specific to each bath. Before studying the 4lQAR, we examine two related, simpler, three-level models. The V energy transfer system which describes energy exchange between two heat baths mediated by a three-level quantum system, and the three-level QAR which acts as a refrigerator with null steady-state coherences. Using a weak-coupling quantum master equation, we investigate the operation of these two models. Equipped with this background, we are able then to rationalize the properties of the four-level QAR.

3.2.1 V energy transfer system

The V and \( \Lambda \)-type systems, with three atomic or molecular levels interacting with coherent or incoherent reservoirs (representing e.g. electromagnetic radiation fields) have been intensively investigated in quantum optics. In particular, the prospect of generating long-lived coherences in a quantum system has
attracted much attention, with applications to lasing, photovoltaic devices and light harvesting systems [278, 276, 279, 277]. While the dynamics of populations and coherences in V and Λ systems has been investigated in detail, so far, few studies considered the nature of energy transport across such systems [280].

We study the behaviour of the V system out of equilibrium in the steady-state limit. The model includes three levels and three reservoirs, \( \alpha = h, c, d \), see Fig. 3.1. The hot (h) and cold (c) thermal baths exchange energy—mediated by the system. The so-called dephasing (d) bath is responsible for pure decoherence effects. In the site or “local” basis the quantum system includes a ground state \(|1\rangle\) and two excited states, \(|a\rangle\) and \(|b\rangle\), which are made degenerate at energy \(\theta\). These states are coherently coupled, with a coupling strength \(g\),

\[
\hat{H}_S = \epsilon_1 |1\rangle\langle 1| + \theta (|a\rangle\langle a| + |b\rangle\langle b|) + g (|a\rangle\langle b| + |b\rangle\langle a|).
\] (3.4)

The coupling energy \(g\) can be made arbitrarily large or small. In what follows, we set the reference energy at \(\epsilon_1 = 0\). The system \(\hat{S}\) operators mediate energy exchange processes and decoherence effects from the environment,

\[
\hat{S}_h = |1\rangle\langle a| + h.c., \quad \hat{S}_c = |1\rangle\langle b| + h.c.
\]

\[
\hat{S}_d = |a\rangle\langle b| + h.c.
\] (3.5)

In the zero decoherence picture (no d bath), energy is transferred between the hot and cold baths as long as \(g \neq 0\). In the site basis, we picture energy flow as follows: The hot bath excites the \(|a\rangle\) site, which transfers population to the \(|b\rangle\) site through the coherent coupling \(g\). Since the population of \(|b\rangle\)—relative to the ground state—exceeds the equilibrium value as dictated by the cold bath to which it is coupled, energy is released to the cold bath. In the system energy basis, the Hamiltonian and the \(\hat{S}_\alpha\) operators
transform into
\[ \hat{H}_S = \epsilon_1 |1\rangle\langle1| + (\theta - g) |2\rangle\langle2| + (\theta + g) |3\rangle\langle3|, \]
(3.6)
and
\[
\begin{align*}
\hat{S}_c &= \frac{1}{\sqrt{2}} (|1\rangle\langle3| - |1\rangle\langle2| + \text{h.c.}) \\
\hat{S}_h &= \frac{1}{\sqrt{2}} (|1\rangle\langle2| + |1\rangle\langle3| + \text{h.c.}) \\
\hat{S}_d &= |3\rangle\langle3| - |2\rangle\langle2|. \\
\end{align*}
\]
(3.7)

Note the differing signs in \( \hat{S}_c \) and \( \hat{S}_h \). The role of the \( d \) bath is to directly decohere the energy basis dynamics. In the site basis, it mediates the transition between degenerate excited states (giving us a hint as to how the VETS will behave when the \( d \) bath is turned on). Since the excited states are degenerate, the \( d \) bath does not provide energy to the system (in the present weak coupling approach). This is not, however, a limitation of our analysis. One can always write down an energy-conserving decoherence operator between two states of the form given in Eq. (3.7), though the local-basis representation of this operator will be different.

In the energy picture, both excited states are coupled to the ground state via both the hot and cold baths. One may view the model now as having two spins sharing a common ground state, with each spin individually but not independently facilitating energy transfer between the two heat baths. It is also clear now that the \( d \) bath is responsible for decoherence, without energy exchange. As we shall see, since both effective spins are coupled to the same heat baths, coherences are generated in the system energy basis.

### 3.2.2 Three-level QAR

A simple design of an autonomous quantum absorption refrigerator consists of a three-level system as the working medium and three independent thermal reservoirs [5, 265], see Fig. 3.2. Each transition between a pair of levels is coupled to one of the three heat baths, \( c, h \) and \( w \), where \( T_w > T_h > T_c \). In the steady-state limit, the work bath provides energy to the system, allowing the extraction of energy from the cold bath, to be dumped into the hot reservoir. The opposite heating process from the hot bath to the cold can be controlled by manipulating the frequencies of the system. The three-level QAR is described by the system Hamiltonian (\( \epsilon_1 = 0 \))
\[
\hat{H}_S = \theta_c |2\rangle\langle2| + \theta_h |3\rangle\langle3|,
\]
(3.8)
and we set \( \theta_w = \theta_h - \theta_c \). The \( \hat{S}_\alpha \) operators are
\[
\begin{align*}
\hat{S}_c &= |1\rangle\langle2| + |2\rangle\langle1|, & \hat{S}_w &= |2\rangle\langle3| + |3\rangle\langle2| \\
\hat{S}_h &= |1\rangle\langle3| + |3\rangle\langle1|. \\
\end{align*}
\]
(3.9)
A decohering bath is not included in this example; as we discuss below in Sec. 3.3, in the weak coupling limit the system’s dynamics is naturally fully secular, with decoupled populations and coherences.
3.2.3 Four-level QAR

The working medium of the 4lQAR comprises four quantum levels. It further includes three heat baths \((h, c, w)\), as well as a decohering bath \(d\), see Fig. 3.3. In the site basis, the system’s Hamiltonian is

\[ \hat{H}_S = \epsilon_1 |1\rangle\langle 1| + \theta_c (|a\rangle\langle a| + |b\rangle\langle b|) + \theta_h |4\rangle\langle 4| + g (|a\rangle\langle b| + |b\rangle\langle a|). \quad (3.10) \]

We again set the reference energy at \(\epsilon_1 = 0\). The system’s operators \(\hat{S}_\alpha\) are

\[ \hat{S}_c = |1\rangle\langle b| + |b\rangle\langle 1|, \quad \hat{S}_w = |a\rangle\langle 4| + |4\rangle\langle a| \]
\[ \hat{S}_h = |1\rangle\langle 4| + |4\rangle\langle 1|, \quad \hat{S}_d = |a\rangle\langle b| + |b\rangle\langle a|. \quad (3.11) \]

After diagonalisation of \(\hat{H}_S\) we receive

\[ \hat{H}_S = (\theta_c - g) |2\rangle\langle 2| + (\theta_c + g) |3\rangle\langle 3| + \theta_h |4\rangle\langle 4|, \quad (3.12) \]

and

\[ \hat{S}_c = \frac{1}{\sqrt{2}} (|1\rangle\langle 3| - |3\rangle\langle 1| + h.c.), \]
\[ \hat{S}_w = \frac{1}{\sqrt{2}} (|2\rangle\langle 4| + |4\rangle\langle 2| + h.c.) \]
\[ \hat{S}_h = |1\rangle\langle 4| + |4\rangle\langle 1|, \quad \hat{S}_d = |3\rangle\langle 3| - |2\rangle\langle 2|. \quad (3.13) \]

This model is obviously quite complex. Nevertheless, its cooling performance can be explained by studying energy transfer in the VETS model and the cooling behaviour of the 3lQAR. A similar model, lacking
the dephasing bath, has been explored in the past to address questions of heat leaks and endoreversibility of heat engines [269]. Nevertheless, this study was limited to the secular limit, where populations and coherences are decoupled. In Sec. 3.3 we extend this analysis to cover device operation under the combined effects of internal coupling $g$ and coherence effects, while highlighting methodological issues relevant to this setup.

3.3 Method and Operational Characteristics

We study the various systems’ dynamics using the Redfield equation, a projection operator method [43]. This method is derived based on several assumptions: (i) The quantum system weakly couples to its environment, thus the interaction with the different baths is captured within a second order perturbation theory. (ii) The reservoirs are Markovian, and (iii) the initial condition is assumed to be system-bath factorized, with each bath prepared in a canonical thermal state according to its temperature. It is important to note that the Redfield equation in general couples coherences, which are the off diagonal elements of the reduced density matrix (RDM) $\sigma$, to populations, the diagonal elements of $\sigma$. The Redfield equation is commonly implemented in the system energy basis, though site basis implementations were also tested. When the inter-site coupling $g$ becomes large, such a local quantum master equation provides an incorrect long time solution, e.g. showing deviations from the thermal equilibrium state [247, 246, 243, 245, 262]. For a discussion in the context of charge transfer, see for example Refs. [261, 94].

In the energy basis, the time evolution of $\sigma$ obeys the following equation of motion [43] in the
Chapter 3. Coherence in Quantum Thermal Devices

65

Schrödinger representation ($\hbar \equiv 1$),

\[
\dot{\sigma}_{mn}(t) = -i\omega_{mn}\sigma_{mn}(t) - \sum_{\alpha, j,k} \left[ R^{\alpha}_{mj,jk}(\omega_{kj})\sigma_{kn}(t) + R^{\alpha*}_{nk,kj}(\omega_{jk})\sigma_{mj}(t) - [R^\alpha_{kn,mj}(\omega_{jm}) + R^\alpha_{jm,nk}(\omega_{kn})]\sigma_{jk}(t) \right].
\]

(3.14)

Here, $\omega_{mn} = \epsilon_m - \epsilon_n$ are frequencies of the system. The reservoirs act in an additive manner, a direct outcome of the weak system-bath coupling approximation. The dissipation terms in Eq. (3.14) are

\[
R^{\alpha}_{mn,jk}(\omega) = S^{\alpha}_{mn}S^{\alpha}_{jk} \int_0^\infty d\tau e^{i\omega\tau} \langle \hat{B}_{\alpha}(\tau) \hat{B}_{\alpha} \rangle = S^{\alpha}_{mn}S^{\alpha}_{jk} (\Gamma_{\alpha}(\omega) + i\Delta_{\alpha}(\omega)),
\]

(3.15)

with matrix elements $S^{\alpha}_{mn} = \langle m|\hat{S}_{\alpha}|n \rangle$. The average is performed with respect to the canonical thermal state (initial condition) of the $\alpha$ bath. While these $R$ terms, in general, are complex numbers, in what follows we neglect the imaginary part $\Delta$ since it essentially corresponds to energy shifts. For harmonic baths and bilinear coupling the real part of the dissipator is

\[
\Gamma_{\alpha}(\omega) = \begin{cases} 
\frac{1}{2}J_{\alpha}(\omega)n_{\alpha}(\omega) & \omega < 0 \\
\frac{1}{2}J_{\alpha}(\omega)[n_{\alpha}(\omega) + 1] & \omega > 0.
\end{cases}
\]

(3.16)

Here, $J_{\alpha}(\omega) = 2\pi \sum_q |\lambda_{q,\alpha}|^2 \delta(\omega_{q,\alpha} - \omega)$ is the spectral density function of the $\alpha$ bath. We assume an ohmic function, $J_{\alpha}(\omega) = \gamma_{\alpha} \omega e^{-|\omega|/\omega_c}; \gamma_{\alpha}$ is a dimensionless interaction parameter. The cutoff frequency $\omega_c$ is the largest energy scale in the problem. $n_{\alpha}(\omega)$ is the Bose-Einstein occupation function characterized by the temperature of the $\alpha$ bath, $T_{\alpha} = 1/\beta_{\alpha}$ ($k_B \equiv 1$). Note that the temperature of the decohering bath $d$ affects the magnitude of the decoherence rate, yet the $d$ bath does not exchange energy with the system.

While the Redfield equation in general couples the dynamics of populations and coherences, one may invoke the so-called secular approximation and decouple these elements. This approximation can be justified if the natural (coherent) timescale of the system is short relative to its relaxation time—induced by the thermal baths. In some cases, a system will realize finite and relevant system coherences which decay to zero in the steady-state, therefore rationalising a secular approximation only in the long time limit. Furthermore, the equations can be effectively “secularized” if there is strong decoherence process, $\gamma_d \gg \gamma_{h,c,w}$.

In what follows we study the dynamics of the three different models, the VETS, 3QAR, and 4QAR by exercising the Redfield equation in the energy basis (diagonal $\hat{H}_S$). We further compare results to the secularized behaviour (whether justified or not), so as to expose the role of coherences. Appendix C includes the full and secularized Redfield equations for the VETS model, and a discussion over their relative applicability. It should be noted that the Redfield equation is secular by construction for the 3QAR.

To calculate the energy current we organize the Redfield equation as

\[
\dot{\sigma} = -i[\hat{H}_S, \sigma(t)] + \sum_{\alpha} D_{\alpha}\sigma(t),
\]

(3.17)
with the dissipaters $\mathcal{D}_\alpha$ accounting for the effects of each of the baths. In the long time limit, $\dot{\sigma} = 0$, we obtain the steady-state solution $\sigma_{ss}$. Considering the change of the system’s energy, $d\langle \hat{H}_S \rangle / dt = \text{Tr}[\hat{H}_S \dot{\sigma}]$ (recall that the Hamiltonian does not depend on time) any energy exchange corresponds to heat flow. With that, we get the standard formula for the (steady-state) rate of heat exchange with the $\alpha$ reservoir,

$$J_q^\alpha = \text{Tr}[\hat{H}_S \mathcal{D}_\alpha \sigma_{ss}].$$

Below we solve equation (3.14) in the long time limit and find $\sigma_{ss}$. We then calculate the heat current from Eq. (3.18).

### 3.3.1 Energy flow in the VETS model

![Figure 3.4: Heat current in the VETS model. (a)-(d) Solution of the Redfield equation with an increasing decoherence strength between the excited states. (e) When decoherence is sufficiently strong, we retrieve the secular behaviour. $\gamma \equiv \gamma_{h,c} = 0.002$, $\omega_c = 50$, $T_h = 0.15$, $T_c = 0.1$, $T_d = 0.12$.](image)

The Redfield equation of the VETS model is presented in Appendix C and analytic results for the energy current are derived under the secular approximation. While one can derive analytic results for the nonsecular steady-state current, the expressions are quite cumbersome for our applications. All of the results shown in our figures were therefore computed numerically from the full Redfield equation Eq. (3.14).

Fig. 3.4 displays the energy current, from the hot bath to the cold one, as a function of the energy gap $\theta$ and the coherent coupling $g$. We further vary the decoherence rate $\gamma_d$ throughout panels (a)-(e). The following observations can be made: (i) In the absence of a decohering bath the heat current approaches zero when $g$ becomes very small, which is the expected result. (ii) As we turn on decoherence, the two effective qubits (the pairs 1-2 and 1-3) begin to disentangle from each other. Energy then flows between the two heat baths even at small $g$. The large $\gamma_d$ limit in fact corresponds to the secular behaviour, as we show in panel (e). (iii) The energy current is highly non-monotonic as a function of $g$. (iv) In our parameters, secularization takes place once $\gamma_d > \gamma_{h,c}$. (v) The behaviour of the energy current as a function of the spacing $\theta$ is intuitive, and it follows trends observed for the spin-boson model [281]: When the gap is small, the energy current increases with $\theta$ since more energy is transferred per quantum. However, once we further increase the gap, $\theta \gtrsim 1/\beta_\alpha$, thermal occupation at relevant-resonant frequencies is suppressed, and the heat current rapidly drops.
When coherences are neglected, we are able to reach a simple closed-form expression for the energy current, see Appendix C for details. In the asymptotic limit of \( g \rightarrow 0 \) we get
\[
J_q = \gamma \theta^2 \frac{n_h(\theta) - n_c(\theta)}{3n_c(\theta) + 3n_h(\theta) + 2},
\]
where \( \gamma \equiv \gamma_{h,c} \), and \( \gamma_d \gg \gamma \). The current is linear in the coupling parameter \( \gamma \), as expected from a weak coupling system-bath description. The product of the transferred quantum, which is equal to the transition frequency, by the (ohmic) spectral function leads to the quadratic dependence with \( \theta \). Most notably, the current does not vanish at vanishing coupling \( g \). Without the explicit inclusion of \( \gamma_d \), the non-vanishing current \( J_q(g \rightarrow 0) \neq 0 \) simply illustrates the breakdown of the secular approximation at small \( g \) (panel (e)); in the local-site basis, \( J_q(g \rightarrow 0) \rightarrow 0 \). Nevertheless, once \( \gamma_d \) is included this finite current is physically attributed to the action of the decohering bath. It couples the \( |a\rangle \) and \( |b\rangle \) states in the site basis, allowing for energy flow, see Eq. (3.4).

\[
\begin{align*}
\text{Figure 3.5:} & \quad (a) \text{Contour plot of current in the VETS model as a function of the inter-site coupling } g \text{ and decoherence strength } \gamma_d. \\
& \quad (b) \text{Demonstration of a non-monotonic } J_q \text{ vs. } \gamma_d \text{ behaviour. } \gamma \equiv \gamma_{h,c} = 0.002, \omega_c = 50, T_h = 0.15, T_c = 0.1, T_d = 0.12, \theta = 0.5.
\end{align*}
\]

In Fig. 3.5 we display the behaviour of the current as a function of \( g \) and \( \gamma_d \). Generally, the current increases as we suppress coherences in the system. Nevertheless, we reveal an intriguing regime, with \( J_q \) dropping as we increase \( \gamma_d \). Combining internal couplings with decoherence can therefore impact energy transfer in a highly non-trivial manner.

The behaviour of the current as a function of \( g \) is quite complex, and we explain it in Figs. 3.6-3.7. We further display in Fig. 3.7 the currents \( J_q^\pm \), calculated separately for each effective spin (of frequency \( \theta_{\pm} = \theta \pm g \)). Relevant energy scales in the problems are \( \gamma \theta \), which dictates the hot and cold baths-induced decay rates, \( \gamma_d \theta \), which determines the decoherence rate, the coherent coupling \( g \), the bare energy \( \theta \), the temperatures and the reservoir cutoff frequency, which is assumed large. In our simulations, \( \theta \gamma \ll 1 \). Focusing on the \( \gamma_d = 0 \) case (black line) in Fig. 3.6, we identify several regimes.

(i) Ultra small coupling, \( g \ll \gamma \theta \). In this regime, the heat current follows a quadratic scaling \( J_q \propto g^2 \). Fig. 3.7 clearly demonstrates that steady-state coherences in the system are responsible for the low-\( g \) behaviour, which deviates from the secular result. At ultra small \( g \), the population of levels 2 and 3 is essentially equal, and the magnitude of the coherence is significant. (ii) Small coupling regime \( g \sim \gamma \theta \).
Figure 3.6: Heat current in the VETS model as a function of the inter-site coupling $g$. Parameters are the same as in Fig. 3.4, with $\theta = 0.5$, $\gamma \cdot \theta = 0.001$.

The current grows with $g$ and then it saturates. In parallel, the coherence between the excited states drops to zero, and the populations of levels 2 and 3 begin to deviate. In this regime, $(\theta_+ - \theta_-)/\theta$ grows, eventually justifying the secular approximation. (iii) Intermediate coupling, $\gamma \theta < g < \theta$. The heat current quickly rises—then drops. In this regime, the states 2 and 3 are clearly separated, thus the role of coherence/decoherence is inconsequential. Furthermore, while $\theta_+$ is too large to support energy flow, as it exceeds the thermal energy, heat can be readily transferred between the two baths through the $\theta_-$ spin. Nevertheless, once $\theta_-$ diminishes, $j_{\theta_-} \to 0$, and the total current is suppressed. (iv) Strong coupling, $\theta < g < 2\theta$. In this regime the V picture does not hold any longer, since the eigenstate $|2\rangle$ lies below $|1\rangle$. Nevertheless, we can study energy flow in the model. We find that as we continue to increase $g$, the total energy current grows, and it is transferred through the $\theta_-$ spin. (v) Ultra strong coupling $g \gg \theta, 1/\beta_\alpha$. The current quickly drops with $g$ since both transitions, $\theta_\pm$, are too large to support heat flow, with the spin gaps exceeding the thermal energy. We confirmed that these trends are general, showing up with other choices of $\theta$ and $\beta_\alpha$.

The V-type model examined here transfers thermal energy between two heat baths, but it does not operate as a machine since it is missing an additional work source. However, an engine or a cooler can be realized with a V-type model by e.g. periodically driving the transition frequency $\theta$. Such a driven scenario, yet with a perfect degeneracy of excited states in the energy basis, was examined in Ref. [253].

### 3.3.2 Four-level QAR with coherences

Equipped with our understanding of energy flow in the VETS, we are ready to examine the operation of quantum absorption refrigerators. In Appendix C, we first review the behaviour of the 3lQAR model. As we show below, this model can assist in rationalizing the behaviour of the 4lQAR.
We emphasize that in this work we are mostly interested in understanding the cooling performance of the 4QAR at small \( g \), when internal coherences survive and impact its behaviour. Once \( g \sim \gamma_\theta \), with the internal couplings being comparable to the relaxation rate constants to the heat baths, the system’s coherences are lost and the behaviour becomes secular. This incoherent-secular situation was nicely explored in Ref. [269], where different mechanisms responsible for irreversibility in QARs were classified: internal dissipation, which corresponds to the competition between cooling pathways that are optimized at different parameters, and heat leaks, a direct heat exchange between the work and cold baths.

**Cooling Current.** Based on the Redfield equation, we simulate the system’s dynamics and the steady-state energy exchange with the different baths. The cooling current of the 4QAR is presented in Fig. 3.8, where we display only the cooling region, \( J^c_q > 0 \). Overall, we observe trends similar to the VETS. First, in panel (a) we show that in the absence of decoherence processes, \( \gamma_d = 0 \), energy transfer ceases between the states \( |a\rangle \) and \( |b\rangle \) at small \( g \), and the device cannot function continuously. As we increase the decoherence rate constant in panels (b)-(d), we gradually recapture the secular behaviour as depicted

---

Figure 3.7: (a) Current, (b) steady-state population and (c) coherences in the VETS model at \( \gamma_d = 0 \). Parameters are the same as in Fig. 3.6.
Figure 3.8: Cooling current in the 4lQAR. (a)-(d) Solution of the Redfield equation with an increasing decoherence rate between the intermediate states. (e) When $\gamma_d$ is sufficiently strong, we retrieve the secular behaviour. $\gamma \equiv \gamma_{c,h,w} = 0.002$, $\omega_c = 50$, $T_w = 1$, $T_h = 0.15$, $T_c = 0.1$, $T_d = 0.12$, $\theta_h = 1$.

in panel (e), with a large cooling current persisting even at vanishing $g$. The cooling behaviour in the 4lQAR is thus analogous to the transport characteristics of the VETS model.

When comparing the cooling current of the 4lQAR to the 3lQAR, one can show analytically that in the secular, low $g$ limit (when the 4lQAR cooling current is observed to be maximal), the 3lQAR outperforms the 4lQAR for any choice of parameters. One can observe this by simple division of Eqs. (C.9) and (C.19).

We further confirmed (not shown) that the behaviour of the cooling current as a function of $g$ and $\gamma_d$ closely follows trends observed in Fig. 3.5. This correspondence includes the small domain of non-monotonicity, with the cooling current slightly decreasing with an increase of $\gamma_d$ at a particular range of $g$.

Figure 3.9: COP of the 4lQAR for $\gamma_d = 0$ and $\gamma_d/\gamma = 100$ (overlapping). Parameters are the same as in Fig. 3.8. The dashed line corresponds to the Carnot bound for a cooling machine, $\eta_C = \frac{\beta_h - \beta_w}{\beta_h - \beta_n}$, which equals 1.7 in our parameters.
Figure 3.10: (a) COP vs. cooling power for the 4lQAR at $\gamma_d = 0$ while increasing $g$ from $10^{-3}$ to 0.4 as we move inward. The black dashed line corresponds to the secular limit at vanishing $g$, showing an endoreversible operation. To generate these plots, the frequency $\theta_c$ was varied within the cooling window. (b) Maximum cooling current and (c) COP at that value, optimized at every point with respect to $\theta_c$. Parameters are the same as in Fig. 3.8.

Cooling window. In Appendix C, we derive closed-form expressions for the cooling current and cooling condition for the 3lQAR and 4lQAR models respectively—under the secular approximation. In the limit of small $g$ and large $\gamma_d$, the cooling window for the 4lQAR model is

$$\frac{\theta_c}{\theta_h} \leq \frac{\beta_h - \beta_w}{\beta_c - \beta_w},$$

which is identical to the behaviour of the 3lQAR. In the parameters of Fig. 3.8, this “secular” cooling window is defined by $\theta_c < 0.63$. In contrast, when $g$ approaches level spacing, $g \sim \theta_c$, the cooling window of the 4lQAR extends beyond the $\theta_c = 0.63$ bound, as can be seen by the tail of the cooling window in Fig. 3.8, developing at large $g$ and large $\theta_c$.

Coefficient of cooling performance. We define the coefficient of cooling performance (COP) as $\eta \equiv J^c_J^w$, and display it in Fig. 3.9. In what follows we sometimes refer to the cooling COP as “efficiency”, though it can exceed unity. Unlike the cooling current, we find from simulations that the COP does not depend on $\gamma_d$. Furthermore, it excellently follows the $\eta = \theta_c/\theta_w$ curve, as long as $g$ is small and $\theta_c,w$ are maintained as a meaningful representation of the spacing. When $g = 0.1 - 0.3$ the different cooling pathways, through $\theta_c \pm g$, are differentiated. The behaviour in this regime agrees with Ref. [269]

In our model, coherences play an important role in dictating the magnitude of the cooling current. However, the cooling COP largely is independent of internal coherences. In contrast, it is obvious that the efficiency at maximal cooling power depends on the internal coupling $g$ and the decoherence rate, as we show in Fig. 3.10. Our results here agree with [269]. As $g$ increases, the endoreversibility of the engine is lost due to internal dissipation and heat leaks; the refrigerator performance suffers significantly in both power and efficiency, until we exit the cooling window entirely.
In panels (b) and (c) of Fig. 3.10 we examine the role of decoherence on the performance. Panel (b) illustrates the dramatic damping of the current at low $\gamma_d$ and $g$ (optimized with respect to $\theta_c$), as observed previously in Fig. 3.8. Panel (c) displays the COP at maximal cooling current. Since at strong decoherence the cooling behaviour of the 4lQAR corresponds to that of the 3lQAR, under the ohmic dissipation the COP at maximal power should be tightly upper bounded by $\eta_C/2$ [265, 272], which is about 0.8 in our parameters. Obviously, our parameters are not optimized for performance.

Generality of our observations. How universal are our observations? First, considering the present level scheme one could assume distinct baths (e.g., collections of spins, fermions, bosons) as well as different spectral density functions (beyond ohmic). Focusing for simplicity on harmonic environments, we point out that our results in the secular limit, as detailed in Appendix C, are given in terms of rate constants, before making use of a particular model of the spectral density function, $J(\omega)$. This allows us to readily conclude that choices made for the spectral density functions of the baths neither impact the cooling window, which is dictated by the temperatures and the system energies, nor the cooling efficiencies. The details of $J(\omega)$ manifest themselves in the actual value of the cooling current and in the efficiency at maximal cooling current, as was also demonstrated in Ref. [265]. In the weak coupling limit, generalisations beyond harmonic baths are standard [232].

More broadly, we find that in our analysis of the 4lQAR coherences act to suppress the cooling current when $g \rightarrow 0$. Other constructions for a QAR, e.g. with two fully degenerate levels and correlated noise lead to an enhancement of the current in certain regimes due to coherence [44]. These seemingly conflicting results are reminiscent of the rich observations of constructive and destructive interference effects in molecular transport junctions like those studied in Part I, which may delicately depend on the molecular electronic structure and connectivity to the leads [282, 283, 284].

### 3.3.3 Experimental realizations

The energy transfer models described here are generic, and may be realized in atomic or molecular systems [234]. Moreover, one could envision that the states of the system may represent a coarse grained electronic or excitonic states in nanoscale electronic or amorphous materials. Energy conversion systems were studied in e.g. Refs. [285, 286] based on a classical network picture using a kinetic scheme. Building on this graph method, which is purely classical, we can imagine a network that combines both classical (kinetic) and quantum (coherent) transitions.

The VETS model of Fig. 3.1 could represent for example a degenerate two-site (termed donor-acceptor) electronic system embedded between two electrodes, see Fig. 3.11(a). The electrodes are maintained at the same chemical potentials but at different temperatures, $T_h$ and $T_c$. In this system, charge carriers transfer energy. The three states in Fig. 3.1 correspond to empty donor and acceptor sites $|1\rangle \leftrightarrow |00\rangle$, a single electron residing on the donor site $|a\rangle \leftrightarrow |10\rangle$ and a single electron placed on the acceptor site $|b\rangle \leftrightarrow |01\rangle$. Charge transfer (thus energy flow) between the two metals is driven by the temperature bias, and it proceeds through the coherent tunnelling element $g$. The overall net process can be summarized as follows, $|00\rangle \overset{\Gamma_h}{\rightarrow} |10\rangle \overset{g}{\rightarrow} |01\rangle \overset{\Gamma_c}{\rightarrow} |00\rangle$. Alternatively, one could realize the VETS model with two coherently coupled degenerate qubits that mediate energy flow between two heat baths through their excitation and de-excitation, see e.g. Refs. [287, 288].

The 3lQAR utilizes input heat from the work reservoir to extract energy from a cold bath. As we show in Fig. 3.11(b), the model can be realized with a two-site electronic system (or two qubits), similarly to the VETS. However, in the 3lQAR model the donor and acceptor sites are no longer degenerate, with
Figure 3.11: Schemes of nanoscale energy conversion devices that can be captured with our generic models. (a) The VETS model can be realized by a conducting junction with two degenerate electronic states. (b) The 3lQAR may correspond to a non-degenerate electronic junction, with the work bath responsible for internal transitions. (c) The 4lQAR can represent a photovoltaic cell. Heat absorbed from the work reservoir is used to transfer carriers—thus energy—from the cold metal to the hot metal. The red, blue and orange arrows represent energy exchange processes with the hot, cold and work heat baths. The effect of the decoherence bath is omitted for simplicity, but it can be further included.

the energy of the donor state placed below the acceptor. As well, in this scenario all transitions are kinetic. The cooling process corresponds to $|00\rangle \xrightarrow{\Gamma_c} |10\rangle \xrightarrow{\Gamma_c} |01\rangle \xrightarrow{\Gamma_c} |00\rangle$.

The 4lQAR can be realized within a photovoltaic cell, with the current flowing between the two metals being assisted by the absorption of solar energy ($T_w$). The system comprises two degenerate species, donor and acceptor, each represented by a ground state and an excited state (HOMO and LUMO, respectively, in the language of molecular orbitals). We assume that the donor is only coupled to the left (cold) metal, while the acceptor is coupled to the right (hot) lead. Furthermore, the acceptor is excited by the solar energy, allowing energy to flow against the temperature difference. The model is sketched in Fig. 3.11(c). The four states of the 4lQAR correspond to an empty system $|1\rangle \leftrightarrow |00\rangle$, the donor specie in the HOMO state with an empty acceptor site $|b\rangle \leftrightarrow |0\rangle$, the complementary state with the charge localized on the acceptor site $|a\rangle \leftrightarrow |0\rangle$, and the highest energy state, with the acceptor in the excited (LUMO) state $|4\rangle \leftrightarrow |0\rangle$. The $|a\rangle$ and $|b\rangle$ states are coherently coupled with a tunnelling element $g$. A cooling process corresponds to the cycle $|00\rangle \xrightarrow{\Gamma_w} |\downarrow\rangle \xrightarrow{\Gamma_w} |0\rangle \xrightarrow{\Gamma_w} |0\rangle \xrightarrow{\Gamma_w} |00\rangle$. Alternatively, the 4lQAR can be realized by three sequential qubits. Excitations transfer coherently between the first two degenerate qubits, and incoherently (assisted by the work bath) between the second and third non-degenerate qubits.
The multi-level models of heat machines explored in this work can therefore represent a variety of
devices, such as photovoltaic cells and thermoelectric junctions, while making use of both classical-kinetic
and quantum-coherent resources.

Most proposals for experimental realizations of quantum heat machines are based on single or small
numbers of atoms or ions, or other atomic and molecular models e.g. for qubits, wherein transitions
between energy levels can be controlled by an optical process. Due to the difficulty in realizing even the
most basic nonequilibrium setups, which require interactions with multiple heat baths, research in this
direction has so far focused on capturing the basic thermodynamic predictions of the QHM literature in
simple systems [289]. To confirm the predictions made in this work, we would first propose not to build
the full 4lQAR, but rather the simpler VETS.

Our main findings on the role of coherence in a nonequilibrium energy-transfer device all follow from
the behaviour of the VETS, which the 4lQAR follows in all key aspects. V and Λ-type systems have
been studied for some time in the quantum optics literature [290]. Recently, a detailed experimental
proposal was put forward [291] for the construction of a V-system with controllable excited state splitting,
bathed in an incoherent radiation field. The goal of this setup has been to study transient noise-induced
coherences, a close relative of the nonequilibrium steady-state coherences we predict and employ in our
system. With the further addition of a second radiation field at a different temperature, and some
scheme to measure the heat current, such a setup may work well to confirm our key predictions on the
VETS, and by extension on the role of coherence in general.

All of our predictions are based on the fundamental assumptions of Markovian Redfield theory:
weak system-bath coupling and a memoryless bath. In theory this broadly means that the system-
bath coupling parameter is small compared to the frequencies of the closed subsystem, and the bath
autocorrelation time is the shortest timescale in the problem. We generally expect in this regime that the
system-bath coupling parameter in the equation for an observable like power should be simply factored
out, giving a prefactor to some order. In experimental practice, for example in the proposal noted above
[291], this means that the system should be irradiated by a low-intensity incoherent light source, such
as sunlight.

3.3.4 4lQAR summary

We studied the impact of coherences on the cooling performance of generic multi-level QHMs with
steady-state noise-induced coherences. We were able to use what we learned from the VETS and 3lQAR
to rationalize the behaviour of the 4lQAR, where we observed the following:

(i) Generally, the presence of coherences in the 4lQAR degrade its cooling performance. Introducing
decohherence essentially “secularizes” the coherent dynamics, by suppressing the off-diagonal elements
of the steady-state, energy basis reduced density matrix. As a result, at strong decoherence we re-capture
the secular dynamics for any internal coupling $g$, and undo the negative effects of coherences.

(ii) Varying the internal coupling $g$ within the system results in rich behaviour as the QAR crosses
between different regimes of operation. Moreover, the interplay of internal coupling in the system and
decoherece rate reveals a small non-monotonic effect of coherence in the device power.

(iii) The cooling efficiency of the refrigerator, defined as the ratio of extracted heat from the cold bath
over input heat from the work reservoir, does not depend on the survival of steady-state coherences in
the system. In fact, the cooling efficiency of the 4lQAR precisely follows the behaviour of the incoherent
3lQAR model when the internal coupling, $g$, is small. In contrast, the efficiency at maximal cooling
current is quite sensitive to the magnitude of the internal couplings and therefore can be affected and manipulated by internal coherences.

(iv) The Redfield equation, despite its known pathologies regarding positivity, is well-behaved at steady-state across a very wide parameter regime explored in this work, and it gives numerical and analytical insight missing in other approaches. The global and local secular quantum master equations catastrophically fail outside their respective regimes of applicability (large and small $g$ respectively). This fact is not surprising, yet it is important to visualize this failure in the context of QHMs. Specifically, we found that when the global secular equation is applied to a fundamentally nonsecular system it provides erroneous predictions for the cooling current. Nevertheless, our simulations demonstrated that it gives correct results for the cooling COP. We expect this to be a general observation, unless one could devise a system which can realize at least two different thermodynamic cycles, where the relative activity of those cycles is a function of coherence.

(vi) More generally, we demonstrate that the operation of a composite quantum heat machine can be explained from the behaviour of its components, allowing us to identify key operational principles in energy conversion devices. We were able to interpret quite well the operation of the 4lQAR based on our study of its constituent parts, and will continue use this approach in Sec. 3.4.

3.4 Secular Analysis of QHE Operation

In Section 3.3 we were able to demonstrate a situation wherein system energy basis coherences survive to the steady-state, and have a deleterious impact on device performance. This observation stands in contrast to the preponderance of work on the subject, wherein the studied devices realize a performance (particularly power) boost when coherences survive [9, 10, 271, 44]. The role of coherence on the operational characteristics of a QHM is in general model-dependent, and the amount of coherence which survives to the steady-state, let alone the instrumentality of coherences, is not obvious. Given this uncertainty, it may be instructive to consider coherence in QHMs from a different perspective, where we can see and understand its impacts in a unified context.

Recent works have attacked this issue by algebraically eliminating coherences from the master equation, and solving the resulting equations of motion in a new basis which includes populations only [271, 44]. This process essentially corresponds to transformation of all the system operators into a new basis, wherein the coherences and populations are explicitly decoupled. A similar transformation has been employed in other works, though this decoupling was not an explicit goal [12, 292, 255].

Particular attention has been paid to the inherent “quantumness” of QHMs which operate with steady-state coherences; the basic question being, if one can transform the equations governing the device such that they incorporate only populations, what then is quantum-mechanical about it? One potential source of quantumness, beyond energy basis coherence, to enter is in the time-evolution itself, via violations of certain Leggett-Garg inequalities. We will not opine on this issue, except to mention that for autonomous QARs like those studied here, steady-state violations have not yet been found [44]. In quantum Otto engines however, violations have been discovered [45], and indeed there appears to be a smooth transition between “quantum” and “classical” kinetic regimes.

To address the ambiguity around the role of coherence, we demonstrate a simple numerical approach that yields an intuitively interpretable picture of QHMs affected by steady-state coherences. We then apply this approach to simple models inspired by the literature, and show how their operation can be
understood on a coherence-free or secular basis

3.4.1 Secular transform

Whereas the secular approximation simply deletes population-coherence interactions from the reduced system equations of motion, the secular transform preserves their effects, while yielding a Hamiltonian which can be understood without requiring consideration of coherences in the new basis. In their recent (and quite insightful) works, the authors of Refs. [271, 44] analytically eliminated coherences from their master equations under certain conditions, and thus extracted useful information. While it is attractive to have complete analytical knowledge on the system under study, the working equations can become unwieldy for even three-level devices if they act in a nonsecular way. Therefore, we retreat to a numerical approach that is significantly easier to apply, and delivers similar insights.

Due to the hermiticity of the density matrix, we can always diagonalize it — effectively secularizing it by removing coherences. This is by itself quite simple, and results in a system wherein coherences cannot play a role. If we further apply the same transformation to the system Hamiltonian and coupling operators, \( \hat{H}_S \) and \( \hat{S}_\alpha \), we retrieve a model of the system with identical steady-state operational characteristics (current, efficiency), but which is completely secular in the steady-state.

We begin by defining the unitary transform operator, \( U^d(t) \), that takes us from the system energy basis to the secular basis, derived from a simple diagonalisation procedure,

\[
\sigma^d(t) = (\hat{U}^d(t))^\dagger \sigma(t) \hat{U}^d(t).
\]  

Since the system density evolves in time, the transform is necessarily time-dependent. We focus on steady-state operational characteristics, and therefore always consider the \( t \to \infty \) or steady-state (ss) limit. Applying this transform to the system energy basis operators in the long-time limit, we retrieve the objects of interest, the local operators which define the new model system.

\[
\hat{H}^d_S = (\hat{U}^d)^\dagger \hat{H}_S \hat{U}^d
\]

\[
\hat{S}_\alpha^d = (\hat{U}^d)^\dagger \hat{S}_\alpha \hat{U}^d.
\]

\( \hat{H}^d_S \) is the transformed local system Hamiltonian, and \( \hat{S}_\alpha^d \) is the system part of the system-bath coupling. The transform is quite simple, but as we show, it yields quite interesting information on the coherent dynamics of the system, without having to engage with complications introduced by the coherences themselves. It should go without saying that applying this transform on a system which is already secular naturally results in no change.

When practically implementing this transform, we begin by numerically running Redfield dynamics until the system reaches steady-state. We then diagonalise the resulting energy basis reduced density matrix, and using the unitary operators obtained in this procedure, transform the other system operators. What follows is a graphical depiction of the resulting transformed model systems. We proceed with two simple models to demonstrate the characteristics of the transform and some of our basic findings, which we call the “Class 1” and “Class 2” VETS. This further informs our discussion of the propriety of secular vs nonsecular master equations, via comparison of the secular and energy bases.
Degenerate

Near-Degenerate

Non-Degenerate

Energy Basis

Secular Basis

Site Basis

\[ |1⟩ |α⟩ |β⟩ \]
\[ 2Γℏ 2Γc \]
\[ |2⟩ |3⟩ \]
\[ γℏ γc \]
\[ (−) \]
\[ 2g \]
\[ Δ \]
\[ γℏ γc \]
\[ (−) \]
\[ 2g \]
\[ (1a) (1b) (1c) \]
\[ (2a) (2b) (2c) \]
\[ (3a) (3b) (3c) \]

Figure 3.12: Model diagrams of the VETS described in 3.2, when the upper states are degenerate, near-degenerate and non-degenerate (zero electronic coupling, \( g \), small \( g \), and large \( g \)). Going across the rows, are representations of the model in various bases: the energy basis, so-called secular basis and the site basis (basis which considers the excited states as coupled). In the centre square, (2b), \( Δ \), \( γ_h \) and \( γ_c \) are complex system and system-bath coupling factors, and \( ω \) is a real energy splitting.

3.4.2 Class 1 VETS

The Class 1 VETS is identical to the first model we explored in Sec. 3.3, which was originally motivated by a desire to examine the combined effects of a dephasing bath and inter-site coupling, \( g \). When one diagonalises this model into its energy basis, we retrieve the model shown in the first column in Fig. 3.12 (1a)-(3a), with dephasing omitted for simplicity. On the far left and right, we have the familiar energy and site bases respectively, and in the centre, the new secular basis. The rows correspond to the exactly degenerate, \( g = 0 \), near degenerate \( g \ll ω_{2,3} \) (with \( ω_{2,3} \) the splitting between the excited energy states \( |2⟩ \) and \( |3⟩ \)), and non-degenerate \( g \sim ω_{2,3} \) cases for the upper states. The factors of \( 2Γ_α \) in (1b) and (1c)-(3c) indicate that the strength of the system bath coupling for the transition is double that in the energy basis. Note the terms marked \( Γ^{(−)} \) in (1a)-(3a) and (2b)-(3b) indicate that the relevant system coupling operator comes with a negative sign in the energy basis, see Eq. 3.7. We include the detailed Hamiltonians in Appendix D. This sign factor arises from the transformation from site picture...
to energy, and is quite instrumental in the interference pattern observed in steady-state operation. We demonstrate the effect of switching this sign in our examination of the Class 2 VETS. The minimal conditions for observing noise-induced coherences like those studied here are: the system must be driven out of equilibrium by two or more heat baths, and a bath exchanging energy with the system must couple to two or more degenerate or nearly degenerate transitions. This second condition describes so-called “correlated noise” [255]. Note that if we use uncorrelated noise, we always find zero steady-state coherence for these types of autonomous QHMs.

We can re-examine our results from Section 3.3 on the VETS operational characteristics, and directly observe the role of coherences on the device operation. We begin by considering the degenerate case. From the energy basis picture (1a), it is not a priori obvious that we will observe zero current, see Figs. 3.4, 3.6. Indeed, from a purely secular point of view (if one imagines coherences do not exist), this system appears analogous to two spins, sharing a ground state (|1⟩), which each independently exchange energy via excitation from a hot bath and dissipation to a cold bath. This picture however fails catastrophically; since the noise sources (baths) couple to both effective “spins”, their overall effect is correlated. This correlation is manifested in a large noise-induced coherence, see Fig. 3.7, which has a dramatic impact on the device, effectively deactivating it. This result would not ordinarily be obvious from simple inspection of the energy basis model.

Looking now at the result for the secular basis (1b), we find quite an interesting and intuitive result. The effect of noise-induced coherence, translated into a purely secular basis, is to decouple the bath transitions, and localise each bath to one excitation channel. Where we earlier had both |1⟩ → |2⟩ and |1⟩ → |3⟩ mediated by both hot and cold baths, we end up with |1⟩ → |α⟩ mediated by hot only and |1⟩ → |β⟩ by cold only. Plainly, this device is incapable of exchanging energy between the respective baths, and so the current observed is zero.

The site basis (1c) shares a ground state with the energy basis, but includes electronic coupling between its degenerate excited states. Note that properly, there is no site basis when g = 0, as it would then be identical to the energy basis. To capture the degenerate case we take the limit of g → 0 from the finite-g model, to maintain continuity and distinction from the energy basis. Interestingly, the secular and site bases exactly coincide in this degenerate limit.

Jumping to the non-degenerate or g ≫ ω_{2,3} case, we see that the energy basis (3a) and secular bases (3b) coincide. This comports very well with our prior knowledge of the propriety of the secular approximation in quantum master equations. When g becomes large, there are no slowly oscillating terms in the master equation, and it is well known that in this context it is appropriate to employ a secular or rotating-wave approximation. Thus, it is perhaps redundant to observe that when we expect the system to be effectively described by a secularized energy basis master equation, that the secular basis is simply the same basis; the system as-is is already secular, so the transform has no effect. Without the complications of coherences then, we can very easily understand the operation of this device in a secular manner, at face-value. The two effective spins (now non-degenerate) exchange energy independently, and though still technically correlated, the baths impart no steady-state coherence on the system. In a turnabout, the site basis (3c) now gives a less clear picture through which to naively analyse the operation of the VETS. At large g, the current in the device falls due to the reduction of the bath-induced rates J(ω)n(ω), when the transition frequencies, ω_{2,1}, ω_{3,1}, become large, an effect one cannot read off of the site basis picture. It should then be no surprise that a local-basis Lindblad equation also fails catastrophically here.
We now consider the in-between case (2a)-(2c), where the levels $|2\rangle$ and $|3\rangle$ are not degenerate, but coherence persists in the energy basis. Here, the energy basis (2a) is difficult to interpret; we still cannot predict the effect coherence has on energy transfer, or for that matter the presence of coherence at all. The site basis (2c), particularly at small $g$, gives a good account: we expect the rate of population transfer between sites $|a\rangle$ and $|b\rangle$ to scale with their interaction strength, and thereby allow energy to flow through the device. The secular picture (2b) presents as a hybrid between energy and site bases, and in fact smoothly transitions between them with changing $g$. In this non-degenerate yet nonsecular case, the secular basis presents again an unambiguous picture. The new terms — real $\omega$ and complex $\gamma_\alpha, \Delta$ — result from the diagonalisation of the reduced system density, and fine-tune the dynamics to yield zero steady-state coherence despite retaining correlated noise. These new parameters also smoothly transition from their degenerate to non-degenerate counterparts in the energy and site bases respectively, with $0 < \omega < 2g$, $0 < |\Delta| < g$, $0 < |\gamma_\alpha| < \Gamma_\alpha$. Interestingly, a master equation written in this secular basis is actually nonsecular, the populations and coherences are generally still coupled; only, the computed parameters precisely result in zero coherence at steady-state. Only in the fully degenerate case is a transformation to a strictly secular master equation possible [44, 293, 291].

In panel (2b), we see a mixture of energy basis and site basis features: the levels $|\alpha\rangle$ and $|\beta\rangle$ are non-degenerate, with $\omega < 2g$, and coupled, with $|\Delta| < g$. Further, the bath-induced transitions affect each excitation pathway unequally, with hot and cold baths adopting a primary transition ($|1\rangle \rightarrow |\alpha\rangle$ and $|1\rangle \rightarrow |\beta\rangle$ respectively). As we decrease $g$ and move towards the degenerate case, $\Delta$ and $\omega$ (objects which appear only in the secular basis, in the non-degenerate, nonsecular regime (2b)) shrink, and the bath transitions fully localise. Conversely with increasing $g$, we move towards a picture resembling the energy basis, with the baths equally sharing both effective spins, $\omega \rightarrow 2g$, and interestingly again $\Delta \rightarrow 0$. Thus, $\Delta$, exists only in the non-degenerate yet nonsecular regime, where the action of the coherences move from being dominant in the degenerate limit to nonexistent in the secular.

In the example of the VETS, it seems that when $g$ is small, the site basis provides the best intuitive understanding of the device operation. This basically follows the reasoning of local secular Lindblad equations, which operate fairly well in this regime, where global secular approaches fail. When $g$ is large coherences do not exist and the energy basis provides the correct picture. This is unsurprising, for this is the regime where we expect secular approaches to behave well. One may then ask, what is the utility of computing the secular basis? Since $\sigma$ is hermitian, the secular basis is guaranteed to exist. While in many cases, it may be that there is some basis which well explains the behaviour of a given system, it is not a given that we can easily determine what that basis is. By contrast, we always have access to a secular basis, which we can understand without having to consider explicitly any of the ambiguities of steady-state coherences. Particularly in larger and more complex systems, finding a basis which sensibly demonstrates the dynamics may be extremely difficult, whereas finding the secular basis requires only propagation and diagonalisation.

We have omitted the role of a dephasing bath, like that used in Sec. 3.3, partially for simplicity, and partially because its operation can be very easily understood: the role of the dephasing bath is always to drive the system further towards the secular limit. In terms of Fig. 3.12, it will push the secular basis to appear more like the energy basis, the degree of secularisation depending on the strength of the dephasing.
Figure 3.13: Same as 3.12, except with only positive terms in $\hat{S}_{h,c}$, which gives rise to a different site basis and overall behaviour. After degeneracy is broken, the secular basis and energy basis become identical (there are no steady-state energy basis coherences in the non-degenerate model).

3.4.3 Class 2 VETS

We now analyse the Class 2 VETS, where the system couplings take all the same sign $\hat{S} \propto (|1\rangle\langle 2| + |2\rangle\langle 1|) + (|1\rangle\langle 3| + |3\rangle\langle 1|)$. Whereas the Class 1 model was intuitively derived from the site basis, the Class 2 is perhaps what one would naively construct in the energy basis, and indeed it is a building block in many proposed setups. Many studies of noise-induced coherence in 4QARs have taken advantage of this basic unit [9, 10, 12, 44, 292], which as we will see harnesses steady-state coherences to boost energy transfer rates over the secular case. The Class 2 VETS is simpler than the Class 1, as coherences appear only in the limit of exact degeneracy of the two higher states in the energy basis, and therefore the secular basis is identical to the energy basis for any finite splitting, $g$ (see Fig. 3.13, (1a)-(1c).

In the degenerate limit $g = 0$ (1a)-(1c), the secular transform can be done numerically or analytically [44], changing the system from the familiar V shape, to a single spin and a decoupled “dark” state (1b)-(1c). In the decoherence literature, the dark state is known as a protected state, or decoherence-free subspace [294], and is desirable in certain situations due to its isolation from interactions with any
baths. We are primarily interested in the single effective spin, which is identical to the prior twin-spins, but has double the effective system-bath coupling strength. The effect of coherence is the same as we observed for the Class 1 VETS in Fig. 3.12, except instead of the two bath interactions localising on separate transitions, they now mediate the same transition, enabling energy exchange. Thus, with an appropriate initial condition (no population trapped in the dark state), we achieve higher power with the single, more strongly interacting spin, than with the twin spins, acting independently.

We demonstrate this boost in Fig. 3.14 where we show the ratio of power evolved in the system when coherences are active, compared to when they are deleted with a secular approximation. One can rationalise the observed boost by considering that with all the population concentrated in a smaller subspace, and stronger couplings between the two states, the overall population transfer and therefore energy transfer rates increase. We see that the worst the non-secular setup can do is about the same as the secular case, and in the best case it can realize a significant boost.

The site basis is actually more obscure than the energy/secular bases at finite $g$. We rationalize the behaviour of a spin interacting with two baths (2a)-(2b), (3a)-(3b) by simple arguments on the form of the various transition rates. The site basis on the other hand (2c), (3c), requires intuition on the effect of the state which does not interact with the environment, $|b\rangle$, which is non-trivial.

When the secularizing transformation does not impact the system Hamiltonian (i.e. in the fully-degenerate limit), one can use a secular-Lindblad master equation to run dynamics in the secular basis. The transient dynamics of this system are not in general identical to those of the pre-transform model, but the steady-state operational characteristics are indistinguishable. Indeed, if one has knowledge only of the device performance, the secular and original models are physically indistinguishable, without “looking under the hood” of the model system [271].

It should be noted at this time that, beyond manipulation of $g$, there is another avenue to realize steady-state coherences in otherwise secular models, such as the model in panel (2b) of Fig. 3.13. In this work, we only consider system-bath coupling operators which equally couple the ground state to each
of the excited states. When this coupling is non-symmetric, e.g. the cold bath promotes the transition \(|1⟩ \rightarrow |2⟩\) more or less than \(|1⟩ \rightarrow |3⟩\), we realize a new source of steady-state coherence. Dealing with this effect, similar to nonzero \(g\), is analytically tricky, and indeed it is not in general possible to recast the master equation into a completely secular form, even in the degenerate case \([44]\). Asymmetric, yet correlated coupling can induce coherence in the \((2b)\) system, at small \(g\), resulting in a system which cannot be easily understood in the energy basis, and so the secular basis becomes useful again. The effects induced by such a coupling asymmetry are not identical, but are very broadly similar to what we find at small \(g\), and so for brevity we omit a detailed analysis in this work.

### 3.4.4 4-Level QARs with degeneracy

We now apply what we learned in 3-level QHMs to 4lQARs, to rationalize observations made here and in the literature.

![Energy Basis](1a)

![Secular Basis](1b)

![Site Basis](1c)

![Energy Basis](2a)

![Secular Basis](2b)

![Site Basis](2c)

![Energy Basis](3a)

![Secular Basis](3b)

![Site Basis](3c)

Figure 3.15: 4lQAR identical to the one studied in Sec. 3.3, considering the energy basis, secular basis and site basis at zero, small and large \(g\).

We begin with the 4lQAR from Sec. 3.3, where coherences at small \(g\) were found to be detrimental
to coherence. The operational principles are nearly identical to the Class 1 VETS from Fig. 3.12: at vanishing $g$ (1a)-(1c), the bath couplings localise to only one transition, shutting off population transfer between $|a⟩$ and $|b⟩$. Without this population transfer, the engine cannot cycle, and therefore the currents are all zero, as in Fig. 3.8. Again we see that until $g$ becomes large (3a)-(3c), the site basis is quite instructive to rationalize the increase in the current with increasing $g$. The secular basis smoothly transitions between energy and site bases with increasing $g$, bearing features of both in the near-degenerate $g$ regime (2b), with again $0 < \omega < 2a$, $0 < |\Delta| < a$, $0 < |\gamma_\alpha| < \Gamma_\alpha$.

![Figure 3.16: Same as 3.15, except with only positive terms in $\hat{S}_c$, which gives rise to a different site basis and overall behaviour. After perfect degeneracy is broken, the secular basis and energy basis become identical (there are no steady-state energy basis coherences in the non-degenerate model).](image)

We can further examine the case with all-positive terms in $\hat{S}_{h,c}$, with a close connection to the Class 2 VETS in Fig. 3.13. Here we again clearly see in the degenerate case (1a)-(2c), that upon secularization we create a dark state, and increase the coupling strength to the remaining cold and work transitions. The result is directly analogous to the Class 2 VETS (see Fig. 3.14); with an appropriate initial condition the population is concentrated in only three sites instead of four, and with a stronger system-bath coupling we observe faster population transfer rates, and therefore an overall power boost. Also as in the Class 2 VETS, we see that when the degeneracy is broken (2a)-(2c), coherence and its
boosting effect are lost, and so the energy basis and secular basis become identical.

### 3.4.5 Dicke states in degenerate spin systems

In Ref. [292], the authors observe an interesting physical phenomenon: when identical, single-spin QHMs (Hamiltonians shown in Appendix D) are added together and their respective hot and cold baths are treated *independently*, the power output scales linearly with the number of spins. Since the spins are noninteracting, this is the expected result. When the hot and cold baths are taken to act collectively on all the spins, realizing what we would call correlated noise, the power improves *nonlinearly* with the number of spins. The authors rationalize this boost by transforming their system to the so-called Dicke basis, which diagonalizes certain spin operators [42], where they can rationalize the power boost using straightforward arguments.

We show here using a simple example that the Dicke basis which explains the power boost due to cooperative effects is identical with the secular basis for the multi-spin system, which we have used to explain power boosts due to long-lived quantum coherence. For simplicity we omit the driving field, and therefore our model is not a heat engine but simply an energy transfer device. The working principles and role of noise-induced coherence, however, should be the same.

In Fig. 3.17, we show the model system for two degenerate spins, each coupled to a hot and cold bath. Diagonalising the steady-state density and computing the secular basis, we find a very familiar result to Figs. 3.13 and 3.16. In (1a) and (1b), we show the cooperative result, in which there are only two baths - hot and cold - and their collective action on the two spins gives rise to noise-induced coherence. The role of energy basis coherence can be re-expressed in the secular basis as increasing the coupling between three of the states, excluding one as a dark state, and giving rise to the observed power boost. We further show in panels (2a) and (2b) that when the baths are treated independently, i.e. each spin has its own hot and cold bath, there is no bath-induced coherence, and so the secular and energy bases are identical. In this situation, we simply have a system of two independent spins, and therefore the power scales linearly with the number of spins added.

The energy and secular bases we employ above are commonly denoted as the $2 \otimes 2$ and $3 \oplus 1$ bases respectively [295]. This notation highlights how the composite system of two spins can be decomposed into two separate systems, with three levels and one level respectively. Our secular basis coincides with the Dicke basis, therefore we can easily explain the boost in power from cooperative effects via the effects of noise-induced coherences. This result is general with the addition of additional spins, and the power will increase nonlinearly with an appropriate initial condition, so long as they are all degenerate. For the addition of non-degenerate spins, no cooperative boost is expected, as coherences do not survive to the steady-state (see the second row of Fig. 3.16).

### 3.5 Conclusions

In Section 3.4, we took a step back to try to understand the role of coherence more generally for the class of QHMs which operate with noise-induced coherences. In order to reconcile the cases wherein coherences are found to be beneficial to device performance, with the case earlier in this Chapter where they are detrimental, we sought a unified basis for analysis of the effects of noise-induced coherences. Due to the difficulty and lack of generality of analytical approaches, we used a simple numerical technique to generate a basis without steady-state coherences, which we could understand without needing to
interpret the action of coherences. We then applied this technique to several relevant setups to extract general information.

We found that the question of the appropriate basis within which to interpret QHM operation was highly model and parameter dependent, with the secular basis following the energy basis, the site basis, or a mixture of both depending on the situation. We further found that the effect of noise-induced coherences (interpreted via the secular basis) is to localise the system-bath couplings between two (or more) near-degenerate states and a third state, to a single transition. Depending on the states connected and the degree of localisation, itself determined by the degree of coherence, via the degree of degeneracy, the result might boost or negate energy current through the device. We applied these principles to four-level setups from the literature, and were able to explain their operation on these terms.

Going forward, there are several avenues that should be explored in this area. First, an interesting result of this study which deserves future attention is the insensitivity of the QAR efficiency to coherence/decoherence, in contrast to the quite dramatic effects observed in the current. It is not at all clear that this is a required or general result, and deserves further attention. While we studied one marker of
“quantumness” (magnitude of off diagonal elements of the reduced density matrix in the energy basis), it is interesting to further examine other measures for quantumness and delocalisation in quantum energy transport systems and QHMs, such as state purity, inverse participation ratio, entanglement, discord, and adherence to Leggett-Garg inequalities [239, 287, 288, 296]. Certain setups, such as those in the near-degenerate regime and including asymmetrically coupled transitions mediated by single baths, may produce certain exotic behaviours, though one should always be able to describe such a system with a “classical”, or “kinetic”, secular master equation, via our secularization procedure.

While quantum thermodynamical machines have been traditionally analysed under a strict weak-coupling approximation, it is now recognized that to properly characterize the performance of quantum engines and refrigerators, and moreover to achieve new functionality, one must develop methods that are not limited in this respect [281, 272, 54, 297, 298, 46, 299, 300, 301, 302, 49, 303, 55, 304]. The exploration of quantum coherent effects in strongly coupled heat machines is an important next step. In Chapter 4, we present a new, numerically exact methodology to assist in the study of quantum thermal devices operating in this regime.
Chapter 4

Development of the Iterative Full-Counting Statistics Path Integral

4.1 Introduction

Understanding energy transfer in nanoscale systems is of central importance for the design of energy efficient devices [305, 306, 307], and for uncovering fundamental physical bounds on the rates of computation and information flow [308, 309, 310, 311]. How do particles and energy travel through nanostructures, quantum dots, small or large organic and biological molecules? At the nanoscale, quantum effects may play an instrumental role in the management of waste heat and the function of electronic, thermal and thermoelectric devices. Furthermore, understanding quantum heat flow is a critical step for further developments in quantum thermodynamics [312, 313, 4].

Counting statistics is a powerful, well established technique in quantum statistical mechanics [314, 315]. It allows one to construct the nonequilibrium probability distribution of exchanged particles, heat, or work. From the richer literature, we recount here studies on cumulants of charge transport in mesoscopic and nanoscale devices [316, 317, 318, 319, 36], efficiency fluctuations in e.g., thermoelectric junctions, [36, 320], work statistics in closed-driven systems [314, 315, 321], and photon emission statistics in single molecules [322, 323, 324]. Heat conduction problems are fundamental to thermodynamics; the statistics of phononic heat exchange can be solved exactly only in the noninteracting (classical and quantum harmonic) case [325, 326, 327].

We focus on the problem of quantum heat transfer in nanojunctions. Beyond the average heat current, fluctuations are of significant interest, in particular at the nanoscale when they are substantial [314, 315]. A full-counting statistics (FCS) analysis provides the probability distribution function $P_t(Q)$ of the heat $Q$ transferred within a time interval $t$. Obtaining this function in interacting systems is a formidable task, achieved through the development of e.g. perturbative [328, 329, 330, 326, 55, 331, 332, 333, 327] and numerically-exact [334, 335, 336, 337] treatments. FCS calculations not only hand over the cumulants of heat exchange, but allow one to test fundamental relations, such as the steady-state heat exchange fluctuation symmetry [338, 314, 315].
The non-equilibrium spin-boson (NESB) model generalizes the dissipative spin-boson model [339] to include two or more heat baths. As such, it serves as a test-bed to explore the fundamentals of quantum heat flow in anharmonic nanojunctions [220, 340, 281]. In the NESB model, the spin represents an anharmonic mode, constructed from a truncated harmonic spectrum, and the heat baths are described by a collection of harmonic oscillators (phonons). The NESB model is an extremely rich platform for studying nonlinear effects in quantum transport [307], including the operation of thermal diodes [220, 340], transistors [341], and heat machines [342, 343, 328]. To simulate the transients and steady-state behaviour of heat exchange in the NESB model, efforts have been made to generalize methodologies originally developed for time evolving the reduced density matrix. A partial list includes perturbative (Born-Markov) quantum master equation tools [220, 340, 344], the noninteracting blip approximation (NIBA) [220, 340, 329, 329], the nonequilibrium polaron-transformed Redfield equation [332, 333], Green’s function methods [345, 346, 347, 348, 331], wavefunction approaches [349], hierarchical equations of motion [288, 300, 334], path integral methodologies [350, 351, 352, 353, 68], and mixed quantum-classical equations [354].

In this work, we present and apply a new tool for the study of the full counting statistics (FCS) of heat exchange in nanojunctions. Our numerically exact path integral method, which we name the “iterative full counting statistics path integral” (iFCSPI) method, provides the steady-state cumulants of heat exchange, focusing on the first cumulant, the current. Focusing on the NESB model we perform simulations of the heat current beyond the weak system-bath coupling and the nonadiabatic (weak tunnelling) transport limits.

The iFCSPI is built on the influence functional path integral representation of quantum dissipative dynamics [355], with the influence functional modified to include counting information. The implementation of the iFCSPI is based on combining (i) the two-time measurement protocol, which rigorously builds the characteristic function for heat exchange, and (ii) the iterative quasi-adiabatic influence functional path integral approach (iQuAPI) of Makri and Makarov [356, 357], which was originally developed for iteratively time evolving the reduced density matrix. Therefore, similarly to iQuAPI, the convergence of the iFCSPI to the exact limit relies on the existence of a well-defined decorrelation time of the nonlocal influence functional.

Like other iterative influence functional approaches, the iFCSPI relies on discretisation of the system and time coordinates. The standard iQuAPI approach can be difficult to converge depending on the system and bath parameters, though significant progress with improved algorithms based on e.g. path filtering [358, 359] or alternative construction of the propagator has been made in recent years [360, 361, 362, 363, 364, 365, 366]. Nevertheless, to establish our method and understand its strengths and limitations, we here implement iFCSPI based on the elementary iQuAPI algorithm [356, 357].

The chapter is organized as follows. We introduce the NESB model and the FCS formalism in Sec. 4.2. We describe the iFCSPI algorithm in Sec. 4.3, with technical details set aside for Appendix E. Simulation results are presented in Sec. 4.5; convergence and error analysis are discussed in Appendix F. We conclude in Sec. 4.6.
4.2 Full Counting Statistics for Heat Exchange

4.2.1 The nonequilibrium spin-boson model

The iFCSPI approach is presented here in the language of the Feynman-Vernon (FV) influence functional [355]. The main assumptions underlying this approach are that the environment is composed of harmonic oscillators, and that the system-bath interaction Hamiltonian is a linear function in the baths’ displacements. As such, the method naturally fits to describe the Caldeira-Leggett and the spin-boson models [339]. Nevertheless, the iFCSPI method can be extended beyond this construction to setups missing an analytic form for the influence functional and including correlations beyond pairwise interactions [367, 368]. For simplicity, here we implement the iFCSPI within the minimal NESB model.

The Feynman-Vernon path integral approach has been recently used to study work statistics [50] and heat statistics [51, 68, 336] in the Caldeira-Leggett and the spin-boson models. However, these studies were focused on describing the analytical properties of the path integral formula for heat exchange and work (e.g. proving the Jarzynski’s equality for work fluctuations), while our focus here is on the presentation of a feasible numerical implementation to compute heat transfer cumulants.

Let us now describe the NESB model. The total Hamiltonian consists of a spin system $\hat{H}_S$, which is coupled via $\hat{H}_{S\alpha}$ to two reservoirs $\hat{H}_\alpha$ ($\alpha = L, R$),

$$
\hat{H} = \hat{H}_S + \hat{H}_L + \hat{H}_R + \hat{H}_{SL} + \hat{H}_{SR}.
$$

(4.1)

The $L$ and $R$ heat baths are assumed to be prepared at thermal equilibrium at the inverse temperatures $\beta_L$ and $\beta_R$, respectively. In the long time limit, a nonequilibrium steady-state in reached when the thermal baths are set at different temperatures. In the NESB model, the system comprises a single spin,

$$
\hat{H}_S = \frac{\omega_0}{2} \hat{\sigma}_z + \frac{\Delta}{2} \hat{\sigma}_x,
$$

(4.2)

with $\hat{\sigma}_{x,z}$ as the Pauli matrices, $\omega_0$ the spin splitting, and $\Delta$ the tunnelling energy. For simplicity, in what follows we take $\omega_0 = 0$, therefore $\Delta$ becomes the level splitting in the system energy basis. The bath plus system-bath interaction, collectively, the “environmental Hamiltonian” are given by

$$
\hat{H}_{\text{env}} = \sum_{\alpha=L,R} \left( \hat{H}_\alpha + \hat{H}_{S\alpha} \right).
$$

(4.3)

We model the baths by collections of independent harmonic oscillators. These oscillators are bilinearly coupled to the spin, $\hat{H}_{S\alpha} = \hat{S} \otimes \hat{B}_\alpha$, with $\hat{S}$ as the system operator (spin polarization $\hat{\sigma}_z$) and $\hat{B}_\alpha = \sum_k \lambda_{\alpha,k} (\hat{b}_{\alpha,k}^\dagger + \hat{b}_{\alpha,k})$ given in terms of the displacements of the baths’ normal modes. Altogether, the environmental Hamiltonian is given by

$$
\hat{H}_{\text{env}} = \sum_{\alpha,k} \left[ \omega_{\alpha,k} \hat{b}_{\alpha,k}^\dagger \hat{b}_{\alpha,k} + \lambda_{\alpha,k} (\hat{b}_{\alpha,k}^\dagger + \hat{b}_{\alpha,k}) \hat{\sigma}_z \right].
$$

(4.4)

Here, $\hat{b}_{\alpha,k}^\dagger$ ($\hat{b}_{\alpha,k}$) are bosonic creation (annihilation) operators for modes of frequency $\omega_{\alpha,k}$ in the $\alpha$ bath.
The system-bath interaction is characterized by a spectral density function,

$$g_\alpha(\omega) = \pi \sum_k \lambda_{\alpha,k}^2 \delta(\omega - \omega_{\alpha,k}).$$

(4.5)

In simulations we employ an Ohmic function of the form $g_\alpha(\omega) = \gamma_\alpha \omega e^{-\omega/\omega_c}$. The method is general for other physical spectral densities, though the convergence characteristics depend intimately on this choice. The system-bath coupling parameter $\gamma$ is related to the Kondo parameter $K$, $\gamma = \pi K/2$ [339]. $\omega_c$ is the cutoff frequency of the baths, taken here as identical between hot and cold reservoirs.

Figure 4.1: Scheme of the NESB nanojunction, while illustrating with curvy arrows the counting process with the phase factors decorating the system-bath interaction, see Eqs. (4.6)-(4.18). The expansive arrows display the direction of the net heat flow in steady-state. (a) Counting system-bath heat exchange only at the left contact. (b) Counting heat exchange in a symmetrical manner. Model parameters include $\Delta$ as the spin spacing in the energy basis. The baths are characterized by spectral functions $g_\alpha(\omega)$ and an inverse temperature $\beta_\alpha$.

4.2.2 Cumulant generating function for heat transfer

To glean information about transport statistics we compute the generating function of heat exchange. First, we define the energy current operator as the rate of change of energy in one of the reservoirs, $\hat{J}_{Q,\alpha}(t) = -d\hat{H}^H_\alpha(t)/dt$. Operators are written in the Heisenberg representation and evolve with respect to the total Hamiltonian $\hat{H}$. Therefore, the total energy change in the $L$ bath within the time interval $t_0 = 0$ to $t$ is given by the integrated current

$$Q_L(t_t_0 = 0) = \int_{t_0}^t \hat{J}_{Q,L}(t')dt' = \hat{H}_L(0) - \hat{H}^H_L(t).$$

(4.6)
We define energy leaving the left bath towards the system as positive. Note that since the system is not driven by an external field, the energy exchanged is thermal in nature, i.e. heat. Following this definition of heat exchange, we write down its moment generating function based on the two-time measurement protocol \[314, 315, 326\],

\[
Z(t, \xi) \equiv \left\langle e^{i\xi H_L} e^{-i\xi H_L^\dagger(t)} \right\rangle. \tag{4.7}
\]

Here, \(\xi\) is referred to as the “counting field” as it tracks the energy transferred to the bath. The expectation value is evaluated with respect to the total initial density matrix, which is assumed to be system-bath factorized,

\[
\rho_0 = \sigma_0 \otimes \rho_B.
\]

\(\sigma_0\) is the density matrix of the spin system at \(t = 0\). The state of the two baths is initially factorized as well,

\[
\rho_B = \rho_L \otimes \rho_R, \quad \text{each prepared at a thermal equilibrium state,}
\]

\[
\rho_\alpha = e^{-\beta_\alpha \hat{H}_\alpha} \text{Tr}\left[e^{-\beta_\alpha \hat{H}_\alpha}\right].
\]

In the long time limit, the cumulant generating function (CGF) for heat exchange is defined as

\[
G(\xi) = \lim_{t \to \infty} \frac{1}{t} \ln Z(t, \xi) = \lim_{t \to \infty} \frac{1}{t} \sum_{n=1}^{\infty} \frac{(i\xi)^n}{n!} \langle \langle Q_L^n(t, 0) \rangle \rangle, \tag{4.8}
\]

with \(\langle \langle Q_L^n(t, 0) \rangle \rangle\) standing for the cumulants for heat exchange between the system and the \(L\) bath within the interval \([0, t]\). Explicitly,

\[
G(\xi) = (i\xi) \frac{\langle Q_L(t, 0) \rangle}{t} \bigg|_{t \to \infty} + \frac{(i\xi)^2}{2} \frac{\langle \langle Q_L^2(t, 0) \rangle \rangle}{t} \bigg|_{t \to \infty} + \ldots, \tag{4.9}
\]

where we calculate cumulant in the long time limit when the CGF reaches a constant value. To find the steady-state heat current, we take the first derivative of the CGF with respect to the counting parameter \(\xi\),

\[
\langle J_Q \rangle = \frac{dG(\xi)}{d(i\xi)} \bigg|_{\xi=0}. \tag{4.10}
\]

Higher cumulants are computed as higher derivatives.

The counting field has the effect of “dressing” the forward and backward time evolution operators \(e^{\pm i\hat{H}t}\). This can be observed from Eq. (4.7) after making some rearrangements,

\[
\begin{align*}
Z(t, \xi) &= \left\langle e^{i\xi H_L} \hat{U}_\xi(t) e^{-i\xi H_L} \hat{U}_\xi(t) \right\rangle \\
&= \text{Tr}\left[e^{-\frac{i}{2} \hat{H}_L} \hat{U}_\xi(t) e^{\frac{i}{2} \hat{H}_L} \rho_0 e^{-\frac{i}{2} \hat{H}_L} \hat{U}_\xi(t) e^{\frac{i}{2} \hat{H}_L}\right] \\
&= \text{Tr}\left[\hat{U}_{-\xi}(t) \rho_0 \hat{U}_\xi(t)\right] \\
&= \text{Tr}_S[\text{Tr}_B[\rho_\xi(t)]] \tag{4.11}
\end{align*}
\]

Throughout this work, \(\xi\)’s are assigned to operators dressed by counting fields. In the last line we define \(\rho_\xi(t)\), which closely resembles the standard density operator, but evolving with modified, counting field dependent propagators. Similarly, \(\text{Tr}_B[\rho_\xi(t)]\) can be regarded as the counting field dependent reduced
The dressing of the propagators is defined as

\[ \hat{U}_{-\xi}(t) = e^{-\frac{\xi}{2} \hat{H}_L} \hat{U}(t) e^{\frac{\xi}{2} \hat{H}_L} = e^{-i\hat{H}_{-\xi} t}, \]
\[ \hat{U}_{\xi}^\dagger(t) = e^{\frac{\xi}{2} \hat{H}_L} \hat{U}^\dagger(t) e^{-\frac{\xi}{2} \hat{H}_L} = e^{i\hat{H}_{\xi} t}, \] (4.12)

and we used the fact that \( \hat{A} e^{iH_s t} \hat{A}^\dagger = e^{i\hat{A}^\dagger H_s \hat{A}} \) for a unitary \( \hat{A} \) to define the dressed Hamiltonians \( \hat{H}_{\pm \xi} \) above. This transformation impacts only the system-bath interaction part of the Hamiltonian. For example, the forward time evolution operator \( e^{-i\hat{H}_{-\xi} t} \) is given in terms of

\[ \hat{H}_{-\xi} = \hat{H}_S + \hat{H}_L + \hat{H}_{SL}^\xi + \hat{H}_{SR}, \] (4.13)

where the transformed system-bath Hamiltonian is

\[ \hat{H}_{SL}^\xi = \sigma_z \sum_k \lambda_{L,k} (\hat{b}_{L,k}^\dagger e^{-i\omega_{L,k} \xi/2} + \hat{b}_{L,k} e^{i\omega_{L,k} \xi/2}). \] (4.14)

The counting field therefore enters as phase factors inside the interaction Hamiltonian. For a schematic representation of the model and the counting process, see Fig. 4.1(a). From here, one can follow the regular derivation of the Feynman-Vernon influence functional, and obtain the counting-field dependent analogue. In Appendix E we show a detailed derivation based on a cumulant and discuss the exact derivation of the influence functional following Ref. [68].

Back to Eq. (4.11), in order to extract information on the heat current, we need to time evolve the counting field dependent reduced density matrix, obtain the generating function \( Z(t, \xi) \) and compute the cumulant generating function \( G(\xi) \) via a numerical derivative in the long time limit. To find the steady-state heat current, one further needs to take the derivative of the CGF with respect to the counting parameter, see Eq. (4.10).

To facilitate error cancellation as explained in Appendix F, it is necessary in this implementation to apply the counting field in a symmetrized manner with respect to the two baths; for a schematic representation, see Fig. 4.1(b). This puts the iFCSPI in a somewhat similar situation to the computational methods used in Refs [349, 345]. Therefore, we repeat steps (4.6)-(4.11): We define the symmetrized heat exchange in the interval \([0, t]\),

\[ Q(t) = \frac{1}{2} \left[ \hat{H}_L(0) - \hat{H}_L^R(t) \right] - \frac{1}{2} \left[ \hat{H}_R(0) - \hat{H}_R^R(t) \right], \] (4.15)

and the generating function of heat exchange

\[ Z(t, \xi) = \left\langle e^{i\xi (\hat{H}_L - \hat{H}_R)/4} e^{-i\xi \left( (\hat{H}_L^R(t) - \hat{H}_R^R(t))/2 \right)} \right\rangle. \] (4.16)

These definitions again allow us to arrive at Eq. (4.11), but with symmetrized time evolution operators

\[ \hat{U}_{-\xi}(t) = e^{-i\xi(\hat{H}_L - \hat{H}_R)/4} \hat{U}(t) e^{i\xi(\hat{H}_L - \hat{H}_R)/4} \] (4.17)

and

\[ \hat{U}_{\xi}^\dagger(t) = e^{i\xi(\hat{H}_L - \hat{H}_R)/4} \hat{U}^\dagger(t) e^{-i\xi(\hat{H}_L - \hat{H}_R)/4}. \] (4.18)
Note that in the symmetrized representation, the sign of the counting field is flipped between the two baths, and its magnitude is halved.

### 4.3 FCS Path Integral

A variety of approaches have been used to compute FCS for quantum heat transport problems using the two-time measurement protocol, including Green’s functions [331, 327], quantum master equations [329, 55, 332, 333], hierarchical equations of motion [334] and mixed quantum-classical methods [354]. Here, we implement the two-time measurement protocol within the machinery of the iQuAPI scheme developed by Makri and Makarov [356, 357].

Though we introduce this method in the context of the NESB presented above, it is important to note that this iFCSPI approach is completely general for any size or form of \( \hat{H}_S \) and \( \hat{H}_{SB} \), so long as they comport with the assumptions given below.

#### 4.3.1 The influence functional

We start by presenting the influence functional path integral. We discretize the time evolution, then break the time evolution operators into “free” (system) and “environmental” parts using the symmetrized Trotter decomposition formula. For example, the forward time evolution is organized as

\[
\begin{align*}
\langle s_N | e^{-i\hat{H}_S\delta t} | s_{N-1}^+ \rangle \cdots \langle s_1^+ | e^{-i\hat{H}_S\delta t} | s_0^\pm \rangle \langle s_0^- | \sigma_0 | s_0^+ \rangle \langle s_0^- | e^{i\hat{H}_{SB}\delta t} | s_1^- \rangle \cdots \langle s_{N-1}^- | e^{i\hat{H}_{SB}\delta t} | s_N \rangle \\
\times \text{Tr}_B \left[ e^{-i\hat{H}_{env}(s_N)\delta t/2} e^{-i\hat{H}_{env}(s_{N-1}^-)\delta t/2} \cdots e^{-i\hat{H}_{env}(s_1^-)\delta t/2} \right] \rho_B \left[ e^{i\hat{H}_{env}(s_0^-)\delta t/2} \cdots e^{i\hat{H}_{env}(s_{N-1}^-)\delta t/2} \right] I_R^{\xi/2} (s_0^+, s_1^+, \cdots, s_N) I_L^{\xi/2} (s_0^-, s_1^-, \cdots, s_N)
\end{align*}
\]

(4.20)

Here, + (−) refers to the forward (backward) time evolution. Since we are evaluating a trace over the system, \( s_N^+ = s_N^- = s_N \) for the outer sum. The free evolution is contained in \( K(s_j^+, s_{j+1}^-) = \langle s_{j+1}^- | e^{-i\hat{H}_S\delta t} | s_j^+ \rangle \langle s_j^- | e^{i\hat{H}_{SB}\delta t} | s_{j+1}^- \rangle \). The influence functionals, \( I_R^{\xi/2} (\{s^\pm\}) \) carry the details of the environment, its interaction with the system, and the counting field. Since the baths are independent, their respective influence functionals factorize to a simple product, see Appendix E. The counting parameter appears in both influence functionals since we used the symmetrized definition of the FCS.

An analytic form for the influence functional can be derived assuming that: (i) The baths include harmonic oscillators. (ii) Each bath is prepared at thermal equilibrium. (iii) The system-bath coupling
is linear in the bath coordinates. One obtains then the FV influence functional, which is dressed here by the counting parameters \[68\],

\[
I_\alpha^{\xi}(\{s^\pm\}) = \exp \left[ - \int_0^t d\tau \int_0^{\tau'} d\tau' [s^+(\tau)s^+(\tau')\eta_\alpha(\tau - \tau') - s^-(\tau)s^+(\tau')\eta_\alpha(\tau - \tau') + \xi] - s^+(\tau)s^-(\tau')\eta_\alpha(\tau' - \tau) \right],
\]

(4.21)

Recall that in the symmetrized implementation \(\xi\) is chopped by a factor of 2, and it further receives a negative sign for the \(R\) terminal. In Appendix E we include a derivation of the counting field dependent influence functional based on a weak-coupling expansion, which is useful though not necessarily exact beyond the linear coupling-harmonic bath model. Here, \(\eta_\alpha(t)\) is the autocorrelation function of the \(\alpha\) bath’s operators that are coupled to the spin,

\[\eta_\alpha(t + \xi) = \langle \hat{B}_\alpha^\xi(t)\hat{B}_\alpha^{-\xi}(0) \rangle,\]

(4.22)

where e.g. from Eq. (4.14),

\[
\hat{B}_L^{\xi}(t) = \sum_k \lambda_{L,k} \left[ \hat{b}_{L,k}(t)e^{-i\omega_{L,k}\xi/2} + \hat{b}_{L,k}(t)e^{i\omega_{L,k}\xi/2} \right].
\]

(4.23)

We explicitly evaluate Eq. (4.22) and get

\[\eta_\alpha(t + \xi) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{g_\alpha(\omega)e^{\frac{\omega}{\hbar} + \xi}}{\sinh \frac{\omega}{\hbar}} e^{-i\omega(t + \xi)},\]

(4.24)

where we extend the range of the spectral density to negative frequencies, \(g(\omega) = -g(-\omega)\). We conclude that the impact of the counting field is a multiplicative phase factor onto the standard integrand.

To evaluate Eq. (4.20) we time-discretize the influence functional and accompanying correlation functions. This is accomplished in the same way as in Ref. [356], and we receive

\[
I_\alpha^{\xi}(\{s^\pm\}) = \exp \left[ - \sum_{k=0}^{N} \sum_{k'}^{k} \left( s^+_k s^+_k \eta_{kk'^+\alpha}^{++\xi} - s^-_k s^+_k \eta_{kk'^-\alpha}^{-+\xi} - s^-_k s^-_k \eta_{kk'^-\alpha}^{+-\xi} + s^-_k s^-_k \eta_{kk'^-\alpha}^{--\xi} \right) \right].
\]

(4.25)

The \(\eta_{kk'^\pm\alpha}^{\pm\pm\xi}\) coefficients are the discretized versions of Eq. (4.24), given in Eq. (E.13). The influence functional contains four different types of correlation functions, rather than the two that appear in the standard derivation for the reduced density matrix [356], see Appendix E. The coefficients \(\eta^{++}\) and \(\eta^{-}\) do not depend on the counting field, and are complex conjugates, \((\eta_{kk}^{++})^* = \eta_{kk}^{--}\). The two new correlation functions, \(\eta^{+-\xi}\) and \(\eta^{-+\xi}\) are dressed by the counting field, and they approach \(\eta^{++}\) and \(\eta^{--}\), respectively, at \(\xi = 0\) when one retrieves the standard influence functional for the reduced density matrix. Note that \(\eta^{+-\xi} \neq (\eta^{-+\xi})^*\), thus the counting field destroys the blip-sojourn symmetry of the standard influence functional, which underlies blip decomposition based path integral approaches [362].
4.3.2 Iterative time evolution

Attempting to evaluate Eq. (4.20) directly is impractical, in particular, when looking for steady-state properties. The cost scaling of this full path integral is exponential, $d^{2N}$, where $d$ is the dimensionality of the Hilbert state of the system and $N$ is the number of time steps. We therefore implement an iterative scheme, in the mould of the celebrated iQuAPI approach.

Following the reasoning of Makri and Makarov [356], the correlation function (or kernel) $\eta(t)$ has a finite range (captured by a decorrelation timescale) if the environment is characterized by a smooth and continuous spectrum. This observation allows the development of an iterative time evolution scheme that is numerically exact when sufficiently long memory, $\Delta k = k - k'$, is accounted for, and when the Trotter error is minimized, $\delta t \to 0$. The introduction of the counting field simply shifts the time axis. Therefore, the same principles underlying the development of the iQuAPI apply to the iFCSPI method, and by propagating the path integral using the counting field dependent influence functional we should converge to the exact generating function.

We now provide the working expressions for the iterative time evolution scheme. First, recall the definition of counting field dependent reduced density matrix and the characteristic function,

$$\sigma^\xi(t) \equiv \text{Tr}_B[\rho^\xi(t)], \quad Z(t, \xi) = \text{Tr}_S[\sigma^\xi(t)]. \quad (4.26)$$

We define the truncated IF, which is used for time evolution,

$$I^\Delta_{a,\xi}(s_{k-\Delta k}, s_{k-\Delta k+1}, \ldots, s_{k+}) = \exp \left[ -\sum_{k'=k-\Delta k}^{k} \left( s_k^+ s_k^- \eta_{k'\alpha} - s_k^- s_k^+ \eta_{k'\alpha} - s_k^+ s_k^- \eta_{k'\alpha} + s_k^- s_k^+ \eta_{k'\alpha} \right) \right]. \quad (4.27)$$

It includes the pairwise coupling terms between $s_k$ and previous time steps within the memory time. Time evolution is dictated by

$$\sigma^\xi_{\Delta k}(s_{k-\Delta k}, s_{k-\Delta k+1}, \ldots, s_{k+}) = \sum_{s_{k-\Delta k-1}} \sigma^\xi_{\Delta k}(s_{k-\Delta k-1}, s_{k-\Delta k}, \ldots, s_{k-1}) K(s_{k-1}, s_k) I_L^{\Delta k,\xi/2}(s_{k-\Delta k}, \ldots, s_{k+}) I_R^{\Delta k,\xi/2}(s_{k-\Delta k}, \ldots, s_{k+}), \quad (4.28)$$

where we introduce the augmented reduced density matrix $\sigma^\xi_{\Delta k}$ (also known as the reduced density tensor), which carries the path information within $\tau_m = \Delta k \delta t$. It is initialized by performing non-iterative time evolution using Eq. (4.20), up to $t_{\Delta k} = (\Delta k - 1)\delta t$, omitting summation of the path segments. To get the time-local value, we construct an additional truncated IF as in Eq. (4.27), but with the final time step $k = N\delta t$ (see Appendix E). We use this truncated IF in the last time evolution step Eq. (4.28), and sum over the intermediate times,

$$\sigma^\xi(t_k) = \sum_{s_{k-\Delta k}, \ldots, s_{k-1}} \sigma^\xi_{\Delta k}(s_{k-\Delta k}, \ldots, s_{k+}). \quad (4.29)$$

The counting-dressed reduced density matrix has $d^2$ elements. We trace over the diagonal elements, $s_k = s_k^+ = s_k^-$ to construct the characteristic function of heat exchange at time $t_k$, $Z(t_k, \xi) = \sum_{s_k=1}^{d} \langle s_k | \sigma^\xi(t_k) | s_k \rangle$. 
Examining the form of Eq. (4.25), it is trivial to show that $I_{\alpha}^{\xi=0}(|s\rangle \langle s|) = I_{\alpha}(|s\rangle \langle s|)$. Therefore, from the trace conservation that is inherent to the iQuAPI algorithm we conclude that $Z(t, \xi = 0) = 1$.

### 4.4 Full-Counting Statistics in the Dephasing Model

Before presenting calculations of the current in the NESB, we use the formalism derived above to compute the full-counting statistics for heat exchange in the so-called “dephasing” or “pure decoherence” model. This model is identical to the NESB defined in Eq. (4.1), except that the inter-site coupling, $\Delta$, is zero,

$$
\hat{H} = \hat{H}_S + \hat{H}_{env},
$$

$$
\hat{H}_S = \frac{\hbar_0}{2} \hat{\sigma}_z = \frac{\hbar_0}{2} |1\rangle \langle 1| - \frac{\hbar_0}{2} |2\rangle \langle 2|,
$$

$$
\hat{H}_{env} = \sum_{\alpha=L,R} \left( \hat{H}_\alpha + \hat{\sigma}_z \otimes \hat{B}_\alpha \right),
$$

where we have explicitly defined the spin states as $|1\rangle$ and $|2\rangle$. The system and bath Hamiltonians fully commute and there are no bath-induced dynamics other than damping of system coherences [369]; the upshot of this is that since [$\hat{H}_S, \hat{H}_{env}$] = 0, energy flow through the system is prohibited, $\langle J_Q \rangle = 0$. Further, due to its simplicity, we can find a relatively neat analytical form for the cumulant generating function, which we present now.

We begin from the definition of the generating function in Eq. (4.11), where only one of the baths is dressed by the counting field. Since there is no Trotter splitting in this approach, no errors will be introduced and therefore no symmetrisation of the counting field is required,

$$
Z(t, \xi) = \text{Tr} \left[ e^{-i\hat{H}_S t + i\hat{H}_{env} t} \rho e^{i\hat{H}_S t} \right].
$$

Since $\langle 2|e^{-i\hat{H}_S t}|1\rangle = \langle 1|e^{-i\hat{H}_S t}|2\rangle = 0$, off-diagonal elements in the initial reduced density cannot impact the generating function. Further, it can be easily shown that initial population in $|2\rangle$ plays an identical role to that in $|1\rangle$, we can therefore assume all the population is initially in state $|1\rangle$ and simplify this expression quite substantially

$$
Z(t, \xi) = \text{Tr}_B \left[ \langle 1|e^{-i\hat{H}_S t + i\hat{H}_{env} t} \rho e^{i\hat{H}_S t} |1\rangle \langle 1| e^{i\hat{H}_S t} |1\rangle \right].
$$

The system and bath parts of the Hamiltonian commute, and therefore we can freely break the propagators without incurring an error,

$$
Z(t, \xi) = \langle 1|e^{-i\hat{H}_S t + i\hat{H}_{env} t} \rho e^{i\hat{H}_S t} |1\rangle \langle 1| e^{i\hat{H}_S t} |1\rangle \text{Tr}_B \left[ \langle 1| e^{-i\hat{H}_{env} t} |1\rangle \langle 1| e^{i\hat{H}_{env} t} |1\rangle \rho_B \right]
$$

$$
= \text{Tr}_B \left[ \langle 1| e^{-i\hat{B}_{env}^\xi t} |1\rangle \langle 1| e^{i\hat{B}_{env}^\xi t} |1\rangle \rho_B \right]
$$

$$
= \text{Tr}_B \left[ e^{-i(\hat{B}_L^\xi \xi + \hat{B}_L + \hat{B}_R + \hat{H}_R) t} e^{i(\hat{B}_L^\xi \xi + \hat{B}_L + \hat{B}_R + \hat{H}_R) t} \rho_B \right].
$$

Where in the last line we have used $\langle 1| e^{i\hat{\sigma}_z} |1\rangle = 1$.

Following the derivation in Appendix E, we can find a familiar result in continuous time

$$
Z(t, \xi) = \exp \left[ -\int_0^t d\tau \int_0^\tau d\tau' \left( \eta_L(\tau - \tau') - \eta_L(\tau - \tau' + \xi) - \eta_L(\tau' - \tau + \xi) + \eta_L(\tau' - \tau) \right) \right].
$$
The correlation functions associated with the right bath cancelled out since it was not dressed by a counting field. We simplify further by defining a new correlation function which explicitly takes on the “counting” part of the influence functional, omitting the “standard” part

\[\eta^\Xi(\tau - \tau' + \xi) = \eta(\tau - \tau' + \xi) - \eta(\tau - \tau')\]

\[\eta^\Xi(\tau' - \tau + \xi) = \eta(\tau' - \tau + \xi) - \eta(\tau' - \tau),\]  

(4.34)

and coming to our compact formal expression

\[Z(t, \xi) = \exp \left[ \int_0^t d\tau \int_0^{\tau} d\tau' [\eta^\Xi_L(\tau - \tau' + \xi) + \eta^\Xi_L(\tau' - \tau + \xi)] \right].\]  

(4.35)

Since we did not split the propagator, we can evaluate this directly to retrieve the exact generating function at time \(t\). There are several ways to organize the resulting expression, with the following as our preferred option,

\[Z(t, \xi) = \exp \left[ \frac{2}{\pi} \int_0^\infty d\omega g(\omega) \sin^2\left(\frac{\omega \xi}{2}\right) \left[n_L(\omega)(e^{i\omega \xi} - 1) + (n_L(\omega) + 1)(e^{-i\omega \xi} - 1)\right] \right],\]  

(4.36)

where \(n(\omega)\) is the Bose-Einstein distribution function. We find that this expression matches well with numerical evaluation using Eq. (4.20).

Figure 4.2: (a)-(b) Real and imaginary parts of the cumulant generating function for the \(L\) bath in the dephasing model, as a function of time. Parameters are \(\omega_c = 50\), \(T_L = T_R = 5\), \(\gamma = 0.01\), \(\xi = 0.01\).

In Fig. 4.2 we show example behaviour of Eq. (4.36). What one notices first and most importantly, both the real and imaginary parts of the generating function have nonzero slope, and therefore energy is being exchanged. From Eq. (4.36), we can see that the \(R\) bath, or any other bath which is not dressed by a counting field do not enter into the expression. Therefore, the energy exchange cannot depend on the temperature bias, or any features of the \(R\). This makes sense when we consider our definition for the heat in Eq. (4.6). By applying a counting field to the \(L\) bath, we are tracking the gained or lost in that
bath over time. In what follows, we consider this to be equal to the heat current through the system, \( \langle J_Q \rangle \), however, this is only strictly true at steady-state due to the conservation of energy. Transiently, as we see here, the baths exchange energy with the system-bath interaction itself for a finite time, but no energy whatsoever is exchanged with the system or other baths.

### 4.5 Results in the Nonequilibrium Spin-Boson Model

In this section we present simulations of the cumulant generating function for the nonequilibrium spin-boson model defined under Eq. (4.1).

#### 4.5.1 Choice of parameters

The iterative path integral method provides the exact answer when the time step is infinitely short, \( \delta t \to 0 \), and the entire range of the memory kernel is covered, \( \Delta k = N \). In practice, we minimize the Trotter error by taking a small enough time step \( \delta t \), while aiming to adequately capture the memory of the bath, by increasing \( \Delta k \), which controls the range of the memory retained. Convergence is approached by adjusting these parameters until the result remains constant for multiple iterations.

Balancing the Trotter error with the memory-truncation error is tricky: Shortening the time step increases the number of steps required to span the memory kernel. Since the computational effort scales as \( d^2 \Delta k \), with \( d \) the dimension of the Hilbert space of the system, simulations with the basic iQuAPI algorithm are typically limited to \( \Delta k \lesssim 10 \) [356]. Advanced algorithms based on path filtering [358] or tensor decomposition [363], for example, extend this limit by an order of magnitude or more—at the cost of additional algorithmic complexity and introduction of new convergence parameters. In particular, filtering approaches are not trace conserving. Other approaches to improving on the basic iQuAPI include those based on blip decomposition [362] or mixed quantum-classical setups [360, 361], but these appear incompatible with the iFCSPI algorithm. To lucidly present our method and its computational challenges, we therefore limit ourselves to the basic iQuAPI algorithm of Refs. [356, 357].

To facilitate convergence, our simulations are typically performed using the following parameters: spin splitting \( \Delta = 1 \), and high averaged temperature, \( \bar{T} = (T_L + T_R)/2 = 5 \). We assume an Ohmic spectral density function for the baths and work in the scaling limit with a high cutoff frequency \( \omega_c = 10 - 50 \). Since the iFCSPI method is not restricted to the linear response regime (and in fact, converges well far from equilibrium), we play with biases in the range \( T_L - T_R = 0 - 2 \). For the dimensionless system-bath coupling we use \( \gamma = 10^{-3} - 1 \), but convergence was achieved only at weak-to-intermediate coupling, \( \gamma \lesssim 0.15 \). With these parameters, iFCSPI simulations typically converge with \( \Delta k = 4 - 7, \delta t = 0.05 - 0.2 \). We also define the memory span \( \tau_m = \Delta k \delta t \). Roughly, we find that iFCSPI simulations converge when \( \tau_m \gtrsim 1/\bar{T} \).

The iFCSPI protocol has comparable convergence characteristics to iQuAPI. We found that it is slightly more difficult to converge the imaginary part of the CGF than the reduced density matrix, and much more difficult to converge the real part of the CGF. After presenting as an example the CGF, in the rest of the chapter we focus on the behaviour of the first cumulant of heat exchange, the heat current.
4.5.2 Perturbative methods

In order to assess the viability of the iFCSPI we compared its results to several other methods, which are perturbative in the interaction parameter $\gamma$ or the tunnelling element $\Delta$:

(i) The Markovian Redfield quantum master equation (QME) is a second order perturbative approach, the same used in Chapter 3, valid for a system weakly coupled to a Markovian environment [43]. The resulting heat current expression only includes resonant heat exchange processes. We use expressions developed in Refs. [220, 340], and more recently reviewed in Ref. [331]. We refer to this approach as the “Redfield QME” method.

(ii) The Majorana fermion Green’s function (Majorana-GF) approach is perturbative is the system-bath coupling, but it can capture non-resonant processes beyond the Redfield QME. The working expressions were organized in Ref. [331].

(iii) Polaron transforming the spin-boson model, one can derive expressions for the heat current that are related to the noninteracting blip approximation (NIBA) literature [332, 333, 352]. Under the Markov approximation we organize the NIBA QME [220, 340, 330, 329], which is valid for intermediate-strong system-bath coupling when $\bar{T} \gg \Delta$. We note that a more accurate polaron transformed method was developed more recently: It interpolates between the Redfield limit and NIBA [332, 333], or goes beyond the Markovian limit [352]. Here we limit ourselves to the high temperature Markov equation that was described in Refs. [220, 329], referred below to as “NIBA” expression for heat exchange.

4.5.3 Cumulant generating function

The behaviour of the function $\ln Z(t, \xi)$ is displayed in Fig. 4.3. The imaginary part of the function is odd in the counting parameter. In panel (b) we show the cumulant generating function as it approaches steady-state.
and reaches its nonequilibrium steady-state. Taking the derivative with respect to $i\xi$ provides the averaged heat current. The real part of $\ln Z(t,\xi)$ is displayed in panel (c). As expected, it is even in the counting parameter, see Eq. (4.8). While our results for the imaginary part of $Z(t,\xi)$ easily converge with respect to the time step and memory size (here with $\delta t = 0.3$, $\Delta k = 5$), the real part of this function requires stringent conditions for convergence, beyond what our implementation can currently meet.

We compute the steady-state current via numerical derivatives of the cumulant generating function, following Eq. (4.10). The cumulant generating function reaches its steady-state limit when $\ln[Z(t,\xi)]$ becomes linear in time. At that point, one evaluates a numerical derivative with respect to $t$ to extract $G(\xi)$. Here $\xi$ is always the smallest timescale of the system, and particularly, small compared to $\delta t$. It is further not difficult to check the convergence with respect to $\xi$, to ensure one captures only the linear behaviour of the cumulant generating function. In our simulations we typically take $\xi$ on the order $\delta t/100$.

### 4.5.4 Heat current

![Figure 4.4: (a) Steady-state heat current in the NESB model as a function of the dimensionless system-bath coupling parameter $\gamma$ with $\Delta k = 7$ and different time steps $\delta t$. Results are compared to NIBA simulations. (b) Weak coupling results are compared to the Redfield QME and the Majorana Green’s function approaches. (c)-(d) Exemplifying convergence of results at $\gamma = 0.1$ as a function of (c) $\Delta k$ while fixing the time step and (d) $\delta t$ for a fixed memory time. Parameters are $\Delta = 1$, $\omega_c = 50$, $T = 5$, $T_L - T_R = 0.5$.](image-url)

**System-bath coupling.** Figure 4.4 displays the behaviour of the heat current as a function of the coupling strength to the baths. We compare the behaviour of the iFCSPI to other approaches, and to facilitate comparison we define a dimensionless parameter, $\frac{\Delta}{\bar{T}}$. We expect iFCSPI simulations to comfortably converge when $\gamma \Delta \ll 1$. Here, $\gamma \Delta$ is the system-bath interaction energy in the Redfield limit; the bath-induced transition rate in the Redfield QME is proportional to this factor through its dependence on $g(\omega)$, assuming an Ohmic form. The Redfield formalism holds for the NESB so long as the interaction energy is assumed smaller than the energy spacing in the system, i.e. $\gamma \Delta \ll \Delta$ or $\gamma \ll 1$. NIBA is valid at high temperatures in the nonadiabatic limit, $\Delta < \bar{T}$. 


The agreement with weak-coupling approaches is excellent when $\gamma$ is small, as we observe in panel (b), while at weak-intermediate coupling, $\gamma \gtrsim 0.1$ (or equivalently, $\frac{\gamma}{\bar{T}} \gtrsim 0.02$), the results deviate by about a factor of 1.5-2 as we pass out of the range of validity for the Redfield and Majorana approaches.

As we push the iFCSPI method into the stronger system-bath coupling regime, $\gamma > 0.25$ (or equivalently, $\frac{\gamma}{\bar{T}} > 0.05$), convergence becomes difficult in the current implementation. Results are compared to the Markovian NIBA approach [329], which is known to be qualitatively correct at strong coupling for Ohmic dissipation, though in general it overestimates the current. We understand a priori that we will not be able to converge the iFCSPI at strong coupling with our current implementation, simply due to the prohibitive computational cost of additional system-bath memory. That being said, the method converges quite well up to $\gamma \approx 0.2$, and the qualitative behaviour of iFCSPI simulations is fair over the full range. The peak position is close to that from NIBA, and it follows the expected turnover behaviour.

Panels (c) and (d) in Fig. 4.4 exemplify the convergence of the iFCSPI at weak-intermediate coupling. We first show the convergence as a function of the memory time covered by increasing $\Delta k$ with a short time step. We then demonstrate a fixed-memory analysis, where the total memory time is kept fixed, $\tau_m = \Delta k \cdot \delta t$, and the number of time steps required to cover this memory range is increased, eventually converging with a short enough time step.

Figure 4.5: (a) Steady-state heat current in the NESB model as a function of temperature difference $T_L - T_R$. iFCSPI simulations are compared to Redfield and Majorana-GF approaches. (b)-(c) Convergence is achieved for both small and large temperature bias as illustrated upon varying (b) the memory range $\Delta k$ with a fixed $\delta t = 0.07$, and the (c) time step $\delta t$ with a fixed $\Delta k = 7$. The arrow in panel (b) points to the direction of converging results. Parameters are $\Delta = 1, \gamma = 0.1, \omega_c = 50, \bar{T} = 5$.

Temperature difference. In Fig. 4.5 we study the behaviour of the heat current as a function of the temperature difference, up to a large bias, observing a linear dependence. This is the expected result when the coupling to the hot and cold reservoirs is symmetric, as in our work, but is not general [298]. This trend agrees with weak coupling approaches across the full range of temperature biases examined; for a symmetric junction, the Redfield approaches predicts $\langle J_Q \rangle \propto \frac{(T_L - T_R)}{T}$ [220, 340, 232]. While weak coupling methods are qualitatively correct for the presented parameters, the Redfield QME overestimates the heat current by almost a factor of two throughout, which is quite significant. We note that our results fully converge both at small, $(T_L - T_R)/\Delta < 1$, and large, $(T_L - T_R)/\Delta > 1$, temperature differences,
see panels (b)-(c). With algorithmic improvements, one could test the behaviour of the heat current as a function of temperature difference at strong coupling. Furthermore, by introducing a spatial asymmetry with different coupling energies at the two boundaries one could assess the extent of the thermal diode effect, which so far was predicted and evaluated based on perturbative methods [220, 340].

Figure 4.6: (a) Steady-state heat current as a function of the tunnelling element $\Delta$ in the weak system-bath coupling regime. We present three curves for the iFCSPI with different time steps $\delta t$. iFCSPI results are compared to Redfield QME (full), Majorana-GF (dashed-dotted), and NIBA (dashed) results. The latter is known to fail in the large $\Delta$ regime. (b) Demonstration of convergence behaviour: series of results from $\Delta k = 1 - 6$ for $\delta t = 0.05$. The arrow points to the direction of increasing $\Delta k$. The case $\Delta k = 7$, which is presented in panel (a) is highlighted in filled circles. Parameters are $\gamma = 0.01$, $\omega_c = 50$, $\bar{T} = 5$, $T_L - T_R = 0.5$.

Coherent tunnelling/level splitting. Fig. 4.6 shows the behaviour of the current as we increase the eigenenergy splitting, $\Delta$, which corresponds to the tunnelling energy in the site basis. Note that we enter an effective low temperature regime as we increase $\Delta$, and it is more difficult to converge the iFCSPI when $\Delta \gtrsim \bar{T}$. That being said, the iFCSPI maintains excellent agreement with weak coupling approaches up to $\frac{\Delta}{\bar{T}} \approx 0.02$, and is in qualitative agreement for the full range. The three lines shown for the path integral are each converged in terms of memory length $(\Delta k \cdot \delta t)$, and we approach the correct answer by successively reducing the time step $\delta t$. NIBA follows the expected $\langle J_Q \rangle \propto \Delta^2$ trend [329], and it breaks down when $\frac{\Delta}{\bar{T}} \gtrsim 0.01$. In panel (b) we display convergence in $\Delta k$ for the shortest time step, and we find that the method converges for the full range of $\Delta$, for the given $\tau_m$.

4.6 Conclusions

We introduced an iterative influence functional path integral approach to simulate the full counting statistics of heat exchange in quantum impurity models. This iFCSPI generalizes the celebrated iQuAPI, going beyond iterative evolution of the reduced density matrix to study energy transfer statistics in a numerically exact manner.

The numerical implementation of the iFCSPI relies on a discretized representation of the system’s coordinates. To test the this new approach, we applied it to the nonequilibrium spin-boson model and focused on the average heat current in steady-state. We studied the heat transfer behaviour as a function
of system-bath coupling and tunnelling splitting, demonstrating turnover behaviour in both cases. The iFCSPI method can be employed far from equilibrium at large temperature difference since its working expressions are not based in a linear response assumption. Though not elaborated on in this work, one can employ the iFCSPI to retrieve transient energy exchange statistics by considering the behaviour of the generating function between its initial condition and the steady-state limit.

Key challenges associated in converging iFCSPI simulations were elaborated on. Most critically, Trotter splitting leads to spurious heat current at zero temperature difference when the time step $\delta t$ is finite. Nevertheless, this error is precisely cancelled out in junctions with identical bath spectral functions and upon symmetrizing the counting fields at the two boundaries. Besides numerical exactness, a key benefit of the iFCSPI approach is the ease of implementation, coming as a straightforward modification to the iQuAPI method. Converging the path integral for parameters in the range $\omega_c > \bar{T} > \Delta > \gamma\Delta$ was feasible even with the basic iQuAPI algorithm.

Beyond the spin-boson model, the principles outlined here can be used to study other models for charge and energy transport based on a path integral representation of the generating function, constructed similarly to Eq. (4.20). For example, FCS of the interacting Anderson dot model [52, 53, 370, 371, 372] or the spin-fermion model can be investigated using an iterative algorithm. Finite-time FCS [373] can be similarly readily explored using the iFCSPI method.

Future work will be focused on implementing the iFCSPI within efficient path integral algorithms developed in the area of dissipative dynamics, such as path filtering [358] and tensor decomposition [363]. Coupled with a sufficiently powerful algorithm, the iFCSPI is a tremendously enabling tool, handing over not only the system reduced density matrix, but also the energy exchange statistics to numerically exact precision. An improved iFCSPI algorithm would enable the exploration of non-Markovianity, strong system-bath coupling effects, quantum coherences and time-dependent driving, offering itself as a powerful instrument for studies of quantum thermal machines.
Part II Summary

In this second and final Part of the thesis, we analysed in-detail the role of coherence in automatous (non-driven) quantum heat machines, and introduced a new, numerically exact method for computing heat transfer statistics, with an eye towards applications in QHMs. In Chapter 3, we presented a model system which, counter to the norm, has its power output completely damped by persistent energy basis coherences. We then presented a general approach for examining the operation of coherence-active QHMs, through a completely secular lens, and used it to analyse several fundamental models and make sense of their operational characteristics without explicit consideration of coherences.

In Chapter 4, we presented and characterized our new iterative full-counting statistics path integral. We showed that this technique has great potential for exact simulations of quantum heat transport, though it will require additional numerical/computational streamlining to bring computational costs down to a reasonable level for most systems of interest.

Our secularized picture can significantly clarify the operational features of QHMs where noise-induced coherences play a role. Without such a tool, intuitive understanding of the role of coherence in these devices is far from straightforward. As regards the iFCSPI, its key limitation currently would seem to be the requirement of symmetrisation of counting fields. The numerical challenges in a study of a complex, multi-bath, multi-level QHM would be far from trivial, but excellent work in recent years on optimising iQuAPI-type algorithms has opened the door to this type of project [358, 363]. To date, however, we have found no means of cancelling the Trotter error in the generating function of heat current, other than via bath symmetrisation, potentially making simulation of multi-bath setups more complicated.
Conclusion

We presented in this thesis studies of the charge and energy transport characteristics of several types of nanodevices. In particular, we focused on mechanistic insights into device operation - how can we efficiently simulate environmental effects, and that is their role? What is the role of coherence, and how can we best analyse it? How can we capture the effect of strong system-bath coupling and non-Markovian effects on heat transfer statistics? We addressed these questions while considering and commenting on the applicability of the methods employed by us and in the broader literature.

Part I of the thesis examined charge transport through molecular junctions, with incoherent environmental effects incorporated into the Landauer technique via Büttiker’s probes. Using the LBP technique, we were in Chapter 1 able to successfully phenomenologically capture many of the physical features of incoherent hopping including length dependence, thermal activation and a Kramer’s-like turnover. We further validated the technique by comparison with experimental data on long, conjugated molecular wires, and found we were able to match the tunnelling to hopping crossover length and current values with good accuracy. Chapter 1 concludes with an application of the LBP to the problem of electrical conductance of stacked vs. alternating ds-DNA. We show that the experimentally observed even-odd trend can be explained by overlaying an oscillating coherent contribution on a linear hopping contribution. This mixture of coherent and environmental effects means that this could not have been understood from the level of bare Landauer theory.

In Chapter 2 we considered the molecular junctions under high voltage using the LBP, beginning with implementation of the voltage probe far-from-equilibrium, before moving on to studies of model systems and applications. When a large voltage bias is applied, we developed two key features; the molecular orbital energies are shifted, deforming the structure of the wire, and the behaviours of dephasing (elastic) and voltage (inelastic) probe conditions diverge. We found that since the dephasing probe was unable to admit dissipation of electronic energy along the molecular bridge, it could not support a large hopping current at high voltage. In contrast, the voltage probe efficiently dissipated energy from incoming electrons into the environment, and so admitted large currents. Understanding the high-bias behaviour of the probes, we analysed the role of an environment on the operation of the most basic electronic device, the diode. We subjected a proposed model for a tunnelling diode to environmental effects, and discovered that its operation is hampered, though not dramatically so, up to reasonable dephasing strength. Pushing the model, we propose an extension which achieved much higher rectification ratios, but which is accordingly more difficult to construct, and more susceptible to environmental effects. We finish Part I with a presentation of two systems wherein the role of the environment is to generate a weak diode effect in an otherwise symmetric system.

Part II shifts the focus of the thesis from charge to heat transport. In Chapter 3 we addressed the problem of noise-induced coherences in quantum thermal machines. Building up from its components,
we thoroughly analysed the behaviour of a four level quantum absorption refrigerator wherein the coherences damped device performance, even deactivating it. This stands in stark contrast to studies where coherence was found to boost the power output, compared to the non-coherent case [10]. To unravel this seeming contradiction, we proposed and utilized a new protocol for the analysis of heat machines, which gives a fully secular picture of device operation, eliminating the ambiguity introduced by the presence of energy basis coherences. We demonstrated the utility of the secular basis by a systematic analysis of a variety of models that support steady-state noise-induced coherences, where we were able to interpret the role of coherence in an intuitive, straightforward manner.

We concluded in Chapter 4 with a presentation of a numerically exact path integral technique, the iterative full-counting statistics path integral (iFCSPI), for computing the cumulants of the heat current from a heat bath coupled to a quantum subsystem. We presented a detailed derivation and discussion of implementation before applying the method to the nonequilibrium spin boson model, and comparing results to other methods. The full-counting statistics path integral, when it converged, found good agreement with the other methods in their respective regimes of validity. Thus we are incentivised to develop superior numerical techniques in the future that will allow us to converge the path integral in a wider parameter space. We further included is a detailed look at the unique error properties of the method, as well as a derivation of the full-counting statistics for the dephasing model.
Appendix A

Supporting Results for Hopping Conductance

A.1 Hopping conduction: construction of Eq. (1.31).

Based on the simulations reported above, as well as additional results included here, we suggest the hopping conductance, Eq. (1.31), $G_H \sim G_0 A(T) \frac{\gamma_2 d^2}{\epsilon_B^4} \frac{1}{N+1}$, with the dimensionless coefficient $l$, positive or negative, see Fig. 1.7. This expression contains the central characteristics of bath-assisted conduction: Ohmic-like conduction for long chains, and the enhancement of $G$ with dephasing strength (for weak dephasing) and with barrier parameters as $\frac{\gamma d}{\epsilon_B^4}$. Recall that Eq. (1.31) was developed assuming parameters in the range $\gamma d, v, \beta^{-1}, \Delta \mu \ll \epsilon_B, \gamma < \epsilon_B$.

We can justify this hopping form with some qualitative arguments: Electrons scatter into the molecule through the resonance most strongly hybridized with the $L$ metal, and leave from the orbital most tightly coupled to the $R$ lead, overall contributing the factor $\frac{\epsilon^2}{\beta^2}$. On the molecule, the probes absorb and emit electrons, dispersing them between molecular orbitals, thus the conductance scales as $\gamma_2^2 d$, describing probe-molecule-probe transitions. The contribution of probe-mediated scattering processes linearly grows with the number of molecular sites (probes), thus the hopping resistance grows as $N$.

The overall temperature dependence in the process is rather weak; the hopping conductance integrates electrons thermally populating many levels in the lead, off-resonant as well as in resonance with molecular orbitals.

Both dephasing and voltage probes disperse electrons between molecular orbitals. However, the dephasing probe does so while maintaining the number of electrons within each energy interval fixed. The voltage probe can absorb/provide energy from/to electrons, and it can thus modify the energy distribution of electrons in the system. At low bias, $\Delta \mu < \gamma d, \beta^{-1}$, the two probes produce very similar conductance characteristics.

A.2 Simulations

In Chapter 1 we established Eq. (1.31) by exploring the dependence of the hopping conductance on $\epsilon_B, \gamma_d$, temperature and length. Here we complement this and examine the role of inter-site tunnelling $v$ and metal-molecule hybridization on $G_H$. In Fig. A.1 we confirm that in the coherent-tunnelling regime
Appendix A. Supporting Results for Hopping Conductance

Figure A.1: Electrical conductance vs. inter-site tunnelling $v$. In the coherent tunnelling limit $G \propto \frac{1}{v^3} \left( \frac{v}{\epsilon_B} \right)^{2N}$. In the hopping regime $G \propto v^2$. Parameters used are $\epsilon_B = 0.5$, $v = 0.05$, $\gamma_B = 0.2$, $\Delta \mu = 0.01$ eV.

$G \propto v^{2N-2}$, but at finite dephasing and for large $N$ we obtain $G \propto v^2$ for $v \ll \epsilon_B$, independent of molecular length (not shown).

Figure A.2: Electrical conductance as a function of the hybridization energy, $\gamma_B = \gamma_R$. When $\gamma_d = 0$ we resolve tunnelling conductance for $N = 3$, $G \propto \gamma_L \gamma_R$ ($\triangle$) and ballistic motion for $N = 7$ when $\gamma_d \ll \epsilon_B$ ($\circ$). The conductance dependency on $\gamma_d$ diminishes upon increasing dephasing strength. We used $T = 300$ K, $\epsilon_B = 0.5$, $v = 0.05$, $\Delta \mu = 0.01$ eV, dephasing probe simulations.

The hybridization energy $\gamma_d$ is expected to only mildly influence hopping conduction, as the resistance should be determined by the wire itself - electron scattering between probes- rather than by the interface of the molecule with the contacts. This behaviour is confirmed in Fig. A.2: Tunnelling conductance ($N = 3$, $\gamma_d = 0$) grows as $\gamma_L \gamma_R$, see Eq. (1.29), but in long chains with $\gamma_d \neq 0$ the effect of the hybridization energy on $G$ is insignificant.
Appendix B

Electronic Matrix Elements for the Ladder Model

For the completeness of our presentation we compile three tables B.1-B.3 from Ref. [175] with values for charge-transfer integrals as used in our simulations for the ladder model of double-stranded DNA. As noted in the literature, \( t_{5'-XY-3'} = t_{5'-YX-5'} \) and \( t_{3'-XY-3'} = t_{3'-YX-3'} \) from symmetry, but \( t_{5'-XY-3'} \neq t_{3'-XY-3'} \), given the directionality of DNA [175].

<table>
<thead>
<tr>
<th>Y</th>
<th>X</th>
<th>G</th>
<th>A</th>
<th>C</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
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<td>-0.077</td>
<td>-0.114</td>
<td>0.141</td>
<td></td>
</tr>
<tr>
<td>A</td>
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<td>-0.004</td>
<td>0.042</td>
<td>-0.063</td>
<td></td>
</tr>
<tr>
<td>C</td>
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<td>-0.002</td>
<td>0.022</td>
<td>-0.055</td>
<td></td>
</tr>
<tr>
<td>T</td>
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<td>-0.031</td>
<td>-0.028</td>
<td>0.072</td>
<td></td>
</tr>
</tbody>
</table>

Table B.1: \( t_{5'-XY-3'} = t_{3'-YX-5'} \) (eV) [175]

<table>
<thead>
<tr>
<th>Y</th>
<th>X</th>
<th>G</th>
<th>A</th>
<th>C</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
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<td>-0.013</td>
<td>0.002</td>
<td>-0.009</td>
<td></td>
</tr>
<tr>
<td>A</td>
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<td>0.031</td>
<td>-0.001</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>C</td>
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<td>-0.001</td>
<td>0.001</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>T</td>
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<td>0.007</td>
<td>0.0003</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>

Table B.2: \( t_{5'-XY-3'} \) (eV) [175]
### Table B.3: $t_{3'}_{X Y - 3'} (eV)$ [175]

<table>
<thead>
<tr>
<th></th>
<th>G</th>
<th>A</th>
<th>C</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
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<td>-0.011</td>
<td>0.022</td>
<td>-0.014</td>
</tr>
<tr>
<td>A</td>
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<td>0.049</td>
<td>0.017</td>
<td>-0.007</td>
</tr>
<tr>
<td>C</td>
<td>0.022</td>
<td>0.017</td>
<td>0.010</td>
<td>0.004</td>
</tr>
<tr>
<td>T</td>
<td>-0.014</td>
<td>-0.007</td>
<td>0.004</td>
<td>0.006</td>
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</table>
Appendix C

Analytics for 3 and 4 Level Quantum Heat Machines

C.1 Energy transfer in the V system

We derive here a closed-form expression for the energy current in the VETS model under the secular approximation. Our starting point is the Redfield equation (3.14) for the reduced density matrix $\sigma$, written in the energy basis (“global Redfield”), which couples the dynamics of populations and coherences. For the VETS model (3.6)-(3.7), the Redfield equation reduces to

\[
\dot{\bar{\sigma}}_{11}(t) = -(R_{12,21} + R_{13,31} + R_{13,31}^*)\sigma_{11}(t) + \sigma_{12}(t) + (R_{21,12} + R_{21,12}^*)\sigma_{22}(t) + (R_{31,13} + R_{31,13}^*)\sigma_{33}(t)
\]
\[
+ (R_{31,12} + R_{31,13}^*)\sigma_{23}(t) + (R_{21,13} + R_{31,12})\sigma_{32}(t),
\]
\[
\dot{\bar{\sigma}}_{22}(t) = -(R_{21,12} + R_{21,12}^*)\sigma_{22}(t) + \sigma_{11}(t) - R_{21,13}\sigma_{23}(t) - R_{21,13}^*\sigma_{32}(t),
\]
\[
\dot{\bar{\sigma}}_{33}(t) = -(R_{31,13} + R_{31,13}^*)\sigma_{33}(t) + (R_{31,13} + R_{31,13}^*)\sigma_{11}(t) - R_{31,12}\sigma_{23}(t) - R_{31,12}^*\sigma_{32}(t),
\]
\[
\dot{\bar{\sigma}}_{23}(t) = +2i\sigma_{23}(t) - (R_{21,12} + R_{21,12}^*)\sigma_{23}(t) + (R_{13,21} + R_{13,21}^*)\sigma_{11}(t) - R_{31,12}\sigma_{22}(t) - R_{21,13}\sigma_{33}(t)
\]
\[
- (R_{22,22} + R_{33,33}^* - R_{33,33} - R_{22,22}^*)\sigma_{23}(t),
\]
\[
\dot{\bar{\sigma}}_{32}(t) = -2i\sigma_{32}(t) - (R_{21,12} + R_{31,13})\sigma_{32}(t) + (R_{13,21} + R_{13,21}^*)\sigma_{11}(t) - R_{31,12}\sigma_{22}(t) - R_{21,13}\sigma_{33}(t)
\]
\[
- (R_{22,22} + R_{33,33}^* - R_{33,33} - R_{22,22}^*)\sigma_{32}(t).
\]

(C.1)

For notational simplicity, we do not explicitly indicate the frequency at which the dissipation elements are calculated, see Eqs. (3.14)-(3.15). Note that there are three types of bath-induced terms in Eq. (C.1): (i) We put together the rate constants induced by the hot and cold baths, $R_{mn,jk}(\omega) = \sum_{\alpha=h,c} R_{\alpha mn,jk}^\alpha(\omega)$. For example, $R_{12,21}(\omega) = \Gamma_h(\omega) + \Gamma_c(\omega)$ (ignoring for simplicity the imaginary term). (ii) On top of that, we use bold faced fonts to highlight terms in which the sum $\sum_{\alpha=h,c} R_{\alpha mn,jk}^\alpha(\omega)$ turns into the difference between the hot and cold dissipation rates, such as in $R_{21,13}(\omega) = \Gamma_h(\omega) - \Gamma_c(\omega)$. The sign difference develops because the operators $\hat{S}_h$ and $\hat{S}_c$ have opposite signs in front of the transitions $|1\rangle|2\rangle + h.c.$, see Eq. (3.7). (iii) We separately identify contributions from the decohering bath, for example, $R_{22,22}^d = -R_{22,33}^d = \Gamma_d(0)$. Because $n(0)$ diverges, the zero-frequency transitions mediated
through the decohering bath require some extra effort to compute. In general, this term is dependent on the functional form of the spectral density. For an ohmic bath, we employ L’Hôpital’s rule to compute the limit

\[
J(0)n(0) = \lim_{\omega \to 0} \frac{\gamma \omega e^{-|\omega|/\omega_c}}{e^{\beta \omega} - 1} = \lim_{\omega \to 0} \frac{\gamma e^{-|\omega|/\omega_c} (\omega_c - \omega)}{\omega_c \beta e^{\beta \omega}} = \frac{\gamma}{\beta}.
\]

(C.2)

Based on Eq. (C.1), we can clearly expose the conditions for which a secular approximation is justified:

(i) Energy basis coherences only survive in the long-time limit if the system is driven out of equilibrium, i.e. there is a temperature bias between the reservoirs. If there is no temperature bias, the system will adhere to the Gibbs state defined by the bath temperatures, which is completely diagonal. This can be proved as follows. When \( T_h = T_c \), we add up the equations of motion for the coherences, \( \sigma_{23} + \sigma_{32} \), and in the long time limit, we assume zero coherences. The only surviving terms then (in bold) have a sign flip between the two (equal temperature) baths, \( R_{ij,kl}(\omega_{ik}) = \Gamma_h(\omega_{ik}) - \Gamma_c(\omega_{ik}) \). This contribution is proportional to \((\gamma_h - \gamma_c)\), resulting in a trivial identity for the population dynamics. Since the algebraic steady-state equation has a unique solution, the trial solution of zero coherences, which does not show contradictions, is valid.

(ii) When \( g \) is large compared to the dissipation rate, the so-called “rotating-wave approximation” becomes well-justified. This translates to the timescale of coherence oscillation being short compared to other timescales of the system, and therefore effectively decoupling coherences from the population dynamics.

(iii) Finally, one can directly “secularize” the dynamics by adding strong decoherence effects, \( \gamma_d \gg \gamma_{h,c,w} \). This contribution exponentially damps the coherence terms, \( \sigma_{23}, \sigma_{32} \), resulting in a secular dynamics.

Working under the secular approximation with population and coherence dynamics decoupled, we find from Eq. (C.1) that the populations follow a kinetic equation \( \dot{\rho} = \sum_{\alpha = h,c} D_\alpha |p\rangle \), with the vector \( |p\rangle = (p_1, p_2, p_3)^T \) and the dissipator

\[
D_\alpha = \begin{pmatrix}
-k_{1\to 2}^\alpha & -k_{1\to 3}^\alpha & k_{2\to 1}^\alpha & k_{2\to 3}^\alpha \\
 k_{1\to 2}^\alpha & -k_{1\to 3}^\alpha & 0 & 0 \\
 k_{1\to 3}^\alpha & 0 & 0 & -k_{3\to 1}^\alpha
\end{pmatrix}
\]

(C.3)

It is useful to define the two relevant frequencies as \( \theta_{\pm} = \theta \pm g \), see Fig. 3.1. The rate constants combine two Redfield dissipation rates, for example, \( k_{1\to 2}^h = R_{12,21}^h + R_{12,21}^{h,\ast} \). Explicitly, they are given by \( k_{1\to 2}^\alpha = \frac{1}{2} J_\alpha(\theta_-) n_\alpha(\theta_-) \) and \( k_{1\to 3}^\alpha = \frac{1}{2} J_\alpha(\theta_+) n_\alpha(\theta_+) \), with the reversed rates \( k_{2\to 1}^\alpha \) and \( k_{3\to 1}^\alpha \) determined from detailed balance. Note, the factor 1/2 within these expressions results from the 1/\( \sqrt{2} \) prefactor in front of the energy basis operators \( \hat{S}_\alpha \) in Eq. (3.7). Here, \( n_\alpha(\theta_{\pm}) = (e^{\beta_{\pm} \theta_{\pm}} - 1)^{-1} \) is the Bose-Einstein distribution function and \( J_\alpha(\theta_{\pm}) \) is the spectral density of the \( \alpha \) bath. In the ohmic limit with a large cutoff frequency, \( \omega_c \gg \theta, g \),

\[
k_{1\to 2}^\alpha = \frac{1}{2} \gamma_\alpha \theta_- n_\alpha, \quad k_{1\to 3}^\alpha = \frac{1}{2} \gamma_\alpha \theta_+ n_\alpha^\ast, \quad (C.4)
\]

We use the short notation \( n_\alpha^{\pm} \equiv n_\alpha(\theta_{\pm}) \). For simplicity, we further assume a symmetric coupling,
Appendix C. Analytics for 3 and 4 Level Quantum Heat Machines

\[ \gamma = \gamma_{c,h}. \] Recall that \( \gamma_{h,c,d} \) are dimensionless coupling parameters.

We readily calculate the energy current (e.g. from the hot bath) using Eq. (3.18), or directly with the approach described in Ref. [275], using partial cumulant generating functions. The energy current from the hot bath includes two contributions from the two transitions ("spins"),

\[
J_q = \theta - \left[ \frac{(k_{1\rightarrow 2}^h k_{2\rightarrow 1}^c - k_{1\rightarrow 2}^c k_{2\rightarrow 1}^h)}{\Psi} \right]
\]

The denominator is

\[
\Psi = (k_{1\rightarrow 3}^c + k_{1\rightarrow 3}^h) (k_{2\rightarrow 1}^c + k_{2\rightarrow 1}^h) + (k_{3\rightarrow 1}^c + k_{3\rightarrow 1}^h) (k_{2\rightarrow 1}^h + k_{2\rightarrow 1}^c + k_{1\rightarrow 2}^c + k_{1\rightarrow 2}^h). 
\]

Equation (C.5) describes the energy current in the VETS model when the population and coherences dynamics are decoupled. The energy current depends on the inter-site coupling \( g \) in a rich manner. First, clearly, the frequencies \( \theta_{\pm} \) are linear functions in \( g \). More involved behaviour arises since the distribution function \( n_{\alpha}^{\pm} \) further depends on the transition frequency, thus it is a nonlinear function of \( g \).

To the lowest order in \( g \), the levels \( \theta_{\pm} \) are degenerate thus \( k_{1\rightarrow 2}^c = k_{1\rightarrow 3}^c \). As a result, the current (C.5) reduces to

\[
J_q = 2\theta \frac{[k_{1\rightarrow 2}^h k_{2\rightarrow 1}^c - k_{1\rightarrow 2}^c k_{2\rightarrow 1}^h]}{2(k_{1\rightarrow 2}^c + k_{1\rightarrow 2}^h) + k_{2\rightarrow 1}^c + k_{2\rightarrow 1}^h + k_{1\rightarrow 2}^c + k_{1\rightarrow 2}^h}, \quad \text{(C.6)}
\]

Using the concrete expressions for the rate constants (C.4), we immediately get

\[
J_q = \gamma \theta^2 \frac{n_h(\theta) - n_c(\theta)}{3n_c(\theta) + 3n_h(\theta) + 2}, \quad \text{(C.7)}
\]

Beyond the lowest order in \( g \), corrections are given by a power series, \( g^{2n} \) with \( n = 1, 2, 3, ... \). We reiterate that Eq. (C.7) is valid when the internal coupling \( g \) is small yet the decoherence constant \( \gamma_d \) is large enough such that the secular approximation is well founded.

C.2 3LQAR

We derive here an expression for the cooling current in the canonical three-level QAR (3LQAR) model. We further discuss the cooling window and the cooler coefficient of performance (termed efficiency here). In the 3LQAR model, each transition is coupled to a separate thermal bath; internal couplings between system’s states are absent. As a result, in this model population and coherences naturally decouple, without the need to further invoke the secular approximation. Using the Redfield equation in a manner analogous to that described in Sec. C.1, we find that the population dynamics follow a kinetic equation
\(|\rho\rangle = \sum_{\alpha=c,h,w} D_\alpha |\rho\rangle\), with the population vector \(|\rho\rangle = (p_1, p_2, p_3)^T\), and the total dissipator

\[
\sum_\alpha D_\alpha = \begin{bmatrix}
-k_{1\rightarrow 2}^c & k_{2\rightarrow 1}^c & k_{h\rightarrow 3}^h \\
-k_{1\rightarrow 2}^h & -k_{2\rightarrow 1}^h & k_{w\rightarrow 3}^w \\
k_{1\rightarrow 3}^c & k_{w\rightarrow 3}^w & -k_{3\rightarrow 1}^c & -k_{3\rightarrow 1}^w
\end{bmatrix}
\] (C.8)

The rate constants for a given transition are given by the Bose-Einstein function and the spectral density, evaluated at the transition frequency,

\[
k_{1\rightarrow 2}^c = J_c(\theta_c) n_c(\theta_c), \quad k_{1\rightarrow 3}^h = J_h(\theta_h) n_h(\theta_h) \quad \text{and} \quad k_{2\rightarrow 3}^w = J_w(\theta_w) n_w(\theta_w).
\]

The reversed rate constants are determined from detailed balance. We assume ohmic spectral functions with large cutoff frequencies. For simplicity, we further take the couplings to be identical at all contacts, \(\gamma = \gamma_\alpha\). Since the Bose-Einstein function is evaluated at the transition frequency, we can use the short notation \(n_\alpha \equiv n_\alpha(\theta_\alpha)\). Following Eq. (3.18), the heat current at the \(c\) bath is given by

\[
J_q^c = \theta_c k_{1\rightarrow 2}^c k_{w\rightarrow 3}^w k_{3\rightarrow 1}^h - k_{1\rightarrow 3}^h k_{2\rightarrow 1}^w / \Psi,
\] (C.9)

with the denominator

\[
\Psi = k_{1\rightarrow 3}^h k_{2\rightarrow 1}^c + k_{1\rightarrow 3}^c k_{2\rightarrow 1}^w + k_{1\rightarrow 3}^h k_{2\rightarrow 3}^w \\
+ k_{2\rightarrow 1}^c k_{3\rightarrow 1}^h + k_{2\rightarrow 1}^w k_{3\rightarrow 2}^h + k_{2\rightarrow 3}^h k_{3\rightarrow 2}^w \\
+ k_{2\rightarrow 1}^c k_{3\rightarrow 1}^h + k_{2\rightarrow 1}^w k_{3\rightarrow 2}^h + k_{2\rightarrow 3}^w k_{3\rightarrow 1}^h.
\] (C.10)

Explicitly, we find that the cooling current is given by

\[
J_q^c \propto \gamma \theta_c [n_c n_w (n_h + 1) - n_h (n_c + 1)(n_w + 1)].
\] (C.11)

Positive cooling current, i.e. the extraction of thermal energy from the cold bath, is achieved when the inequality is satisfied,

\[
(n_c + 1)(n_w + 1)n_h < (n_h + 1)n_w n_c.
\] (C.12)

One can then readily identify the cooling window,

\[
\frac{\theta_c}{\theta_h} < \frac{\beta_h - \beta_w}{\beta_c - \beta_w}
\] (C.13)

It can be also shown that the cooling coefficient of performance is

\[
\eta \equiv J_q^c / J_w^c = \frac{\theta_c}{\theta_w},
\] (C.14)

and that this coefficient is bounded by the Carnot limit,

\[
\eta_C = \frac{\beta_h - \beta_w}{\beta_c - \beta_h}.
\] (C.15)

For the ohmic model, the efficiency at maximal power is tightly bounded by half of the Carnot efficiency [265].
C.3 4lQAR

The 4lQAR combines features from both the VETS and the 3lQAR. As described in Sec. C.1, our starting point is the Redfield equation, working as usual in the energy basis. The structure of the equation would be analogous to (C.1), with an additional level |4⟩ and the work bath w.

We can easily calculate the cooling current in the 4lQAR model within the secular approximation. First, we define four frequencies, \( \theta^\pm_c = \theta_c \pm g \), \( \theta^\pm_w = \theta_w \pm g \), which obey \( \theta_h = \theta^+_c + \theta^-_w \). Under the secular approximation, the populations follow a kinetic equation of motion, \( \dot{\rho} = \sum_{a=h,c,w} D_a |p\rangle \), with the population vector \( |p\rangle = (p_1, p_2, p_3, p_4)^T \) and the total dissipator is,

\[
\sum_a D_a = \begin{bmatrix}
-k^c_{1 \rightarrow 2} - k^c_{1 \rightarrow 3} - k^w_{1 \rightarrow 4} & k^c_{2 \rightarrow 1} & k^c_{3 \rightarrow 1} & k^w_{4 \rightarrow 1} \\
 0 & -k^c_{2 \rightarrow 1} - k^w_{2 \rightarrow 4} & 0 & k^w_{4 \rightarrow 2} \\
k^c_{1 \rightarrow 3} & 0 & -k^c_{3 \rightarrow 1} - k^w_{3 \rightarrow 4} & k^w_{3 \rightarrow 4} \\
k^c_{1 \rightarrow 4} & k^w_{2 \rightarrow 4} & k^w_{3 \rightarrow 4} & -k^h_{4 \rightarrow 1} - k^w_{4 \rightarrow 2} - k^w_{3 \rightarrow 4}
\end{bmatrix}.
\]

The rate constants are

\[
k^c_{1 \rightarrow 2} = \frac{1}{2} J_c(\theta^+_c) n_c(\theta^-_c), \quad k^c_{1 \rightarrow 3} = \frac{1}{2} J_c(\theta^-_c) n_c(\theta^+_c)
\]

\[
k^w_{2 \rightarrow 4} = \frac{1}{2} J_w(\theta^-_w) n_w(\theta^+_w), \quad k^w_{3 \rightarrow 4} = \frac{1}{2} J_w(\theta^-_w) n_w(\theta^+_w)
\]

\[
k^h_{1 \rightarrow 4} = J_h(\theta_h)n_h(\theta_h),
\]

with the reversed rate constants determined from detailed balance. As in Sec. C.1, the factor 1/2 results from the \( 1/\sqrt{2} \) prefactor in front of the operator \( \hat{S} \), Eq. (3.13). We use an ohmic spectral density with a large cutoff. As well, for simplicity, we assume a symmetric coupling, \( \gamma = \gamma_{h,c,w} \). This leads to, e.g., \( k^c_{1 \rightarrow 2} = \frac{1}{2} \gamma \theta^-_c n^-_c \), with \( n^\pm_\alpha = n_\alpha(\theta^\pm) \). We calculate the energy currents using Eq. (3.18) and get

\[
J^c_q = \frac{\theta^+_c}{\Phi}(k^c_{2 \rightarrow 1} + k^w_{2 \rightarrow 4})(k^c_{1 \rightarrow 3} k^w_{3 \rightarrow 4} k^h_{4 \rightarrow 1} - k^c_{3 \rightarrow 1} k^w_{4 \rightarrow 3} k^h_{1 \rightarrow 4})
\]

\[
+ \frac{\theta^-_c}{\Phi}(k^c_{3 \rightarrow 1} + k^w_{3 \rightarrow 4})(k^c_{1 \rightarrow 2} k^w_{2 \rightarrow 4} k^h_{4 \rightarrow 1} - k^c_{2 \rightarrow 1} k^w_{4 \rightarrow 2} k^h_{1 \rightarrow 4})
\]

\[
- \frac{2 \theta^w}{\Phi}(k^c_{1 \rightarrow 2} k^c_{3 \rightarrow 1} k^w_{2 \rightarrow 4} k^w_{4 \rightarrow 3} - k^c_{1 \rightarrow 3} k^c_{2 \rightarrow 1} k^w_{3 \rightarrow 4} k^w_{4 \rightarrow 2}).
\]

This expression agrees with Ref. [269]. Here, \( \Phi \) is a positive normalization factor which is quite cumbersome and has been left out. The first two lines in Eq. (C.18) describe heating and cooling processes through the two transitions \( \theta^\pm \). The last line corresponds to heat leaks, with thermal energy exchanged directly between the work and cold baths. Similarly to the V-system, even in the secular limit the behaviour of the energy current is highly non-monotonic in \( g \), affecting the magnitude of cooling current and the cooling window.

Taking \( g \to 0 \), the mid-gap states in the 4lQAR model become degenerate and we realize a setup that looks and behaves very much like the 3lQAR. In this limit, the current reduces to

\[
J^c_q = \frac{2 \theta^c}{\Psi}(k^c_{1 \rightarrow 2} k^w_{2 \rightarrow 4} k^h_{4 \rightarrow 1} - k^c_{1 \rightarrow 4} k^w_{2 \rightarrow 1} k^w_{4 \rightarrow 2}),
\]

C.3 4lQAR
with

$$\Psi = k^h_{1 \to 4}k^c_{2 \to 1} + 2k^c_{1 \to 2}k^w_{2 \to 4} + 2k^c_{1 \to 2}k^h_{1 \to 1} + k^h_{1 \to 4}k^w_{2 \to 4}$$

$$+ k^c_{5 \to 1}k^h_{1 \to 1} + 4k^c_{1 \to 2}k^w_{4 \to 2} + 2k^h_{1 \to 4}k^w_{4 \to 2}$$

$$+ 2k^c_{2 \to 1}k^w_{4 \to 2} + k^w_{2 \to 4}k^h_{4 \to 1}. \quad (C.20)$$

This result is analogous to the current for the 3lQAR, Eq. (C.9)—with a different denominator (normalization factor), and a factor of 2 here, accounting for the two effective cycles. Note that level ‘3’ in the 3lQAR model serves as level ‘4’ in the 4lQAR model. Also note that the rate constants defined for the 4lQAR are half the value of the rate constants defined for the 3lQAR.

In this $g \to 0$ and large $\gamma_d$ limit, we find that the cooling current of the 4lQAR, Eq. (C.19), is smaller than the one for the 3lQAR, Eq. (C.9), but the cooling window is identical, Eq. (C.13). One can similarly calculate the thermal energy absorbed from the work bath, $J^w_q$, and find that it follows Eq. (C.19), only with the energy prefactor $\theta_w$. Thus, when $g \to 0$ and $\gamma_d$ is large, the coefficient of performance for the 4lQAR is identical to that of the 3lQAR, $\eta = \theta_c/\theta_w$. 
Appendix D

Model Hamiltonians for Noise-Induced Coherence

In this appendix we record the detailed Hamiltonians of the models studied in Chapter 3, Section 3.4. In all of these, as in the main text, we consider a general open-system setup: a small subsystem interacting with multiple infinite bosonic baths, labelled by $\alpha$, through a bilinear interaction.

$$
\hat{H} = \hat{H}_S + \sum_\alpha \hat{H}_\alpha + \sum_\alpha \hat{S}_\alpha \otimes \hat{B}_\alpha \\
\hat{H}_\alpha = \sum_q \hbar \omega_{q,\alpha} \hat{b}_{q,\alpha}^\dagger \hat{b}_{q,\alpha} \\
\hat{B}_\alpha = \sum_q \lambda_{q,\alpha} \left( \hat{b}_{q,\alpha}^\dagger + \hat{b}_{q,\alpha} \right). 
$$

(D.1)

The differences between models will be in the number of baths, and the form of the system operators, $\hat{H}_S$ and $\hat{S}_\alpha$.

D.1 V Energy Transfer System

This system exchanges energy between a hot and cold bath, mediated by a three-level subsystem. There are two types, the Class 1 with mixed positive and negative couplings (Fig. 3.12), and the Class 2 with all positive couplings (Fig. 3.13). For both cases we have the system Hamiltonian

$$
\hat{H}_S = \epsilon_1 |1\rangle \langle 1| + \theta (|a\rangle \langle a| + |b\rangle \langle b|) + g (|a\rangle \langle b| + |b\rangle \langle a|).
$$

(D.2)

The two possible system operators are then, for Class 1

$$
\hat{S}_h = |1\rangle \langle a| + |a\rangle \langle 1|, \quad \hat{S}_c = |1\rangle \langle b| + |b\rangle \langle 1|.
$$

(D.3)

and for Class 2

$$
\hat{S}_h = |1\rangle \langle a| + |a\rangle \langle 1|, \quad \hat{S}_c = |1\rangle \langle a| + |a\rangle \langle 1|.
$$

(D.4)
After diagonalisation to the energy basis we have

\[ \hat{H}_S = \epsilon_1 |1\rangle\langle 1| + (\theta + g) |2\rangle\langle 2| + (\theta - g) |3\rangle\langle 3|, \] (D.5)

and for Class 1

\[ \hat{S}_c = \frac{1}{\sqrt{2}} (|1\rangle\langle 3| - |1\rangle\langle 2| + |3\rangle\langle 1| - |2\rangle\langle 1|) \] (D.6)

\[ \hat{S}_h = \frac{1}{\sqrt{2}} (|1\rangle\langle 2| + |1\rangle\langle 3| + |3\rangle\langle 1| + |2\rangle\langle 1|), \] (D.7)

and Class 2

\[ \hat{S}_c = \frac{1}{\sqrt{2}} (|1\rangle\langle 3| + |1\rangle\langle 2| + |3\rangle\langle 1| + |2\rangle\langle 1|) \] (D.8)

\[ \hat{S}_h = \frac{1}{\sqrt{2}} (|1\rangle\langle 2| + |1\rangle\langle 3| + |3\rangle\langle 1| + |2\rangle\langle 1|). \] (D.9)

We can see that Class 1 corresponds to the VETS defined in Eq. 3.7.

### D.2 4-level Quantum Absorption Refrigerator

Very similar to the VETS, there are two possible setups for this 4lQAR, as shown in Figs. 3.15 and 3.16, with all positive and mixed-sign couplings respectively.

We begin with the system Hamiltonian

\[ \hat{H}_S = \epsilon_1 |1\rangle\langle 1| + \theta_c (|a\rangle\langle a| + |b\rangle\langle b|) + \theta_h |4\rangle\langle 4| + g (|a\rangle\langle b| + |b\rangle\langle a|). \] (D.10)

The system operators are for the Class 1 analogue

\[ \hat{S}_c = |1\rangle\langle b| + |b\rangle\langle 1|, \quad \hat{S}_w = |a\rangle\langle 4| + |4\rangle\langle a|, \quad \hat{S}_h = |1\rangle\langle 4| + |4\rangle\langle 1|, \] (D.11)

and for the Class 2 analogue

\[ \hat{S}_c = |1\rangle\langle a| + |a\rangle\langle 1|, \quad \hat{S}_w = |a\rangle\langle 4| + |4\rangle\langle a|, \quad \hat{S}_h = |1\rangle\langle 4| + |4\rangle\langle 1|. \] (D.12)

After diagonalisation we receive

\[ \hat{H}_S = \epsilon_1 |1\rangle\langle 1| + (\theta_c - g) |2\rangle\langle 2| + (\theta_c + g) |3\rangle\langle 3| + \theta_h |4\rangle\langle 4|. \] (D.13)

The system coupling operators for for Class 1 are

\[ \hat{S}_c = \frac{1}{\sqrt{2}} (|1\rangle\langle 3| - |1\rangle\langle 2| + |3\rangle\langle 1| - |2\rangle\langle 1|), \quad \hat{S}_w = \frac{1}{\sqrt{2}} (|2\rangle\langle 4| + |3\rangle\langle 4| + |4\rangle\langle 2| + |4\rangle\langle 3|) \]

\[ \hat{S}_h = |1\rangle\langle 4| + |4\rangle\langle 1|. \] (D.14)
and for Class 2
\[ \hat{S}_c = \frac{1}{\sqrt{2}} (|1\rangle\langle 3| + |1\rangle\langle 2| + |3\rangle\langle 1| + |2\rangle\langle 1|), \quad \hat{S}_w = \frac{1}{\sqrt{2}} (|2\rangle\langle 4| + |3\rangle\langle 4| + |4\rangle\langle 3| + |4\rangle\langle 2|) \]
\[ \hat{S}_h = |1\rangle\langle 4| + |4\rangle\langle 1|. \]
(D.15)

The Class 1 4lQAR corresponds to the model defined in Eq. 3.13.

### D.3 Multi-Spin Model

This device is constructed out of identical spins, which serve as a heat exchange medium for two baths. The system Hamiltonian for a single spin is
\[ \hat{H}_S = \epsilon_1 |\downarrow\rangle\langle \downarrow| + \epsilon_2 |\uparrow\rangle\langle \uparrow|, \] (D.16)
and the system coupling operators for the hot and cold baths are identical
\[ \hat{S}_{h,c} = |\downarrow\rangle\langle \uparrow| + |\uparrow\rangle\langle \downarrow|, \] (D.17)

Adding two of these together, we retrieve the following for the composite system
\[ \hat{H}_S = 2\epsilon_1 |\downarrow\rangle\langle \downarrow| + \omega (|\uparrow\downarrow\rangle\langle \uparrow\downarrow| + |\downarrow\uparrow\rangle\langle \downarrow\uparrow|) + 2\epsilon_2 |\uparrow\rangle\langle \uparrow|, \] (D.18)
where \( \omega = \epsilon_2 + \epsilon_1 \). The system operators can take two forms: either they operate collectively on the spins, in which case there are only one hot and one cold bath
\[ \hat{S}_{coop}^{(1) h,c} = |\downarrow\rangle\langle \uparrow\downarrow| + |\downarrow\rangle\langle \uparrow\downarrow| + |\uparrow\rangle\langle \uparrow\downarrow| + |\downarrow\rangle\langle \uparrow\downarrow| + h.c., \] (D.19)
or each spin can come with its own baths and system operators
\[ \hat{S}_{h,c}^{(1)} = |\downarrow\rangle\langle \uparrow\downarrow| + h.c., \quad \hat{S}_{h,c}^{(2)} = |\downarrow\rangle\langle \uparrow\downarrow| + h.c. \] (D.20)

Upon transformation to the secular or Dicke basis, the collective system operators transform to
\[ \hat{S}_{coop}^{(1) h,c} = 2\sqrt{2} (|\downarrow\rangle\langle \uparrow\downarrow| + |\uparrow\rangle\langle \uparrow\downarrow| + h.c.). \] (D.21)
Appendix E

Counting-Dressed Influence Functionals

E.1 Counting-Field Dressed Influence Functionals for General Baths

The influence functional (4.21) was derived in Ref. [68] following the original derivation of the Feynman-Vernon influence functional. The derivation relies on harmonic baths and a bilinear interaction Hamiltonian in the displacements of the reservoirs. Here, we construct the counting field-dressed influence functional using perturbation theory and re-exponentiation. This procedure does not rely on the details of the model, and it therefore can be used in more general cases, such as with anharmonic baths, though it will not be exact in all cases.

E.1.1 IF for a single bath

For simplicity, we begin by describing the IF assuming the system is coupled to a single bath, \( L \). The influence functional is derived by focusing on the time-dependent environmental Hamiltonian \( \hat{H}_{\text{env}} = \hat{H}_L + \hat{H}_{SL}(t) \), which evolves along the system’s path \( s(t) \) as \( \hat{H}_{SL}(t) = s(t)\hat{B} \). We later generalize our results to the case of two baths.

We begin with the formal expression for the total influence functional,

\[
I_{L}^{\xi}(\{s^{\pm}\}) = \text{Tr}_{B}\left[\rho_{B}\hat{U}_{\text{env}}^{\xi}[s^{-}(t)]\hat{U}_{\text{env}}^{-\xi}[s^{+}(t)]\right],
\]

(E.1)

where e.g. \( \hat{U}_{\text{env}}^{-\xi}[s^{+}(t)] = \text{Te}^{-i\int_{0}^{t}\hat{H}_{\text{env}}^{-\xi}(s^{\pm},\tau)d\tau} \) is the interaction picture propagator of the environmental Hamiltonian moving on the forward (+) path. Here, we define the interaction picture operators as

\[
\hat{H}_{SL}^{-\xi}(s^{+},t) = s^{+}(t)\hat{B}_{L}^{-\xi}(t), \quad \hat{H}_{\text{env}}^{-\xi}(s^{+},t) = \hat{H}_L + \hat{H}_{SL}^{-\xi}(s^{+},t).
\]

(E.2)

In this equation, the time-dependence \( \hat{B}(t) \) results from the interaction picture, while \( s(t) \) corresponds to the time-dependent coordinate of the system (path) along which the bath coordinates evolve. To simplify our notation, we omit the time argument of the system coordinate, \( s^{\pm}(t) \rightarrow s^{\pm} \) until we arrive...
Appendix E. Counting-Dressed Influence Functionals

We now explicitly write the time evolution operators as a Dyson series, as expressed in Eq. (E.6), where we recover it. Similar definitions hold for the backward time evolution along the system coordinate $s^-$, preparing the time-dependent environmental Hamiltonian $\hat{H}_{\text{env}}(s^-, t)$.

Expression (E.1) can be evaluated by a Dyson expansion and a re-exponentiation procedure as we show next, or by explicit consideration of a time-dependent force on a harmonic oscillator, as in Refs. [374, 335]. We now explicitly write the time evolution operators as a Dyson series,

\[
\hat{U}_{\text{env}}(s^+, t) = e^{-i\hat{H}_L t} \left[ 1 - i \int_0^t d\tau \hat{H}_{\text{env}}(s^+, \tau) - \int_0^t \int_0^\tau d\tau' \hat{H}_{\text{env}}(s^+, \tau') \hat{H}_{\text{env}}(s^+, \tau') + \ldots \right]
\]

\[\hat{U}_{\text{env}}(s^-, t) = \left[ 1 + i \int_0^t d\tau \hat{H}_{\text{env}}(s^-, \tau) - \int_0^t \int_0^\tau d\tau' \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^-, \tau') + \ldots \right] e^{i\hat{H}_L t}.
\]

Multiplying the two propagators and keeping terms up to second order, then rearranging, we retrieve

\[
\hat{U}_{\text{env}}(s^-, t)\hat{U}_{\text{env}}(s^+, t) = 1 - i \int_0^t d\tau \left[ \hat{H}_{\text{env}}(s^+, \tau) - \hat{H}_{\text{env}}(s^-, \tau) \right] + \int_0^t d\tau \hat{H}_{\text{env}}(s^-, \tau) \int_0^t d\tau \hat{H}_{\text{env}}(s^+, \tau)
\]

\[\ldots - \int_0^t \int_0^\tau d\tau' \left[ \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^+, \tau') + \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^+, \tau') \right] + \ldots \quad (E.4)
\]

The third term (product of two integrals) can be rearranged, resulting in

\[
\hat{U}_{\text{env}}(s^-, t)\hat{U}_{\text{env}}(s^+, t) = 1 - i \int_0^t d\tau \left[ \hat{H}_{\text{env}}(s^+, \tau) - \hat{H}_{\text{env}}(s^-, \tau) \right]
\]

\[+ \int_0^t \int_0^\tau d\tau' \left[ \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^+, \tau') + \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^+, \tau') \right]
\]

\[\ldots - \int_0^t \int_0^\tau d\tau' \left[ \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^+, \tau') + \hat{H}_{\text{env}}(s^-, \tau') \hat{H}_{\text{env}}(s^+, \tau') \right] + \ldots \quad (E.5)
\]

Next, we evaluate the trace over the bath with averages performed over the thermal state $\rho_B$, and assuming that the thermal average of the interaction vanishes, $\langle \hat{H}_{\text{SL}} \rangle = 0$. Relying on the bilinear form of the interaction, e.g. $\hat{H}_{\text{env}}(s^+, t) = s^+(t)\hat{B}_{\text{L}}^{-\xi}(t)$, we get

\[
I_{\xi}^c(s^\pm) = 1 + \int_0^\tau d\tau' \left[ s^-(\tau)s^+(\tau')\langle \hat{B}_{\text{L}}^\xi(\tau)\hat{B}_{\text{L}}^{-\xi}(\tau') \rangle + s^+(\tau)s^-(\tau')\langle \hat{B}_{\text{L}}^\xi(\tau')\hat{B}_{\text{L}}^{-\xi}(\tau) \rangle \right]
\]

\[\ldots - s^+(\tau)s^+(\tau')\langle \hat{B}_{\text{L}}^\xi(\tau)\hat{B}_{\text{L}}^\xi(\tau') \rangle - s^-(\tau)s^-(\tau')\langle \hat{B}_{\text{L}}^\xi(\tau')\hat{B}_{\text{L}}^\xi(\tau) \rangle + \ldots \quad (E.6)
\]

Recall that bath operators are written here in the interaction representation. The time-dependence of the system’s coordinate corresponds to the system’s path on which the bath evolves.

Using the stationary bath condition and the cyclic property of the trace we lose the counting parameter in correlation functions of the form

\[
\langle \hat{B}_{\text{L}}^\xi(\tau')\hat{B}_{\text{L}}^\xi(\tau) \rangle = \text{Tr}_B[e^{i\hat{H}_L\xi/2}\hat{B}_{\text{L}}(\tau')e^{-i\hat{H}_L\xi/2}e^{i\hat{H}_L\xi/2}\hat{B}_{\text{L}}(\tau)e^{-i\hat{H}_L\xi/2}\rho_B]
\]

\[
= \text{Tr}_B[\hat{B}_{\text{L}}(\tau')\hat{B}_{\text{L}}(\tau)\rho_B].
\]

\[\quad (E.7)
\]
In contrast, the counting parameter survives in the following combination,

\[
\langle \hat{B}_L^\xi(\tau')\hat{B}_L^{-\xi}(\tau) \rangle = \text{Tr}_B \left[ e^{iH_L\xi/2} \hat{B}_L(\tau') e^{-iH_L\xi/2} \hat{B}_L(\tau) e^{iH_L\xi/2} \rho_B \right] = \text{Tr}_B \left[ e^{iH_L\xi} \hat{B}_L(\tau' - \tau) e^{-iH_L\xi} \hat{B}_L(0) \rho_B \right] = \langle \hat{B}_L(\tau' - \tau + \xi) \hat{B}_L(0) \rangle.
\]

(E.8)

So far, the derivation only includes terms up to second order in the system-bath interaction. Fortunately, for a bilinearly-position coupled harmonic bath, the re-exponentiation of this expression is exact. Therefore, the continuous-time counting-dressed influence functional is given as

\[
I^\xi_L(\{s^\pm\}) = \exp \left[ - \int_0^t d\tau \int_0^\tau d\tau' \left[ s^+(\tau)s^+(\tau')\eta_L(\tau - \tau') - s^-(\tau)s^-(\tau')\eta_L(\tau - \tau' + \xi) - s^-(\tau)s^-(\tau' + \xi) + s^-(\tau)s^-(\tau')\eta_L(\tau - \tau') \right] \right].
\]

(E.9)

Using the interaction Hamiltonian (4.23), we get the correlation function,

\[
\eta_L(\tau - \tau' + \xi) = \langle \hat{B}_L(\tau - \tau' + \xi)\hat{B}_L(0) \rangle = \left\langle \sum_k \lambda^2_{L,k} \left( \hat{b}^\dagger_{L,k} e^{i\omega_{k,L}(\tau - \tau' + \xi)} + \hat{b}_{L,k} e^{-i\omega_{k,L}(\tau - \tau' + \xi)} \right) \left( \hat{b}^\dagger_{L,k} + \hat{b}_{L,k} \right) \right\rangle
\]

\[
= \sum_k \lambda^2_{L,k} \left\{ n_L(\omega_{L,k}) e^{i\omega_{k,L}(\tau - \tau' + \xi)} + \left[ n_L(\omega_{L,k}) + 1 \right] e^{-i\omega_{k,L}(\tau - \tau' + \xi)} \right\}
\]

\[
= \frac{1}{\pi} \int_0^\infty d\omega g_L(\omega) \left\{ \left[ 2n_L(\omega) + 1 \right] \cos \omega(\tau - \tau' + \xi) - i \sin \omega(\tau - \tau' + \xi) \right\}
\]

\[
= \frac{1}{\pi} \int_0^\infty d\omega g_L(\omega) \frac{e^{\beta L\omega/2}}{e^{\beta L\omega/2} - e^{-\beta L\omega/2}} e^{-i\omega(\tau - \tau' + \xi)} + \frac{1}{\pi} \int_0^\infty d\omega g_L(\omega) \frac{e^{-\beta L\omega/2}}{e^{\beta L\omega/2} - e^{-\beta L\omega/2}} e^{i\omega(\tau - \tau' + \xi)}
\]

\[
= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{g_L(\omega) e^{\beta L\omega/2}}{\sinh \left( \frac{\beta L\omega}{2} \right)} e^{-i\omega(\tau - \tau' + \xi)},
\]

(E.10)

where \( n_L(\omega_{L,k}) = \left| e^{\beta L\omega_{L,k}} - 1 \right|^{-1} \) is the Bose Einstein distribution function, and we extended the spectral density function to the negative domain, \( g_L(\omega) = -g_L(-\omega) \). We now discretize the path, e.g. in the forward direction,

\[
s^+(t) = s^+_0 \Theta(t - t_0) + \sum_{k=1}^N (s^+_k - s^+_k - s^+_{k-1}) \Theta(t - t_k),
\]

(E.11)

with the Heaviside function \( \Theta(t) \) and the time series \( t_0 = 0, t_1 = (1 - 1/2)\delta t, t_2 = (2 - 1/2)\delta t, \ldots, t_{N-1} = (N - 1 - 1/2)\delta t, t_N = (N - 1)\delta t \) (where \( N \) is the number of dynamical time steps plus one), and obtain the discrete IF,

\[
I^\xi_L(\{s^\pm\}) = \exp \left[ - \sum_{k=0}^N \sum_{k'=0}^k \left( s_k^+ s_k^+ \eta_{kk'}^+ - s_k^- s_k^+ \eta_{kk'}^- \xi - s_k^+ s_k^- \eta_{kk'}^+ \xi + s_k^+ s_k^- \eta_{kk'}^- \xi \right) \right].
\]

(E.12)

It is here important to note that Eq. E.9 was derived from a Hamiltonian omitting the so-called counterterm, commonly included in such approaches [356]. Since such a term would not be dressed by a counting field, it does not affect the derivation of the generating function. However, in order to maintain
continuity with iQuAPI-based approaches, we did include such a term in our numerical implementation, which amounts to a small adjustment to a few of the correlation functions. The result is the following coefficients:

\[
\eta_{k k', L}^{\mu \nu, \xi} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega A_{L}^{\mu \nu, \xi}(\omega) \frac{\sin^{2}(\omega \delta t/4) e^{-i\omega(k-k')}}{\omega^{2} \sin(\frac{\delta t}{4})}, \quad 0 < k' < k < N
\]

\[
\eta_{k k', L}^{0,0, \xi} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega A_{L}^{0,0, \xi}(\omega)(1 - e^{-i\omega \delta t}), \quad 0 < k < N,
\]

\[
\eta_{N 0, L}^{\mu \nu, \xi} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega A_{L}^{\mu \nu, \xi}(\omega) \sin^{2}(\omega \delta t/4) e^{-i\omega(N\delta t - \delta t/2)},
\]

\[
\eta_{N N, L}^{\mu \nu, \xi} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega A_{L}^{\mu \nu, \xi}(\omega) \left(1 - e^{-i\omega \delta t/2}\right),
\]

\[
\eta_{N k', L}^{\mu \nu, \xi} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega A_{L}^{\mu \nu, \xi}(\omega) \sin^{2}(\omega \delta t/4) e^{-i\omega(N\delta t - k\delta t - \delta t/4)}, \quad 0 < k' < N.
\]

(E.13)

Here \(\mu = \pm 1\), and \(\nu = \pm 1\) correspond to the different (forward and backward) combinations. We put together the spectral function of the reservoir, the thermal factors, and the counting-field phase elements into the function

\[
A_{L}^{\mu \nu, \xi}(\omega) = \frac{g_{L}(\omega)e^{\frac{i\omega}{\delta t}}}{\omega^{2} \sin(\frac{\delta t}{4})} e^{-i\omega(\nu - \mu)/2}, \quad \mu = \pm 1, \quad \nu = \pm 1.
\]

(E.14)

It is important to note that \(\eta(\tau - \tau' + \xi) \neq [\eta(\tau' - \tau + \xi)]^{*}\), equivalent to \(\eta^{- + \xi} \neq \eta^{+ - \xi}\), therefore one must compute these different combinations explicitly. This further precludes a blip decomposition, since the influence functional does not neatly reorganize into a blip-sojourn form: the influence functional with the counting field couples all time points to all others, regardless of their blip or sojourn character.

Next, we generalize this result in two ways.

E.1.2 Generalization I: Two baths with asymmetric counting

Here, we couple the system to two heat baths, but we count energy only in one of the terminals, say \(L\). The environmental Hamiltonian for the forward time evolution branch is given by

\[
\hat{H}_{env}^{-\xi}(s^{+}, t) = \hat{H}_{L} + \hat{H}_{R} + \hat{H}_{SL}^{-\xi}(s^{+}, t) + \hat{H}_{SR}(s^{+}, t).
\]

(E.15)

An analogous expression holds for the backward time evolution expression. The influence functional is given by

\[
I^{\xi}(\{s^{\pm}\}) = \text{Tr}_{B}\left[\rho_{B} \hat{U}_{env}^{\dagger \xi}(s^{+}(t)) \hat{U}_{env}^{-\xi}(s^{+}(t))\right],
\]

(E.16)

yet since the initial condition of the total bath is factorized, \(\rho_{B} = \rho_{L} \otimes \rho_{R}\), the IF is given by a product of two independent terms,

\[
I^{\xi}(\{s^{\pm}\}) = I_{L}^{\xi}(\{s^{\pm}\})I_{R}(\{s^{\pm}\}).
\]

(E.17)

The IF without counting, \(I_{R}(\{s^{\pm}\})\), corresponds to the IF [Eq. (E.12)] evaluated at \(\xi = 0\).
E.1.3 Generalization II: Two baths with symmetric counting

As we explain in the main text and Appendix F, we symmetrise the definition of the moment generating function. Therefore, we count energy transfer at both the \( L \) and \( R \) terminals, and the environmental Hamiltonian is given by

\[
\hat{H}_{	ext{env}}(s^+, t) = \hat{H}_L + \hat{H}_R + \hat{H}_{SL}^{-\xi/2}(s^+, t) + \hat{H}_{SR}^{-\xi/2}(s^+, t) \tag{E.18}
\]

The derivation outlined previously for the IF of the \( L \) bath can be repeated for the \( R \) bath, only with the counting parameter halved and its sign switched throughout all the expressions (E.1)-(E.14). Again, based on the factorized initial condition the total influence function is separable

\[
I^\xi(s^\pm) = I^\xi_L(s^\pm) I^\xi_R(s^\pm), \tag{E.19}
\]

where each term follows Eqs. (E.12)-(E.13).

E.2 Counting-Dressed Influence Functional in Prior Works

The characteristic function in a path integral form was previously derived by Carrega et al. [335] as part of a primarily analytical work on time-dependent heat exchange in the spin-boson model. Their work generalizes the standard-dissipative Feynman-Vernon influence functional to count heat exchange processes in system-boson bath models. That derivation relies on the Gaussian property of harmonic oscillators, which allows tracing out exactly the degrees of freedom of the bath. Though the authors in [335] considered both a different picture of the two-time measurement protocol and an alternate derivation of the influence functional from Sec. E.1, we show here that we arrive at the same result in the continuous time limit. For simplicity, we limit this discussion to include a single heat bath, though the result is general.

First, following [335] we break the influence functional into so-called “normal”, \( I^{(0)} \), and “counting”, \( I^\Xi \), parts,

\[
I^\xi = I^{(0)} I^\Xi. \tag{E.20}
\]

The normal part is the original influence functional, without any effects from the counting field, or simply the influence functional one retrieves when \( \xi = 0 \) at which point the counting part is unity. The normal part \( I^{(0)} \) in Ref. [335] can be easily shown to agree with the standard IF recast in so-called blip-sojourn form using sum and difference coordinates \( \bar{s}(t) \equiv s^+(t) + s^-(t) \), \( \Delta s(t) \equiv s^+(t) - s^-(t) \)[362]. The counting term derived in [335] is somewhat more involved and it reads

\[
I^\Xi = \exp \int_0^t d\tau \int_0^\tau d\tau' \left\{ [\bar{s}(\tau) \bar{s}(\tau') - \Delta s(\tau) \Delta s(\tau')] i L_1^\xi(\tau - \tau') + [\bar{s}(\tau) \Delta s(\tau') - \Delta s(\tau) \bar{s}(\tau')] i L_2^\xi(\tau - \tau') \right\}, \tag{E.21}
\]
with the counting-dressed correlation functions given as

\[ L_1^t(t) = \frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \frac{\sinh(\beta\omega/2 - i\omega\xi/2)}{\sinh(\beta\omega/2)} \cos(\omega t) \sin(-\omega\xi/2) \]

\[ L_2^t(t) = -\frac{i}{\pi} \int_0^\infty \! d\omega g(\omega) \frac{\cosh(\beta\omega/2 - i\omega\xi/2)}{\sinh(\beta\omega/2)} \sin(\omega t) \sin(-\omega\xi/2). \]

(E.22)

Note that we flipped the sign of the counting field, \( \xi \) from the original work to match our notation. This has the effect only of reversing the sign of the current, which is by convention taken positive when flowing towards the system. We expand and multiply the sum and difference coordinates and retrieve the following,

\[ T^\Xi = \exp \int_0^t \! dt \int_0^\tau \! d\tau' \left[ s^-(\tau)s^+(\tau')C_1^\xi(\tau - \tau') + s^+(\tau)s^-(\tau')C_2^\xi(\tau - \tau') \right]. \]

(E.23)

The new correlation functions are organized from the rearrangement of the coordinates, and come out as follows,

\[ C_1^\xi(t) = \frac{2}{\pi} \int_0^\infty \! d\omega g(\omega) \frac{\sin(-\omega\xi/2)}{\sinh(\beta\omega/2)} \left( \cosh(\beta\omega/2 - i\omega\xi/2) \sin(\omega t) + i \sinh(\beta\omega/2 - i\omega\xi/2) \cos(\omega t) \right) \]

\[ C_2^\xi(t) = -\frac{2}{\pi} \int_0^\infty \! d\omega g(\omega) \frac{\sin(-\omega\xi/2)}{\sinh(\beta\omega/2)} \left( \cosh(\beta\omega/2 - i\omega\xi/2) \sin(\omega t) - i \sinh(\beta\omega/2 - i\omega\xi/2) \cos(\omega t) \right). \]

(E.24)

These expressions are somewhat obtuse in their current forms, and we decompose them into their real (\( \mathbb{R} \)) and imaginary (\( \mathbb{I} \)) parts,

\[ \mathbb{R}[C_1^\xi(t)] = \frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \coth\left(\frac{\beta\omega}{2}\right) \left[ \cos(\omega(t + \xi)) - \cos(\omega t) \right] \]

\[ \mathbb{I}[C_1^\xi(t)] = -\frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \left[ \sin(\omega(t + \xi)) - \sin(\omega t) \right] \]

\[ \mathbb{R}[C_2^\xi(t)] = \frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \coth\left(\frac{\beta\omega}{2}\right) \left[ \cos(\omega(t - \xi)) - \cos(\omega t) \right] \]

\[ \mathbb{I}[C_2^\xi(t)] = \frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \left[ \sin(\omega(t - \xi)) - \sin(\omega t) \right]. \]

(E.25)

Combining these terms, we re-express the correlation functions as

\[ C_1^\xi(t) = \frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \left[ \coth\left(\frac{\beta\omega}{2}\right) \left[ \cos(\omega(t + \xi)) - \cos(\omega t) \right] - i \left[ \sin(\omega(t + \xi)) - \sin(\omega t) \right] \right] \]

\[ C_2^\xi(t) = \frac{1}{\pi} \int_0^\infty \! d\omega g(\omega) \left[ \coth\left(\frac{\beta\omega}{2}\right) \left[ \cos(\omega(t - \xi)) - \cos(\omega t) \right] + i \left[ \sin(\omega(t - \xi)) - \sin(\omega t) \right] \right]. \]

(E.26)

We are now ready to show that these expressions, adopted from Ref. [335], agree with Eq. (4.21) from the main body text. First, we define \( \bar{\eta}^\Xi(t + \xi) \equiv \eta(t + \xi) - \eta(t) \), excluding the normal kernel. It can be shown that \( \bar{\eta}^\Xi(\tau - \tau' + \xi) = C_1^\xi(\tau - \tau') \) and \( \bar{\eta}^\Xi(\tau' - \tau + \xi) = C_2^\xi(\tau - \tau'). \) To make this identification clear, we re-express the counting dressed continuous time correlation function, Eq. (4.24) as an integral
from zero to infinity.

\begin{equation}
\eta^\Xi(t + \xi) = \frac{1}{\pi} \int_0^\infty d\omega g(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \cos(\omega(t + \xi)) - i \sin(\omega(t + \xi)) \right] - g(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \cos(\omega t) - i \sin(\omega t) \right]
= \frac{1}{\pi} \int_0^\infty d\omega g(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \left[ \cos(\omega(t + \xi)) - \cos(\omega t) \right] - i \left[ \sin(\omega(t + \xi)) - \sin(\omega t) \right] \right]. \tag{E.27}
\end{equation}

For the second correlation function, we have

\begin{equation}
\eta^\Xi(-t + \xi) = \frac{1}{\pi} \int_0^\infty d\omega g(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \left[ \cos(\omega(t - \xi)) - \cos(\omega t) \right] + i \left[ \sin(\omega(t - \xi)) - \sin(\omega t) \right] \right], \tag{E.28}
\end{equation}

thus \( \eta^\Xi(\tau' - \tau + \xi) = C_\xi^2(\tau - \tau') \). Altogether, when we use these functions in Eq. (E.23) we get

\begin{equation}
I^\Xi = \exp \int_0^t d\tau \int_0^\tau d\tau' \left[ s^-(\tau)s^+(\tau')\eta^\Xi(\tau - \tau' + \xi) + s^+(\tau)s^-\left(\tau'\right)\eta^\Xi(\tau' - \tau + \xi) \right], \tag{E.29}
\end{equation}

which corresponds to Eq. (4.21) in the main text, stripped from the “normal” influence functional.
Appendix F

Influence Functional Error Analysis

F.1 Numerical Error Analysis

Iterative path integral schemes suffer from known numerical challenges, depending on the precise implementation and the system under study. For a recent example, Strathearn and coworkers [363] found that for certain forms of the spectral density function, the path integral may produce nonphysical long-time behaviours. Here, we inherit the errors that come from the Trotter splitting of the propagator and the truncation of the memory kernel. Strategies to converge out these errors, as shown in e.g. Fig. 4.4, are generally successful here.

![Figure F.1](image)

Figure F.1: Error Analysis: An asymmetric counting of energy exchange in the NESB model leads to nonzero heat current at zero temperature difference. We display a fixed-memory analysis of the nonphysical current by reducing the time step as in Figure 4.4. Inset: linear fit demonstrating the behaviour of the spurious current at $\delta t \to 0$. Parameters are $\Delta = 1$, $T_L = T_R = 5$, $\gamma_{L,R} = 0.01$, $\omega_c = 50$.

The familiar Trotter error manifests itself in new ways in the iFCSPI, in steady-state. For example, when naively using a non-symmetric form of the heat current expression for a single bath or multi-bath
Appendix F. Influence Functional Error Analysis

Figure F.2: Error Analysis: (a) Nonzero heat current at zero temperature difference when $\gamma_L \neq \gamma_R$. The counting field is applied symmetrically to the $L$ and $R$ baths, which are coupled asymmetrically to the spin system. (b)-(c) Linear fit of the spurious current, demonstrating its behaviour as $\delta t \to 0$. Parameters are $\Delta = 1$, $T_L = T_R = 5$, $\gamma_{avg} = 0.01$, $\omega_c = 50$.

one develops a significant erroneous current in the long time limit, even at zero temperature bias. We exemplify this issue in Fig. F.1 where we display the iFCSTI steady-state heat current in a junction at equilibrium ($T_L = T_R$), with the counting field dressing only the left bath. To understand the origin of this spurious effect, we perform a fixed-memory analysis so as to determine the scaling of the error with the time step $\delta t$.

We use a range of memory times ($\tau_m = \Delta k \cdot \delta t$) in Fig. F.1: Simulations with $\tau_m = 0.5, 0.8$ reasonably agree with each other, indicating that the total memory time is encapsulated in $\tau_m \sim 0.5$. Most notably, we find that the nonphysical current diminishes with $\delta t$, and that it linearly extrapolates to a value near, but not always exactly at zero for $\delta t = 0$. The discrepancy from zero is usually small and depends on the parameters used. It indicates that the scaling is not strictly linear for all parameter regimes at all values of $\delta t$. An important point is that the same erroneous phenomenon is observed even when the right bath is removed altogether.

The nonphysical current demonstrated in Fig. F.1 can be quenched by reducing the time step $\delta t$ to the required accuracy. Naturally, this approach is difficult to follow numerically, and we opt for a more economic approach, that is, symmetrizing the definition of heat exchange, as we discuss in Sec. 4.2,

\[ Q(t, 0) = \frac{1}{2} \left[ \hat{H}_L(0) - \hat{H}_L^H(t) - \hat{H}_R(0) + \hat{H}_R^H(t) \right]. \]

\( (F.2) \)
This form results in strictly zero current at zero temperature difference for the two-bath case, when 
\( g_L(\omega) = g_R(\omega) \), which we prove in Sec. F.2.

A related error (of finite current at zero temperature bias) arises whenever 
\( g_L(\omega) \neq g_R(\omega) \), which we demonstrate in Fig. F.2. Here again we test the equilibrium scenario and find nonzero current as in Fig. F.1. The erroneous heat current scales linearly with the asymmetry in the system-bath coupling 
\( \Delta \gamma / \gamma_{\text{avg}} \), with 
\( \gamma_{\text{avg}} = (\gamma_L + \gamma_R)/2 \) and 
\( \Delta \gamma = \gamma_L - \gamma_R \). We infer via the scaling with \( \delta t \) that the error (nonzero current) is introduced by the Trotter splitting of the counting-dressed bath Hamiltonians, and that it disappears exactly at finite-large \( \delta t \) only under the choice of identical spectral functions for the baths with symmetric counting fields.

The results presented in Chapter 4 were all computed from the symmetrized definition of the heat and using identical spectral functions for the reservoirs. We emphasize that the iFCSPI method can be used beyond that—once significantly shorter time steps are employed. The symmetrisation of the counting field introduces a significant limitation of the approach as yet, since the method cannot be straightforwardly employed beyond the case of two baths, e.g. to describe the behaviour of a (three bath) quantum absorption refrigerator.

A further challenge encountered with the current implementation of the iFCSPI is that the real part of the generating function is more difficult to converge compared to the imaginary part. To illustrate the technique, we focused here only on the behaviour of the averaged heat current. It bears repeating however, that powerful new algorithms exist that should be able to tackle this issue.

**F.2 Equilibrium Properties**

Using the iFCSPI algorithm, when the following conditions are jointly satisfied, the current through the NESB can be analytically shown to vanish: (i) the counting field is symmetrized about the two baths, (ii) the two baths share identical spectral density functions, \( g(\omega) \), including system-bath coupling strengths, and (iii) the system is at thermal equilibrium, \( T_L - T_R = 0 \). It is physically necessary from for the current to vanish when condition (iii) by itself is met, otherwise current would flow without a bias. An artifact of the iFCSPI method is that conditions (i) and (ii) are also necessary to guarantee thermodynamic consistency. This unfortunately constrains what one is able to do easily with the iFCSPI. We prove this property by showing that the generating function \( Z(t, \xi) \) has no imaginary part when these conditions are all met, and therefore the current vanishes,

\[
\langle J_Q \rangle = \frac{dG(\xi)}{d\xi} \bigg|_{\xi=0} = 0. \tag{F.3}
\]

We define a new discretised correlation function which explicitly separates the “standard” and “counting” parts of the influence functional.

\[
\eta^{\pm,\pm,\Xi} = \eta^{\pm,\pm,\xi} - \eta^{\pm,\pm}. \tag{F.4}
\]

This effectively splits the counting information, \( \eta^{\pm,\pm,\Xi} \), from \( \eta^{\pm,\pm,\xi} \), which contains a mixture of counting and standard influence functional contributions. Trivially, \( \eta^{\pm,\pm,\Xi} = 0 \) for \( \xi = 0 \). If one chose to, it is straightforward to re-cast the path integral in these terms, with a “standard” and “counting” influence functional, though we have not done so in the main text for notational and conceptual simplicity. We
make use of this language below.

When the three conditions noted above are met, we have the symmetry
\[
\eta_{L}^{-,+} = (\eta_{R}^{+,--})^*, \\
\eta_{L}^{+,--} = (\eta_{R}^{-,+})^*,
\]
(F.5)

for any of the discretised $\eta$. Explicitly, for $\eta_{00}^{+,+,+}$, we have
\[
\eta_{00,L}^{+,+,+} - (\eta_{00,R}^{+,+,+})^* = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{g_L(\omega)e^{-\beta\omega}}{\omega^2 \sinh \frac{\beta L}{2}} (1 - e^{-i\omega t})(1 - e^{-i\omega t}^\xi) - \frac{g_R(\omega)e^{-\beta\omega}}{\omega^2 \sinh \frac{\beta L}{2}} (1 - e^{i\omega t})(1 - e^{i\omega t}^\xi).
\]
(F.6)

Conditions (i) and (ii) give us $g_L(\omega) = g_R(\omega) = g(\omega)$ and $\beta_L = \beta_R = \beta$, allowing us to factor out several terms. Simplifying yields
\[
\eta_{00,L}^{+,+,+} - (\eta_{00,R}^{+,+,+})^* = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{g(\omega)}{\omega^2 \sinh \frac{\beta L}{2}} \left[ e^{\frac{\beta L}{2}} (1 - e^{-i\omega t})(1 - e^{-i\omega t}^\xi) - e^{-\frac{\beta L}{2}} (1 - e^{i\omega t})(1 - e^{i\omega t}^\xi) \right] = 0.
\]
(F.7)

The second equality comes from the fact that the function before the brackets is even in $\omega$ and the term in the brackets is odd. Therefore the total integral is odd and sums to zero.

This finding is critical to the operation of the iFCSPI, as without it, there would be no cancellation of the Trotter error, and we would realize unphysical results such as finite current without a bias, or even flowing against a bias.

### F.2.1 Proof for zero current under symmetrized conditions

The influence functional can be decomposed to products of exponents of two-point autocorrelation functions. This property makes it straightforward to analyze piecewise. For example, one may consider the case where $\Delta k = 1$. The influence functional for the particular path segment $[s_k^+, s_{k+1}^-, s_k^+, s_{k-1}^-] = [ij, mn]$ can be written naively as in Eq. (4.25),
\[
I^\xi_{ij,mn} = e^{-i\eta_{ij,mn}^+,ij+ij\eta_{ij,mn}^{+,+} + ij\eta_{ij,mn}^{+,+} - jj\eta_{ij,mn}^{+,+}} e^{-im\eta_{ij,mn}^{+,+} + im\eta_{ij,mn}^{+,+} - jm\eta_{ij,mn}^{+,+}} e^{-nm\eta_{ij,mn}^{+,+} + nm\eta_{ij,mn}^{+,+} - mn\eta_{ij,mn}^{+,+}},
\]
where we have explicitly expanded the sum over the $k \to k$ and $k' \to k'$ self terms, as well as the $k \to k'$ coupling, in the first, third and second exponentials respectively. We shall denote individual exponentials constructed in this way as $\mathcal{I}$, and therefore re-express the above influence functional as
\[
I^\xi_{ij,mn} = \mathcal{I}_{ij,mn} = \mathcal{I}_{ij,mn} \mathcal{I}_{ij,mn} \mathcal{I}_{ij,mn} \mathcal{I}_{ij,mn} \mathcal{I}_{ij,mn},
\]
(F.9)

where it is important to note the $k, k'$ subscripts determine whether the $\mathcal{I}$ is a self term or whether it couples two different time-points. We can see then that the individual $\mathcal{I}$’s represent couplings between points on the discretised time axis. All influence functionals of the type derived in Appendix E can be decomposed in this way, into products of two-point couplings.
We are now ready to prove that the current vanishes when conditions (i-iii) above are met. There are in general six types of coupling terms, which combine to build the full influence functional; four for coupling different time points, \( k \) and \( k' \) and two self-terms for \( k \to k \). These couplings are blips to blips, sojourns to sojourns, blips to sojourns, sojourns to blips, and blip-blip and sojourn-sojourn self couplings. A sojourn is a time point where \( s_k^+ = s_k^- \), and a blip is a time point where \( s_k^+ \neq s_k^- \). In the standard influence functional approach, sojourn-blip and sojourn-sojourn couplings, and sojourn-sojourn self-terms do not contribute, however the addition of the counting field disrupts this symmetry. We prove that the total influence functional is real by showing that the contribution coming from the counting field to \( I \) for all six types is entirely real, and therefore that via Eq. (F.7) the current is zero.

The influence functionals for each bath form a simple product we can decompose term-by-term. For each possible coupling, these products are real under our above-stated conditions, using the identity Eq. (F.3) the current is zero.

The influence functionals for each bath form a simple product we can decompose term-by-term. For each possible coupling, these products are real under our above-stated conditions, using the identity Eq. (F.3) the current is zero.

$\mathcal{I}_{iij,i}^{\mathcal{I}}(ii,mm)\mathcal{I}_{kk',R}^{\mathcal{I}}(ii,mm) = e^{i\cdot m(n_{k-,L} + n_{k-,R})} e^{i\cdot m(n_{k-,L} + n_{k-,R})} \tag{F.10}$

where here \( I_{kk'}^{\mathcal{I}} \) contains only the counting information from the IF, specifically \( \eta_{-,+,\Xi}, \eta_{+,-,\Xi} \). For sojourn-sojourn self-terms ((ii) \( \to \) (ii)),

$\mathcal{I}_{iij,i}^{\mathcal{I}}(ii,ii)\mathcal{I}_{kk,R}^{\mathcal{I}}(ii,ii) = e^{i\cdot i(n_{k-,L} + n_{k-,R})} e^{i\cdot i(n_{k-,L} + n_{k-,R})} = e^{2\cdot i\cdot \eta_{k-,L} + \eta_{k+,R}} \eta_{k+,L} e^{\eta_{k-,L} + \eta_{k-,R}} \tag{F.11}$

We see again that this yields a real value. The approach for blip-blip self-terms ((i) \( \to \) (ij)) is identical, with only the sign of the exponential changed, yet still completely real. For blip-blip couplings ((i) \( \to \) (mm), where \( i \neq j \) and \( m \neq n \), but (ij) may or may not equal (mn)),

$\mathcal{I}_{iij,m}^{\mathcal{I}}(ij,mm)\mathcal{I}_{kk',R}^{\mathcal{I}}(ij,mm) = e^{i\cdot \eta_{k+,L} + \eta_{k+,L}} e^{\eta_{k-,L} + \eta_{k-,R}} \eta_{k-,L} e^{\eta_{k-,L} + \eta_{k-,R}} \tag{F.12}$

Here, \( S \) is a sign factor, equal to \( i \cdot n \), which is \(-1 \) if (ij) = (mm) and \(+1 \) if (ij) = (nm). Either way, the final expression is real.

Blip-sojourn couplings are somewhat more involved. For a particular coupling term (\( i \neq j \), \( k = i \) or \( j \)), the counting field clearly carries an imaginary contribution

$\mathcal{I}_{iij,j}^{\mathcal{I}}(ij,mm)\mathcal{I}_{kk',R}^{\mathcal{I}}(ij,mm) = e^{i\cdot \eta_{k+,L} - \eta_{k-,L}} e^{\eta_{k-,L} - \eta_{k-,R}} \eta_{k-,L} e^{\eta_{k-,L} - \eta_{k-,R}} \tag{F.13}$
where now $S = j \cdot m$. This can be resolved in the $\Delta k = 1$ case by summing all the relevant blip-sojourn path segments for a particular set of time points $k$ and $k'$, and then simplifying. We define the two-point propagator (equivalent to one term in the summand of Eq. (4.20)), which gives the amplitude of a particular path segment,

$$p(ij, mm) = \rho(ij)K(ij, mm)I^0_{k'k^'}(ij, mm)I^0_{kk}(mm, mm)I^\Xi_{kk'}(ij, ij)I^\Xi_{kk'}(mm, mm)I^\Xi_{kk'}(ij, mm),$$

where $I^0$ is an influence functional coupling without any counting field, and $\rho(ij)$ is a reduced density matrix element. We then evaluate the sum over blips $(ij), (ji), j \neq i$, and sojourns $(mm), (nn), m \neq n$. Simplification of the resulting expression is straightforward in several steps from the definition of the influence functionals. In the first step we have already accounted for terms which equal or multiply to 1.

$$p(ij, mm) + p(ji, mm) + p(ij, nn) + p(ji, nn) =$$

$$\rho(ij)K(ij, mm)I_{k'k'}(ij, ij)I^\Xi_{kk'}(ij, mm) + \rho(ij)K(ij, nn)I_{k'k'}(ij, ij)I^\Xi_{kk'}(ij, mm) + ...$$

$$+ \rho(ji)K(ji, mm)I_{k'k'}(ji, jj)I^\Xi_{kk'}(ji, mm) + \rho(ji)K(ji, nn)I_{k'k'}(ji, jj)I^\Xi_{kk'}(ji, mm)$$

$$= -4I_{k'k'}(ij, ij)\sin \left( 2S\Im \left( \eta^+_{kk'} - \eta^-_{kk'} \right) \right) \left[ \Re[\rho(ij)]\Im[K(ij, mm)] + \Im[\rho(ij)]\Re[K(ij, mm)] \right].$$

The final result is completely real-valued for any $\xi$.

Sojourn-blip terms are inconsequential in this analysis, since they contribute only to system coherences, which as we have seen cannot contribute any imaginary component to the generating function via blip-sojourn terms. We have therefore verified that given conditions (i-iii), the iFCSPI approach will not realize net current in thermal equilibrium. The imposition of conditions (i) and (ii) in order to realize a physical equilibrium current may be limiting in some applications. Unfortunately there is as yet no error correction scheme which would allow us to relax these conditions.
Bibliography


[59] A. M. Kuznetsov et al., Charge transfer in physics, chemistry and biology: physical mechanisms of elementary processes and an introduction to the theory (Taylor & Francis, 1995).


