Mathematics underpinning the github repository

Kamil Kurdziel

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Contents

Chapter 1

Open Dynamics

1.1 The Toy Model

The system we will consider is a particle in a symmetric 1-dimensional double-well potential of the form

$$V(q) = -V_1 q^2 + V_2 q^4, \tag{1.1}$$

where the parameters V_1 and V_2 are real and positive. For the remainder of this thesis, we will use the values $V_1 = \frac{3}{2}$ and $V_2 = \frac{3}{4}$. The resulting potential is shown in Figure 1.1. For more information about the units of measure used refer to Appendix A. In this system, we can distinguish between two states A and B corresponding to the left and right side of the potential, respectively. Classically for a point-like particle of mass, m, the state A is defined based on the position at time t, $q(t)$, as $q(t) < 0$. State B is equivalently defined as $q(t) > 0$. The state $q(t) = 0$ is called the transition state. Using the two distinguishable states, we can define two observables, $n_A(t)$ and $n_B(t)$, corresponding to the microscopic probabilities of finding a particle in state A and B, respectively, fulfilling

$$n_A(t) + n_B(t) = 1 \quad \forall t. \tag{1.2}$$

Furthermore we will assume that the particle can exchange energy with its surroundings. In order to model this, we will let the particle interact with a heat bath, which is a suitable approximation for a large number of real life situations. In the eyes of a physicist, a heat bath is a collection of many harmonic oscillators interacting with the particle. Under certain approximations that will be discussed later, averaging over the oscillators will lead to an effective description of the particle in a potential driven by single damping and driving term stemming from the interaction with the environment.

1.2 Open Classical Dynamics

1.2.1 Langevin Equation of Motion

In this section, we will closely follow the derivation of the classical Langevin equation of motion found in [15]. For the classical toy model we can write the system Hamiltonian, H_S, as

$$H_S = \frac{p^2}{2m} + V(q), \tag{1.3}$$

where p and q are the momentum and position coordinates, respectively, of the point-like particle of mass, m, and $V(q)$ is the potential energy. The heat bath consists of many oscillators
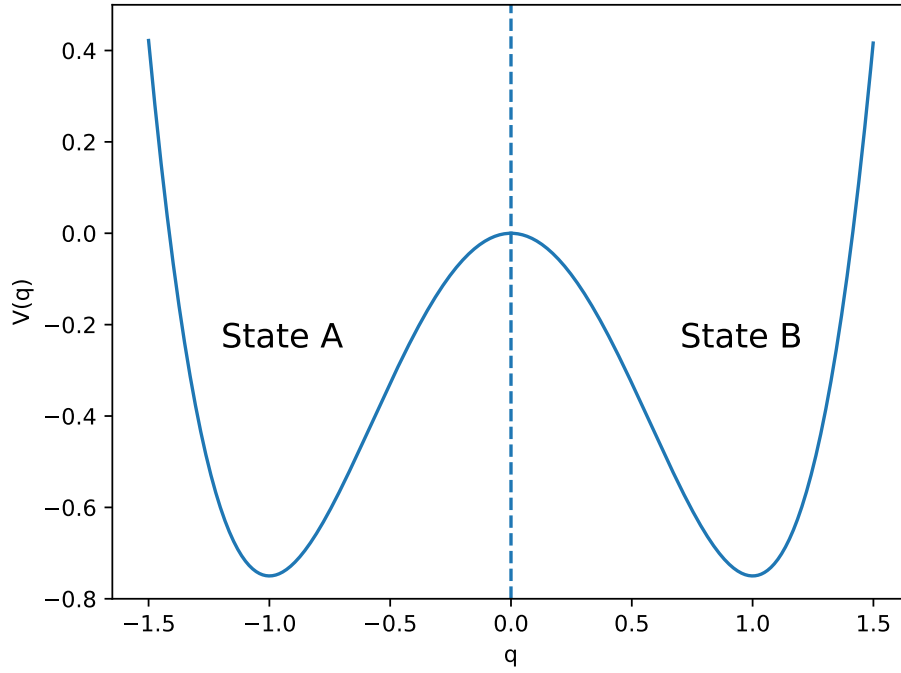
Figure 1.1: The 1-dimensional energy potential defined in Eq. (1.1) *in dimensionless units.*

whose coordinates and conjugate momenta can be denoted by the sets $\{q_j\}$ and $\{p_j\}$, respectively. For simplicity, we will assume that the mass of each oscillator is equal to 1 (see Appendix A for details). In order to capture the interaction, we define a heat bath Hamiltonian, H_B, as

$$H_B = \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 (q_j - \frac{\gamma_j}{\omega_j^2} q)^2 \right), \tag{1.4}$$

where γ_j quantifies the strength of the coupling of the system to the jth oscillator and ω_j is the natural frequency of the jth oscillator.

The equations of motion for the system are given by Hamilton's equations as

$$\begin{aligned} \frac{dq}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -\frac{dV(q)}{dq} + \sum_j \gamma_j (q_j - \frac{\gamma_j}{\omega_j^2} q) \end{aligned} \tag{1.5}$$

and equivalently for the bath oscillators the equations can be written as

$$\begin{aligned} \frac{dq_j}{dt} &= \frac{p_j}{m} \\ \frac{dp_j}{dt} &= -\omega_j^2 q_j + \gamma_j q. \end{aligned} \tag{1.6}$$

Assuming that the time dependence of the position coordinate, $q(t)$, is known, we obtain second order differential equations for the harmonic oscillator coordinates. The formal solution to these equations can be written as

$$q_j(t) = q_j(0)cos(\omega_j t) + p_j(0)\frac{sin(\omega_j t)}{\omega_j} + \gamma_j \int_0^t ds\, q(s) \frac{sin(\omega_j(t-s))}{\omega_j}. \tag{1.7}$$

Integrating by parts the last term in Eq. (1.7) and re-arranging gives

$$q_j(t) - \frac{\gamma_j}{\omega_j^2}q(t) = \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}\right)cos(\omega_j t) + p_j(0)\frac{sin(\omega_j t)}{\omega_j}$$
$$- \gamma_j \int_0^t ds \, \frac{p(s)}{m} \, \frac{cos(\omega_j(t-s))}{\omega_j^2}, \tag{1.8}$$

which can be directly inserted into Eq. (1.5) to obtain the formal Langevin equation

$$\frac{dp(t)}{dt} = -\frac{dV(q)}{dq} - \int_0^t ds \, K(s)\frac{p(t-s)}{m} + F_p(t), \tag{1.9}$$

where we have defined the functions $K(t)$ and $F_p(t)$ corresponding to the memory and the "noise" functions, respectively. Explicitly, these are given as

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2}cos(\omega_j t)$$
$$F_p(t) = \sum_j \gamma_j p_j(0)\frac{sin(\omega_j t)}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}q(0)\right)cos(\omega_j t). \tag{1.10}$$

The next step involves carefully choosing the spectra of coupling coefficients and natural frequencies of the harmonic oscillators. For simplicity, we want the equations of motion to be Markovian, i.e. memory-less. Therefore we assume the spectrum of ω to be continuous and define the density of states, $g(\omega)$, as being proportional to ω^2. Furthermore we assume the coupling coefficient to be constant, i.e. $\gamma_j = \sqrt{\gamma}$ for all values of j and $\gamma > 0$ and we obtain an expression for the memory function

$$K(t) \propto \gamma \int_0^\infty d\omega \, cos(\omega t) \propto \gamma\delta(t), \tag{1.11}$$

which satisfies the Markovian property.

In order to evaluate the noise term, we need to make further assumptions on the harmonic oscillators. We assume that the oscillators are independent and their initial conditions are distributed according to the Boltzmann distribution with respect to the constrained initial condition $q(0)$. Due to the large number of oscillators, we can use the central limit theorem to conclude that the noise term will be a Gaussian process as it is the linear sum of independent terms. Evaluating the first moment and the covariance function gives

$$\langle F_p(t)\rangle = 0$$
$$\langle F_p(t)F_p(t')\rangle = k_b T\gamma\delta(t-t'), \tag{1.12}$$

which defines the so-called "white" noise. The Langevin equations of motion can therefore be written as

$$\dot{q} = \frac{p}{m}$$
$$\dot{p} = -\frac{\partial V}{\partial q} - \frac{\gamma p}{m} + \sqrt{2k_b T\gamma} \, \epsilon(t), \tag{1.13}$$

where $\epsilon(t)$ is a real random stochastic process satisfying the following properties

$$\langle \epsilon(t)\rangle = 0$$
$$\langle \epsilon(t)\epsilon(t')\rangle = \delta(t-t'). \tag{1.14}$$

The Langevin dynamics are in full agreement with our physical intuition. Setting $\gamma = 0$ recovers Newton's equations of motion. The magnitude of the stochastic driving force is proportional to the temperature. For high temperatures we expect more random fluctuations. From ad hoc energy considerations, we expect momentum to be strongly correlated with the square root of temperature as $k_b T \approx \frac{p^2}{2m}$. Lastly, the restoring force is proportional to the coupling coefficient and ensures the particle's energy remains within orders of magnitude of the thermal energy of the surroundings. This term can be viewed as the dissipative term. Having obtained the general equations of motion for a system connected to a heat bath, we are now ready to numerically evaluate individual trajectories of classical particles in our toy model.

1.2.2   Simulation of Classical Dynamics

The Verlet algorithm is a second order accuracy algorithm developed for the numerical simulation of Newton's equations of motion [17]. A modified version of the Verlet algorithm was later developed in order to take into account the dissipative and noise terms in the Langevin equations [18]. The time discretisation of Eq. (1.13) is given by the modified Verlet algorithm

$$
\begin{aligned}
q_{t_{k+1}} &= q_{t_k} + p_{t_k}\Delta t + A_{t_k} \\
p_{t_{k+1}} &= (1 - \gamma\Delta t)p_{t_k} + \frac{\Delta t}{2}(f_{t_{k+1}} + f_{t_k}) + \sqrt{\Delta t}\frac{\lambda}{m}\phi_{t_k} - \gamma A_{t_k},
\end{aligned}
\tag{1.15}
$$

where

$$
\begin{aligned}
A_{t_k} &= \frac{\Delta t^2}{2}(f_{t_k} - \gamma p_{t_K}) + \frac{\Delta t^{\frac{3}{2}}\lambda}{2m}(\phi_{t_K} + \frac{\theta_{t_K}}{\sqrt{3}}) \\
f_{t_K} &= -\frac{1}{m}\frac{\partial V(q)}{\partial q}\Big|_{t_K}
\end{aligned}
\tag{1.16}
$$

and θ_{t_k}, ϕ_{t_k} are independent Gaussian distributed random variables and $\lambda = \sqrt{2mTk_b\gamma}$.

1.3   Open Quantum Dynamics

1.3.1   The Liouville-von Neumann Equations

We will introduce the fundamental equations describing the dynamics of open quantum systems by first reviewing the wave vector and density matrix formalism for closed systems before moving onto open systems. In here, we summarise the notation from [19] and [16].

In quantum mechanics, the Schrödinger equation can be re-written in terms of a unitary time operator, $U(t)$, as an operator equation

$$
i\hbar\frac{\partial}{\partial t}U(t) = H(t)U(t)
\tag{1.17}
$$

with the constraint $U(0) = \mathbb{1}$, where $H(t)$ is the Hamiltonian of the system and $\hbar$ is Planck's constant. The evolution of the state vector is then given by

$$
|\psi(t)\rangle = U(t)|\psi(t=0)\rangle = U(t)|\psi(0)\rangle.
\tag{1.18}
$$

Throughout we will assume the initial time is $t = 0$ for simplicity. This is an appropriate assumption as we can always use a linear transformation to shift the initial time, t_0, to $t = 0$.

At finite temperatures, the system under consideration is found in a mixed state. Therefore, it is necessary to describe the system in terms of the density matrix, or statistical operator,

$$
\rho(t) = \sum_\alpha c_\alpha|\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|,
\tag{1.19}
$$

where $|\psi_\alpha(t)\rangle$ do not necessarily form an orthonormal basis for the system in the Hilbert space $\mathcal{H}$. The expectation value of an observable, $A(t)$, is then given by

$$\langle A(t)\rangle = tr\{A\rho(t)\}. \tag{1.20}$$

Using Eq. (1.19), one can deduce that ρ has trace one, is self-adjoint and positive,

$$tr\{\rho\} = 1, \quad \rho = \rho^\dagger, \quad \forall\Psi(t) \in \mathcal{H} \quad \langle\Psi(t)|\rho(t)\Psi(t)\rangle \geq 0. \tag{1.21}$$

Additionally, we can re-write Eq. (1.19) using the unitary operator as

$$\rho(t) = U(t)\rho(0)U^\dagger(t). \tag{1.22}$$

Differentiating Eq. (1.22) with respect to time and using Eq. (1.17), we immediately get an equation of motion for the density matrix

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[H(t), \rho(t)], \tag{1.23}$$

where $[\cdot, \cdot]$ indicates the commutator. Eq. (1.23) is often referred to as the von Neumann or Liouville-von Neumann equation due to its correspondence with the classical Liouville equation.

For an open quantum system, we need to increase our Hilbert space to incorporate the interaction with the environment. Denoting the Hilbert space of A and B, as $\mathcal{H}_A$ and $\mathcal{H}_B$, respectively, the Hilbert space of the total system is given by tensor product space $\mathcal{H} = H_A \otimes H_B$. The Hamiltonian of the system can be written as

$$H(t) = H_0 + \hat{H}_I(t), \tag{1.24}$$

where $H_0(t) = H_A \otimes I_B + I_A \otimes H_B$. H_A and H_B are the free Hamiltonian's of systems A and B, respectively, and I_A and I_B are the corresponding identity operators. $\hat{H}_I(t)$ describes the interaction between systems A and B. This is the well known interaction picture.

In the interaction picture, we distinguish between three unitary time evolution operators, the total system evolution operator, $U(t)$, free evolution operator, $U_0(t)$ and the interaction evolution operator, $U_I(t)$. These correspond to their respective Hamiltonian's, $H(t)$, $H_0(t)$, and $H_I(t)$ and all of them satisfy Eq. (1.17) subject to the same constraint $U(0) = 1$. The relationship between the unitary time evolution operators is given by

$$U_I(t) = U_0^\dagger(t)U(t). \tag{1.25}$$

In the interaction picture, the expectation value of an arbitrary operator, $A(t)$, can be written as

$$\langle A(t)\rangle = tr\{A(t)U(t)\rho(0)U^\dagger(t)\} = tr_I\{A_I(t)\rho_I(t)\}, \tag{1.26}$$

where the interaction picture operator, $A_I(t)$, and the interaction picture density matrix, $\rho_I(t)$, were introduced

$$\begin{aligned} A_I(t) &= U_0^\dagger(t)A(0)U_0(t) \\ \rho_I(t) &= U_I(t)\rho(0)U_I^\dagger(t) \end{aligned} \tag{1.27}$$

and the subscript on the trace indicates the sum over the orthonormal interaction state vectors $|\phi_I(t)\rangle = U_I(t)|\phi(0)\rangle$ spanning $\mathcal{H}$.

By differentiating Eq. (1.27) with respect to time, we obtain the interaction picture von Neumann equation for the interaction picture density matrix

$$\frac{d}{dt}\rho_I(t) = -\frac{i}{\hbar}[H_I(t), \rho_I(t)]. \tag{1.28}$$

1.3.2   The Caldeira-Leggett Master Equation

In this section, the Caldeira-Leggett model will be derived by closely following the derivation made in [16]. The Caldeira-Leggett model considers a particle of mass m in an arbitrary energy potential, V(q), coupled to a heat bath of harmonic oscillators. The Hamiltonian governing the motion of the particle can be written as

$$H = H_S + H_B + H_I + H_C, \tag{1.29}$$

where $H_S := \frac{p^2}{2m} + V(q)$ is the free particle Hamiltonian, H_B is the Hamiltonian corresponding to the surroundings, H_I represents the interaction of the particle with its surroundings and H_C is known as the counter-term acting only in the Hilbert space $\mathcal{H}_S$ of the particle. H_B is approximated by the interaction of the particle with a large number of harmonic oscillators with mass m_n and natural frequencies ω_n forming a heat bath,

$$H_B = \sum_n \left(\frac{p_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 x_n^2 \right) = \sum_n \hbar \omega_n \left(a_n^\dagger a_n + \frac{1}{2} \right), \tag{1.30}$$

where x_n and p_n are the position and momentum operators respectively corresponding to the nth harmonic oscillator. The $a_n^\dagger$, a_n denote the creation and annihilation operators of the bath modes. Assuming that the coordinate q of the particle m is coupled linearly to the coordinates of the bath oscillators q_n, the interaction Hamiltonian can be written as

$$H_I = -q \sum_n \kappa_n q_n = -q \sum_n \kappa_n \sqrt{\frac{\hbar}{2m_n \omega_n}} (a_n^\dagger + a_n), \tag{1.31}$$

where the sum is weighted by the coupling constants κ_n. The counter-term is included as to renormalise the potential $V(q)$, to include the physical frequencies of motion of the particle m. For a more detailed explanation, refer to [16]. In the Caldeira-Leggett approximation, the counter-term is of the form

$$H_C = q^2 \sum_n \frac{\kappa_n^2}{2m_n \omega_n^2}. \tag{1.32}$$

Therefore the total Hamiltonian can be written as

$$H = \frac{p^2}{2m} + V_c(q) + \sum_n \hbar \omega_n \left(a_n^\dagger a_n + \frac{1}{2} \right) - q \sum_n \kappa_n \sqrt{\frac{\hbar}{2m_n \omega_n}} (a_n^\dagger + a_n), \tag{1.33}$$

where we have defined $V_c(q) := V(q) + q^2 \sum_n \frac{\kappa_n^2}{2m_n \omega_n^2}$.

In order to derive the master equation, we start with the Markovian quantum master equation

$$\frac{d}{dt} \rho_I^S(t) = -\frac{1}{\hbar^2} \int_0^\infty ds \, tr_B \{ [H_I(t), [H_I(t-s), \rho_I^S(t) \otimes \rho_I^B]] \}, \tag{1.34}$$

where the superscripts S and B correspond to the system of interest and the heat bath, respectively, and the subscript is used to denote the interaction picture operators. For a detailed derivation of Eq. (1.34) see Appendix B. Eq. (1.34) is given in the interaction picture, but we can easily transform it back into the Schrödinger picture. The starting point is

$$\rho_I^S(t) = U_0^\dagger \rho^S(t) U_0(t), \tag{1.35}$$

where $\rho_I^S(t)$ and $\rho^S(t)$ are the interaction picture density matrix and the Schrödinger picture density matrix of system S, respectively. Differentiating Eq. (1.35) and re-arranging yields

$$\frac{d}{dt} \rho^S(t) = -\frac{i}{\hbar} [H_0(t), \rho^S(t)] + U_0(t) \frac{d\rho_I^S(t)}{dt} U_0^\dagger, \tag{1.36}$$

where we have identified $H_0 = H_S + H_B + H_C$. Using Eq. (1.34) and noticing that $[H_B, \rho^S(t)] = 0$, gives the Born-Markov approximation for the Brownian particle

$$\frac{d}{dt}\rho^S(t) = -\frac{i}{\hbar}[H_S(t) + H_C(t), \rho^S(t)] - \frac{1}{\hbar^2}\int_0^\infty ds tr_B\{[H_I(t), [H_I(t-s), \rho^S(t) \otimes \rho_B]]\}, \quad (1.37)$$

where $H_I(t)$ is defined in Eq. (1.31). The next steps involved in the derivation of the Caldeira-Leggett model involve approximating the integral found in Eq. (1.37). It is beyond the scope of this work to go into the details here, but we will refer the curious readers to references [16] and [20]. Assuming the heat bath is in thermal equilibrium, the spectral density of ω can be approximated by a smooth function of ω and that $q(t-s)$ can be approximated by free dynamics, we arrive at the Caldeira-Leggett master equation

$$\frac{d}{dt}\rho_S(t) = -\frac{i}{\hbar}[H_S, \rho_S(t)] - \frac{i\eta}{\hbar}[q, \{p, \rho_S(t)\}] - \frac{2m\eta k_b T}{\hbar^2}[q, [q, \rho_S(t)]], \quad (1.38)$$

where $\{\cdot, \cdot\}$ indicates the anti-commutator [20].

The three terms on the right hand side describe physical phenomena acting on the Brownian particle. The first term corresponds to the free dynamics of the particle. The term proportional to the relaxation rate, η, is a dissipative term, where the energy from the Brownian particle is lost to the heat bath resulting in irreversible dynamics. The final term, which is proportional to temperature, describes the thermal fluctuations driving the Brownian particle.

1.3.3 The Caldeira-Leggett Master Equation in Lindblad form

For a Markovian quantum master equation of the form

$$\frac{d}{dt}\rho_S = \mathcal{L}\rho_S, \quad (1.39)$$

$\mathcal{L}$ is the generator of a quantum dynamical semi-group. In 1976, Lindblad showed that the most general form of the generator that preserves positivity is

$$\mathcal{L}\rho_S = -\frac{i}{\hbar}[H, \rho_S] + \sum_j (L_j\rho_S L_j^\dagger - \frac{1}{2}\rho_S L_j^\dagger L_j - \frac{1}{2}L_j^\dagger L_j\rho_S), \quad (1.40)$$

where L_j are known as Lindblad operators and H is not necessarily equal to H_S, but can contain additional terms due to the interaction of the system with the environment [21].

In Section 1.3.1, it was established that the density matrix operator, $\rho(t)$, has to have trace one, be self-adjoint and positive, Eq. (1.21), for all times. The Caldeira-Leggett master equation does not preserve positivity for all times, thus violating the probability interpretation of quantum mechanics. In order to obtain meaningful results, Eq. (1.38) is re-written into Lindblad form using the most common approach taken in literature [16] [13] [22].

For the Caldeira-Leggett master equation an appropriate guess for the single Lindblad operator, L, would be

$$L = Aq + Bp, \quad (1.41)$$

where A, B are complex coefficients to be determined and q, p are the coordinate and momentum operators, respectively. Substituting Eq. (1.42) into Eq. (1.40) and comparing terms with Eq. (1.38), the non-Hermitian Lindblad operator is defined as

$$L = \sqrt{\frac{4m\eta k_b T}{\hbar^2}}q + i\sqrt{\frac{\eta}{4mk_b T}}p. \quad (1.42)$$

An alert reader will notice that H defined in Eq. (1.40) has been modified by an interaction term with the heat bath

$$H = H_S + \frac{\eta}{2}(qp + pq) \tag{1.43}$$

and that a minimally invasive modification is added to the Caldeira-Leggett master equation

$$-\frac{\eta}{8mk_bT}[p, [p, \rho_S]] \tag{1.44}$$

to bring it into Lindblad form [16]. In the high-temperature limit, this term is negligible.

1.3.4 Stochastic Schrödinger Equation

One approach of obtaining quantum dynamics of any quantum system connected to a heat bath is to derive the appropriate stochastic Schrödinger equation. One could view this as the quantum analogue of the Langevin equation of motion. In the derivation of the stochastic Schrödinger equation, we will closely follow the derivation found in [19] and [23].

The projection operator, ρ_S, for an N-dimensional Hilbert space, $\mathcal{H}$, can be written as the expectation value over a distribution of all of the realisations of the wave functions, ψ^r:

$$\rho = \mathbb{E}_r[|\psi^r\rangle \langle \psi^r|]. \tag{1.45}$$

For an open system, the environment introduces "noise" to the system of interest S, which is captured mathematically by the interaction term in the Hamiltonian. We can model this "noise", by introducing Brownian motion to the individual realisations of the wave functions. In differential form, the stochastic equations for wave functions, ψ^r, can be written as

$$|d\psi^r\rangle = |v\rangle \, dt + |u\rangle \, dW_t^r, \tag{1.46}$$

where $|v\rangle \, dt$ corresponds to drift and $|u\rangle \, dW^r$ represents the random fluctuations. dW^r are independent real Wiener processes with the following properties

$$\mathbb{E}[dW_t^r] = 0, \quad E[dW_t^j dW_t^i] = \delta_{ij}dt \quad \forall i, j, \tag{1.47}$$

where δ_{ij} denotes Kronecker delta function. To preserve normalisation, we need to impose the following condition

$$\langle \psi^r | u \rangle = 0. \tag{1.48}$$

Taking the derivative of Eq. (1.45), we obtain

$$d\rho = \mathbb{E}_r[|d\psi^r\rangle \langle \psi^r| + |\psi^r\rangle \langle d\psi^r| + |d\psi^r\rangle \langle d\psi^r|], \tag{1.49}$$

where the last term has to be kept due to Itô calculus. Expanding $|d\psi^r\rangle$, keeping only first order terms with respect to time gives

$$\frac{d\rho}{dt} = \mathbb{E}_r[|\psi\rangle \langle v| + |v\rangle \langle \psi| + |u\rangle \langle u|]. \tag{1.50}$$

In order to determine $|u\rangle \langle u|$ and $|v\rangle$, we can define the operator

$$\rho_\psi = |\psi\rangle \langle \psi|. \tag{1.51}$$

Using this operator the equations for $|u\rangle \langle u|$ and $|v\rangle$ are

$$|u\rangle \langle u| = (I - \rho_\psi)\frac{d\rho}{dt}(I - \rho_\psi), \quad |v\rangle = \frac{d\rho}{dt}|\psi\rangle - (\frac{1}{2}\langle \psi|\frac{d\rho}{dt}|\psi\rangle + ic)|\psi\rangle, \tag{1.52}$$

where ic is a non-physical imaginary phase change constant determined by convention to agree with the Schrödinger equation in the absence of the heat bath. Using Eq. (1.52) and Eq. (1.40), we can determine $|u\rangle\langle u|$ and $|v\rangle$ for the Caldeira-Leggett master equation in Lindblad form and obtain the stochastic Schrödinger equation by substituting back into Eq. (1.46)

$$|d\psi\rangle = -\frac{i}{\hbar}H|\psi\rangle\,dt + ((\langle L^\dagger\rangle L - \frac{1}{2}L^\dagger L - \frac{1}{2}\langle L^\dagger\rangle\langle L\rangle)\,|\psi\rangle\,dt + (L - \langle L\rangle)\,|\psi\rangle\,dW, \qquad (1.53)$$

where the superscript r was dropped.

Equation (1.53), can be re-written in Itô form in the following way

$$|d\psi\rangle = \mu(\psi(t))dt + \sigma(\psi(t))dW_t, \qquad (1.54)$$

where we have introduced the diffusion, $\mu(\psi(t))$, and drift, $\sigma(\psi(t))$ terms

$$\mu(\psi(t)) = -\frac{i}{\hbar}H|\psi\rangle + ((\langle L^\dagger\rangle L - \frac{1}{2}L^\dagger L - \frac{1}{2}\langle L^\dagger\rangle\langle L\rangle)\,|\psi\rangle$$
$$\sigma(\psi(t)) = (L - \langle L\rangle)\,|\psi\rangle\,. \qquad (1.55)$$

For the Caldeira-Leggett equation, the Hamiltonian and the Lindblad operators were defined as

$$H = \frac{p^2}{2m} + V(q) + \frac{\eta}{2}\{p,q\}$$
$$L = \frac{\sqrt{4m\eta k_b T}}{\hbar}q + i\sqrt{\frac{\eta}{4mk_b T}}p. \qquad (1.56)$$

The drift and diffusion terms encapsulate the effect of the heat bath on the system. As one would expect, the diffusion term arises purely due to the interaction with the heat bath. The strength of the thermal "kicks" is proportional to the deviation from the Lindblad expectation value. Physically, one could imagine this "kick" being proportional to the deviation from the thermal equilibrium. The overall Hamiltonian is now the sum of the system Hamiltonian plus the additional commutator term from the interaction. Although this may be surprising at first glance, it is just convenient to write it in this form. Due to it being a linear sum, we can always separate out the interaction and system Hamiltonians. Setting $\eta = 0$ recovers the Schrödinger equation for an isolated system.

In order to be able to compare classical and quantum dynamics, we need to show that in the classical limit the stochastic Schrödinger equation converges with the Langevin equation for the same parameters of temperature and coupling coefficients. In this thesis, we will only state the final result and refer the reader to [13] for a comprehensive derivation. The equations of motion converge in the following scenario

$$\gamma = 2\eta$$
$$T^c = T^q, \qquad (1.57)$$

where the superscripts c and q refer to the classical and quantum cases, respectively. For the rest of this thesis, we will not use the subscripts on the temperature as in both cases we are referring to the same parameter.

1.3.5 Convergence of Individual Dynamics with the Density Matrix

The corresponding density matrix equation to the stochastic Schrödinger equation is the original Lindblad equation

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[H,\rho] + L\rho L^\dagger - \frac{1}{2}\rho L^\dagger L - \frac{1}{2}L^\dagger L\rho \qquad (1.58)$$

with the time independent Hamiltonian, H, and Lindblad, L, operators defined in Eq. (1.56). Given an initial condition, $\rho(t = 0)$, this equation can be solved exactly by transforming from the Hilbert space, $\mathcal{H}$, into the Liouville space, $\mathcal{L}_{N \times N}$. The solution of this equation is given by

$$\rho(t) = e^{\mathcal{L}t} \rho(0), \tag{1.59}$$

where $\mathcal{L}$ is the Liouville operator. For a more comprehensive derivation of the solution to the Lindblad equation, refer to Appendix D.

In terms of numerical simulations, the density matrix $\rho_R(t_i)$ at time t_i is defined in the following way

$$\rho_R(t_i) = \mathbb{E}_r[|\psi^r(t_i)\rangle \langle \psi^r(t_i)|] = \frac{1}{R} \sum_{r=0}^{R} |\psi^r(t_i)\rangle \langle \psi^r(t_i)| \quad \forall t_i \in \{0, t_1, ..., t_{M-1}, t_M\}, \tag{1.60}$$

where $|\psi^r(t_i)\rangle$ is an N-dimensional matrix defined at time t_i in an arbitrary finite N-dimensional Hilbert space, $\mathcal{H}_N$ and where time has been partitioned into a discrete set, $\{0, t_1, ..., t_{M-1}, t_M\}$. Furthermore, r denotes the rth realisation of the stochastic Schrödinger equation and R denotes the total number of realisations. In the limit of R going to infinity and the time step going to zero, the density matrix $\rho_R(t_i)$ will converge to the exact density matrix operator $\rho(t)$.

Of particular interest are expectation values of the observable A of an open system. Having obtained a way of simulating individual trajectories, the expectation value of A at time t_i is given by

$$\langle A(t_i) \rangle = \mathbb{E}[\langle \psi(t_i)| A |\psi(t_i)\rangle] = \frac{1}{R} \sum_{r=0}^{R} \langle \psi^r(t_i)| A |\psi^r(t_i)\rangle \tag{1.61}$$

with the standard error, $\sigma_A(t_i)$, given by

$$\sigma_A(t_i) = \frac{1}{R(R-1)} \sum_{r=0}^{R} (\langle \psi^r(t_i)| A |\psi^r(t_i)\rangle - \langle A(t_i) \rangle)^2. \tag{1.62}$$

Using the density matrix notation, the expectation value of A at time t_i is given by

$$\langle A(t_i) \rangle = Tr(\rho(t_i)A) = \sum_{j=0}^{N} \langle \phi_j| \rho(t_i)A |\phi_j\rangle, \tag{1.63}$$

where $|\phi_j\rangle$ are the orthogonal states forming the finite N-dimensional Hilbert space, $\mathcal{H}_N$, and $\rho(t_i)$ is obtained by solving Eq. (1.59) explicitly.

For the toy model, the dimension of the Hilbert space is chosen to be 80 and the Runge-Kutta scheme requires a time step of $\Delta t = 0.001$ in order to give meaningful dynamics.

1.3.6 Simulating Density Matrix Dynamics

In this short section, we will briefly present the density matrix dynamics for four different sets of parameters T and η that will later be useful in the understanding of quantum transition rates. The density matrix evolution presented here can be used in conjunction with the results obtained in the previous section to further the understanding between microscopic and macroscopic phenomena.

The initial density operator, $\rho(t = 0)$, that is used in the simulations is defined as

$$\rho(t = 0) = P_A \rho_{eq}, \tag{1.64}$$

where ρ_{eq} corresponds to the thermal equilibrium density matrix

$$\rho_{eq} = e^{-\frac{H}{k_B T}}/Tr\left(e^{-\frac{H}{k_B T}}\right), \tag{1.65}$$

where H is the Hamiltonian operator. Furthermore, $P_A(t)$ corresponds to the quantum heaviside operator, which takes the form

$$P_A = \int_{-\infty}^{0} dx\, |x\rangle\langle x|. \tag{1.66}$$

The quantum heaviside operators will be covered in greater depth in Section 2.5.

Chapter 2

Transition Rate Theory

2.1 Statistical Mechanics Approach to a Double Well Potential

Statistical mechanics deals with physical systems that have a large degree of freedom. For example, when considering a box of N particles, each particle can be described by its position and momentum. Without any external forces, once the initial conditions are specified for the system at $t = 0$, the system is deterministic for all $t > 0$. In most situations, the initial conditions are not known and ensemble averages arise by averaging over the set of all possible initial conditions. The observable, $A(t) = A(t; q^N, p^N)$, is not observed directly, but rather the average over all experimental possibilities of A(t) is observed

$$\tilde{A}(t) = \int dq^N dp^N F(q^N, p^N) A(t; r^N, p^N), \tag{2.1}$$

where $F(q^N, p^N)$ is the probability distribution of the set of all possible initial conditions. Once the system reaches equilibrium at time, T, where $T > 0$, then for all $t > T$ the value of $\tilde{A}(t)$ will remain constant.

For a two state system separated by an energy barrier, we can define two observables, $n_A(t)$ and $n_B(t)$, corresponding to macroscopic probabilities of finding a particle in state A and B, respectively. From Eq. (2.1), we can immediately write

$$n_A(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_0 dp_0 F(q_0, p_0) \theta_A(q(t)), \tag{2.2}$$

where (q_0, p_0) is the set of initial conditions with probability distribution $F(q_0, p_0)$. For the toy model, $\theta_A(q(t))$ is the heaviside step function defined as

$$\theta_A(q) = \begin{cases} 1, & \text{if } q(t) \leq 0 \\ 0, & \text{if } 0 < q(t). \end{cases} \tag{2.3}$$

Thus $n_A(t)$ and $n_B(t)$ fulfil the condition

$$n_A(t) + n_B(t) = 1 \quad \forall t. \tag{2.4}$$

In the limit $k_B T << E_B$, we assume that the mean field equations for the dynamics of the system can be written as

$$\begin{aligned} \frac{dn_A(t)}{dt} &= k_{BA}(t) n_B(t) - k_{AB}(t) n_A(t) \\ \frac{dn_B(t)}{dt} &= -k_{BA}(t) n_B(t) + k_{AB}(t) n_B(t), \end{aligned} \tag{2.5}$$

where the forward and back rates, $k_{AB}(t)$ and $k_{BA}(t)$, have been introduced. The forward rate $k_{AB}(t)$ describes the strength of the "diffusion rate" of the macroscopic probability of being in state A to being in state B at time t. The same definition holds for the back rate with the "diffusion rate" being from state B to state A.

The classical transition rate, $k^c(t)$, for this system can be defined as

$$k^c(t) = \frac{k_{AB}(t) + k_{BA}(t)}{2}. \tag{2.6}$$

The assumption $k_B T << E_B$, where E_B is the energy barrier, is crucial for defining a transition rate. In the classical picture, the kinetic energy of the particle is of the order of $k_B T$. For higher temperatures, the particle will move freely between the two states implying the states can be macroscopically thought of as being a single state making the concept of a transition rate redundant. In other words, the transition events should be rare in order to be able to define transition rates.

In writing the mean field equations, we have made the assumption that the system is closed in the sense that there is no diffusion of the macroscopic probabilities from the system. In this thesis, we have chosen to use these mean field equations to simplify the derivation of the classical transition rate, $k^c(t)$. It is worth noting that the addition of diffusion terms in Eq. (2.5) would yield the same result for the transition rate. For a more complete derivation, refer to Appendix B of [9].

2.2   Onsager Regression Hypothesis

In this thesis, we will not derive the results of the regression hypothesis, but merely state it and instead refer the keen reader to [14]. Qualitatively, the Onsager regression hypothesis states that the relaxation of macroscopic systems found in a non-equilibrium state due to perturbations by small linear external forces are governed by the same laws as the regression of spontaneous microscopic fluctuations in equilibrium systems. Mathematically, the regression of spontaneous fluctuations is denoted by time correlation functions. The instantaneous fluctuations or deviations, $\delta A(t)$, of an observable, $A(t)$, at time t can be written as

$$\delta A(t) = A(t) - \langle A \rangle, \tag{2.7}$$

where $\langle A \rangle$ is the time-independent equilibrium average. Information about the system is obtained by studying the correlation, $c_A(t)$, between instantaneous fluctuations at time t and the spontaneous deviations at time $t = 0$,

$$c_A(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_0 dp_0 F(q_0, p_0) \delta A(0) \delta A(t), \tag{2.8}$$

where $F(q_0, p_0)$ is the equilibrium phase-space distribution.

In equilibrium, the correlation function only depends on the separation of the times rather than the absolute value of time. This property can be written as

$$c_A(|t_2 - t_1|) = \langle \delta A(t_1)\delta A(t_2) \rangle = \langle \delta A(t_2)\delta A(t_1) \rangle, \tag{2.9}$$

where $\langle A \rangle$ denotes

$$\langle A(t) \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_0 dp_0 F(q_0, p_0) A(t; q_0, p_0). \tag{2.10}$$

Furthermore, classically $A(0)$ commutes with $A(t)$ implying the special case

$$c_A(t) = \langle \delta A(0)\delta A(t) \rangle = \langle \delta A(-t)\delta A(0) \rangle. \tag{2.11}$$

Considering the limit of small and large times, one can obtain the relations

$$c_A(0) \to \langle \delta A(0)^2 \rangle, \text{ as } t \to 0$$
$$c_A(t) \to \langle \delta A(0) \rangle \langle \delta A(t) \rangle \to 0, \text{ as } t \to \infty, \tag{2.12}$$

as we expect the instantaneous fluctuations at large times to become uncorrelated to the initial deviations. This principle is known as the regression of instantaneous fluctuations.

Having introduced the notion of time correlation function and regression of instantaneous fluctuations, we can now state the mathematical formulation of Onsager regression hypothesis. Imagine a system in equilibrium being perturbed by a small linear force and let $t = 0$ denote the time at which the perturbed system is allowed to relax to equilibrium. In this linear regime, the relaxation obeys the following relation

$$\frac{A(t) - \langle A \rangle}{A(0) - \langle A \rangle} = \frac{c_A(t)}{c_A(0)}. \tag{2.13}$$

The physical motivation behind this relation is that for a system close to equilibrium, one cannot distinguish between the instantaneous deviations driven by an external linear force and spontaneous fluctuations of the system itself. Therefore, the relaxation of spontaneous fluctuations should coincide with the decay to equilibrium of $\Delta A(t) = A(t) - \langle A \rangle$.

2.3 Classical Transition Rate Theory

2.3.1 General Form

For the 1-dimensional double well described in Section 1.1, we can obtain an expression for the classical transition rate, $k^c(t)$. First, we will assume that there exists a time scale in the linear regime for which $k_{AB}(t)$ and $k_{BA}(t)$ are time independent, i.e. constant. Using the constraint in Eq. (2.4), the solution of Eq. (2.5) becomes

$$n_A(t) = (n_A(0) - \langle n_A \rangle)e^{-\frac{t}{\tau_{rxn}}} + \langle n_A(t) \rangle, \tag{2.14}$$

where we have defined the characteristic relaxation time scale, τ_{rxn}, in terms of the transition rates

$$\tau_{rxn} = \frac{1}{k_{AB} + k_{BA}}. \tag{2.15}$$

Substituting this expression into the Onsager regression hypothesis, Eq. (2.13), and using the definition in Eq. (2.9), we obtain

$$\exp\left\{-\frac{t}{\tau_{rxn}}\right\} = \frac{\langle \theta_A(0)\theta_A(t) \rangle - \langle \theta_A^2 \rangle}{\langle \theta_A^2 \rangle - \langle \theta_A \rangle^2}, \tag{2.16}$$

where $\theta_A(t)$ is defined in Eq. (2.3). This equation provides a direct link between the transition rate constant on the left hand side and the microscopic behaviour of the system together with ensemble averages on the right hand side. This equation holds for any system, where two states can be distinguished and the characteristic relaxation time scale exists. This equation is valid only for equilibrium systems being perturbed by a small linear force.

Taking the time derivative of this equation and noticing the relation $\langle \theta_A^2 \rangle - \langle \theta_A \rangle^2 = \langle \theta_A \rangle \langle \theta_B \rangle$, gives

$$-\frac{1}{\tau_{rxn}} \exp\left\{-\frac{t}{\tau_{rxn}}\right\} = \frac{\langle \theta_A(0)\dot{\theta}_A(t) \rangle}{\langle \theta_A \rangle \langle \theta_B \rangle}. \tag{2.17}$$

From the properties of classical time correlation functions, refer to Eq. (2.11), one can obtain the relation $\langle \dot{\theta}_A(0)\theta_A(t)\rangle = -\langle \theta_A(0)\dot{\theta}_A(t)\rangle$ and rewrite the above expression as

$$\frac{1}{\tau_{rxn}}\exp\left\{-\frac{t}{\tau_{rxn}}\right\} = \frac{\langle \dot{\theta}_A(0)\theta_A(t)\rangle}{\langle\theta_A\rangle\langle\theta_B\rangle} = \frac{\langle \dot{q}(0)\delta(q_0-0)\theta_B(t)\rangle}{\langle\theta_A\rangle\langle\theta_B\rangle}, \tag{2.18}$$

where in the last equality the expression $\dot{\theta}_A(0) = -\dot{q}(0)\delta(q_0 - 0)$ is evaluated using chain rule, and two facts were recalled: $\theta_A(t) = 1 - \theta_B(t)$ and $\langle \dot{q}_0\delta(q(0) - 0)\rangle = 0$. The last statement is true as velocity is an odd vector function and the equilibrium ensemble distribution of velocities is even and uncorrelated with position configurations.

The initial assumption made in this derivation is that there exists a time scale for which the forward and backward transition rates are constant. This is true in the regime

$$\tau_{mol} << t << \tau_{rxn}, \tag{2.19}$$

where the time scale required for transient behaviour to relax, τ_{mol}, has been introduced. See Figure 2.1 for more details. Eq. (2.19) implies that for such times $\exp\left\{-\frac{t}{\tau_{rxn}}\right\} \approx 1$. Substituting this into Eq. (2.18) and remembering the definition of the classical transition rate, $k^c(t)$ in Eq. (2.6), we obtain

$$k^c(t) = \frac{\langle \dot{q}(0)\delta(q_0-0)\theta_B(t)\rangle}{2\langle\theta_A\rangle\langle\theta_B\rangle}, \forall t \in T_{plateau}, \tag{2.20}$$

where $T_{plateau}$ denotes the set of all times where the classical transition rate reaches a non-zero plateau.

Remembering that $k_{BA} = \frac{\langle n_A\rangle}{\langle n_B\rangle}k_{AB}$ and using the fact $\langle\theta_A\rangle = \frac{\langle n_A\rangle}{\langle n_A\rangle+\langle n_B\rangle}$, we can obtain the following expressions from Eq. (2.20)

$$\begin{aligned} k_{BA} &= \frac{1}{\langle\theta_A\rangle}\langle \dot{\theta}_B(0)\theta_B(t)\rangle \\ k_{AB} &= \frac{1}{\langle\theta_B\rangle}\langle \dot{\theta}_A(0)\theta_A(t)\rangle \end{aligned} \tag{2.21}$$

that are valid for all $t \in T_{plateau}$. For a symmetric potential well the following equality holds $\langle\theta_A\rangle = \langle\theta_B\rangle$, giving a final expression for the classical transition rate as

$$k^c(t) = \frac{\langle \dot{q}(0)\delta(q_0-0)\theta_B(t)\rangle}{\langle\theta_B\rangle} \qquad \forall t \in T_{plateau}. \tag{2.22}$$

Having derived an expression for the classical transition rate, $k^c(t)$, in Eq. (2.22), it is worthwhile explaining its physical meaning. For a classical particle to move from state A into state B, requires the particle to transition through the position $q = 0$. Classically, one would therefore expect the transition frequency to be proportional to the flux through the barrier separating the two states. The flux term of moving from A to B is contained in the numerator of Eq. (2.22). In order to compute the transition rate, the individual trajectories of classical particles have to be simulated using the initial condition $q(0) = 0$ and averaging over the probability distribution for initial momenta. This is called the path-sampling approach to computing the transition rate. For an extended discussion of this phenomenological classical transition rate constant refer to [6].
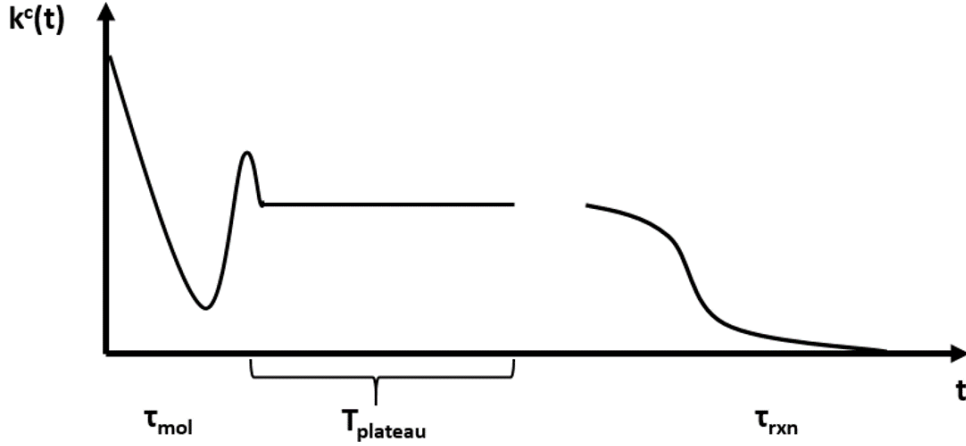
Figure 2.1: The figure shows the behaviour of a classical transition rate, $k^c(t)$. The diagram shows the three different time scales. The τ_{mol} represents the time scale required for transient behaviour to relax. $T_{plateau}$ denotes the set of all times for which the transition rate reaches a non-zero plateau value. In this interval, Eq. (2.22) provides an accurate description of the system only if the transitions constitute rare events. The largest time scale is τ_{rxn} and this is the time required for the system to diffuse back into an equilibrium state. Adapted from [14].

2.3.2 Transition State Theory and Transition Coefficient

The main assumption of transition state theory is that once a particle crosses the barrier its trajectory will not recross the dividing surface. Therefore, one can view the transition state theory approximation to the classical rate as the limit of small t, i.e.

$$k^c_{TST} = \lim_{t \to 0} k^c(t). \tag{2.23}$$

In order to account for corrections to the transition state theory, we can define a transmission coefficient, κ, by

$$k^c(t) = \kappa(t)k^c_{TST}, \tag{2.24}$$

where physically $\kappa(t)$ corresponds to the fraction of successful or undeterred transitions from state A to B. It is worth noting that the transmission coefficient is a highly system- specific and non-trivial quantity encapsulating information about the topology of the system, coupling to the environment and the various time scales.

The transmission coefficient exhibits the same time dependent behaviour as the classical transition rate as k^c_{TST} is a constant. In this thesis, the focus will be on computing the transmission coefficient from which for the classical transition rate can be deduced using Eq. (2.24). Re-arranging Eq. (2.24) gives

$$\kappa(t) = \frac{k^c(t)}{k^c_{TST}}, \tag{2.25}$$

where the value of $\kappa(t)$ will always range between 1 and -1, which will be shown later. In the last part of this section, we will focus on obtaining an expression for $\kappa(t)$.

In thermal equilibrium, the probability distribution function, $F(q_0, p_0)$, is given by

$$F(q_0, p_0) = \frac{1}{Z} \exp\left\{ -\frac{H(q_0, p_0)}{k_B T} \right\}, \tag{2.26}$$

where $H(q_0, p_0)$ is the Hamiltonian of the system and Z is the partition function given by

$$Z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_0 dp_0 \exp\left\{ -\frac{H(q_0, p_0)}{k_B T} \right\}. \tag{2.27}$$

In general, the Hamiltonian is of the form

$$H(q_0, p_0) = T(q_0, p_0) + V(q_0) = \frac{p_0^2}{2m} + V(q_0), \tag{2.28}$$

where $T(q_0, p_0)$ denotes the kinetic energy and $V(q_0)$ denotes the energy potential. Here we are considering a specific form of the Hamiltonian with the energy potential defined in Section 1.1. Substituting Eq. (2.26) into Eq. (2.22) yields

$$k^c(t) = \frac{1}{Z\langle\theta_B\rangle} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_0 dp_0 \frac{p_0}{m} \delta(q_0 - 0)\theta_B(t) \exp\left\{-\frac{H(q_0, p_0)}{k_B T}\right\}, \tag{2.29}$$

which can be simplified to

$$k^c(t) = \frac{1}{mZ\langle\theta_B\rangle} \exp\left\{-\frac{V(0)}{k_B T}\right\} \langle p_0 \theta_B(t)|_{q_0=0}\rangle_{p_0} \tag{2.30}$$

by evaluating the position integral and introducing the notation $\langle\cdot\rangle_{p_0}$ to denote the average over the distribution of all possible initial momenta.

From the definition of k_{TST}^c, Eq. (2.23), we can immediately write

$$\begin{aligned} k_{TST}^c &= \lim_{t\to 0} \frac{1}{Z\langle\theta_B\rangle} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq_0 dp_0 \frac{p_0}{m} \delta(q_0 - 0)\theta_B(t) \exp\left\{-\frac{H(q_0, p_0)}{k_B T}\right\} \\ &= \frac{1}{mZ\langle\theta_B\rangle} \exp\left\{-\frac{V(0)}{k_B T}\right\} \langle p_0 \rangle_{p_0^+} \end{aligned} \tag{2.31}$$

where we have used that $\lim_{t\to 0} \theta_B(t) = \theta(\dot{q}(0))$, evaluated the position integral and introduced the $\langle\cdot\rangle$ notation for simplicity.

Substituting Eq. (2.30) and Eq. (2.31) into the definition of the transmission coefficient, Eq. (2.25) gives

$$\kappa(t) = \frac{1}{\langle p_0\rangle_{p_0^+}} \langle p_0\theta_B(t)|_{q_0=0}\rangle_{p_0}. \tag{2.32}$$

As stated before the value of the transmission coefficient is strictly bounded between -1 and 1. Physically $\kappa = 1$ corresponds to the situation, where all of the particles starting at $q = 0$ at time t will be found in state B with positive momentum. This is the upper bound for the numerator and it is the only case when it can equal the denominator. A value of $\kappa = -1$ corresponds to the same scenario, but with momentum at time t being in the opposite direction.

The approximation for the classical transition rate, $k^c(t)$, is recovered by substituting Eq. (2.32) and Eq. (2.31) into Eq. (2.24) to give

$$k^c(t) = \frac{1}{mZ\langle\theta_B\rangle} \exp\left\{-\frac{V(0)}{k_B T}\right\} \langle p_0\theta_B(t)|_{q_0=0}\rangle_{p_0}. \tag{2.33}$$

With a defined energy potential all of the terms in the above equation can be evaluated either analytically or numerically.

2.4   Simulation of Classical Transition Rates

In Section 1.2, we derived the Langevin equations of motion, which allow us to numerically compute the classical transition rate, $k^c(t)$, for the toy model. N individual trajectories are modelled using Eq. (1.15) with the initial conditions $\{(q_0^0, p_0^0), ..., (q_0^N, p_0^N)\}$, where momentum is sampled from a Boltzmann distribution and the initial position is $q = 0$.

Numerically the classical transition rate, k_N^c, for the toy model is given by the discrete version of Eq. (2.33)

$$k_N^c(t) = \frac{2}{mZ} \frac{1}{N} \sum_{j=0}^{N} p_0^j \theta^c(q_t^j)|_{q_0^j = q*}, \tag{2.34}$$

where the partition function, Z, is evaluated numerically as 11.718 and N is chosen sufficiently large for the sum to converge. Furthermore, we evaluate the term $\langle \theta_B \rangle = \frac{1}{2}$ and the exponential factor, which is equal to 1.

2.5 Quantum Transition Rate Theory

2.5.1 Quantum Transition Rate: Proposal 1

In the derivation of the classical transition rate, time correlations provide the link between microscopic and macroscopic phenomena. Inspired by this approach, one of the easiest way to obtain the quantum transition rate, $k^q(t)$, is to verify the validity of Eq. (2.16). If the correlation function decays exponentially over time, the gradient of the plot will give us the transition rate. In order to implement the method, we have to define this equation in the quantum formulation.

The starting point is the correlation function

$$c(t) = \langle \theta_A(q(0)) \theta_A(q(t)) \rangle, \tag{2.35}$$

where in the classical case the θ_A is defined by the heaviside function. The corresponding operator in quantum mechanics for the toy model can be defined as

$$P_A(t) = \int_{-\infty}^{0} dx \, |x\rangle \langle x| \tag{2.36}$$

acting on the wave function or density operator to give the probability of being in state A. We can define a similar operator for state B in the following way

$$P_B(t) = \int_{0}^{\infty} dx \, |x\rangle \langle x|. \tag{2.37}$$

The classical and quantum operators satisfy the same properties. The quantum heaviside operators satisfy the following relations

$$\begin{aligned} P_A(t)P_A(t) &= P_A(t) \quad \forall t \\ P_B(t)P_B(t) &= P_B(t) \quad \forall t \\ P_A(t) + P_B(t) &= \mathbb{1} \quad \forall t. \end{aligned} \tag{2.38}$$

Using the quantum heaviside operator, $P_A(t)$, we can write the correlation function as

$$c(t) = \langle P_A(0)P_A(t) \rangle = Tr(P_A \rho(t))|_{\rho_0 = P_A \rho_{eq}}, \tag{2.39}$$

where ρ_{eq} corresponds to the thermal equilibrium density matrix defined in (1.65).

The superoperator method (see Appendix D) can be used to evolve the density matrix in time. The reasons for choosing the initial density matrix are twofold. For non-equilibrium systems driven by a linear force, perturbations are governed by the same laws as the regression of spontaneous microscopic fluctuations in equilibrium classical systems. Therefore, this is an appropriate guess. The second reason is that this can be verified experimentally as preparing a thermal equilibrium state should not be problematic.

The quantum transition rate, $k^q(t)$, is obtained by re-arranging Eq. (2.16) and using quantum operators to yield

$$k^q(t) = \frac{\ln 4(Tr(P_A \rho(t))|_{\rho(0)=P_A \rho_{eq}} - 0.5)}{-2t},$$
(2.40)

where remembering that in equilibrium $\langle P_A \rangle = 0.5$ and using the properties of P_A we evaluated $\langle P_A P_A \rangle$. The problem with implementing this solution is that the transition rate has a hyperbolic shape and identifying the relevant time region to average over is problematic. Instead rather than using this formula, the numerator is plotted on the y-axis and time on the x-axis and the gradient is computed.

2.5.2 Quantum Transition Rate: Proposal 2

A more natural approach of viewing the quantum transition rate problem is to assume that the wave function will have to cross the transition state in order to cross the barrier. Classically, this idea is encaptured in Eq. (2.22). This equation can be re-written as

$$k(t) = \frac{\langle j(x=0)\theta_B(t) \rangle}{\langle \theta_B \rangle},$$
(2.41)

where $j(x=0)$ denotes the flux at the transition state and θ_B is the heaviside operator for state B.

In quantum mechanics, the current density flux is obtained from the continuity equation

$$\nabla \cdot \mathbf{j}(r) = -\dot{\rho},$$
(2.42)

where

$$\rho(t) = |\psi|^2.$$
(2.43)

Using Schrödinger's equations we can evaluate the right hand side of the continuity equation. Equating it to the left hand side, we can define the current in Dirac notation as an operator

$$j(x) = \frac{1}{2m}\{|x\rangle \langle x| p + p^\dagger |x\rangle \langle x|\}.$$
(2.44)

For the toy model, the quantum transition rate could be defined in the following way

$$k^q(t) = 2Tr(j(x=0)\theta_B \rho(t))|_{\rho(0)=P_A \rho_{eq}},$$
(2.45)

where ρ_{eq} is defined in Eq. (1.65). It should be noted that in the previous sentence, the word "could" was deliberately used. In the classical version of this equation, Eq. (2.22), the initial distribution of the system is not specified. We have deliberately chosen this initial condition in order to be able to compare the numerical values against the quantum transition rate defined in Proposal 1, see Section 2.5.1.

The quantum transition rate given in Eq. (2.45) can also be interpreted physically. Assume that at time we obtain a certain density matrix, $\rho(t)$. The θ_B projects it onto state B, i.e. we are now only looking at a fraction of the wave function found in state B. Then the current density operator, $j(x=0)$, measures the "flow" of the wave function through the transition state. The transition rate is therefore a measurement of the influx of the probability distribution into or out of state B. This formulation is in line with the definition of forward and backward rates made in the mean field approximations made in Section 2.1. Therefore, the transition rate is only valid when it reaches a plateau, i.e. a constant value.

Appendix A

Units of Measure

The toy model used throughout this thesis is defined in terms of rescaled units. The model is developed with the intention of modelling the dynamics of a hydrogen atom in an iron lattice and more specifically a hydrogen atom moving in separated tetrahedral sites in α-Fe. The relevant scaling parameters for this physical system are

$$d_0 = 1.014\text{Å}, \quad m_0 = 1.674 \times 10^{-27} kg, \quad E_0 = 0.089 eV, \tag{A.1}$$

where E_0 has been calculated in [4]. The dimensionless units were obtained by the scaling

$$\left[\frac{m}{m_0}\right] = \left[\frac{E_B}{E_0}\right] = \left[\frac{d}{d_0}\right] = 1, \tag{A.2}$$

where E_B is the energy barrier, d is the distance between the two energy states and $[\,\cdot\,]$ means "dimensions of". For our energy potential, d is equal to 2 and $E_B = \frac{3}{4}$.

The length scales defined in Eq. (A.1) are used to rescale the other parameters in our model. The most relevant ones are time, t, the coupling coefficient, γ, and temperature, T. Fixing the Boltzmann constant, k_B, to 1, gives the temperature rescaling $T_0 = E_0$. From dimensional analysis, one can obtain the time and coupling length scales

$$t_0 = d_0\sqrt{\frac{m_0}{E_0}}$$
$$\gamma_0 = \frac{1}{t_0} = \frac{1}{d_0}\sqrt{\frac{E_0}{m_0}} \tag{A.3}$$

with

$$\left[\frac{\gamma}{\gamma_0}\right] = \left[\frac{t}{t_0}\right] = 1, \tag{A.4}$$

where all of the numerical parameters are now in "dimensionless units". The time scaling parameter is calculated as $t_0 = 8.016 \times 10^{-2}$ ps and $\gamma_0 = 0.012$ Ps using the values given in Eq. (A.1). Planck's constant is also rescaled and is given by $\hbar = 0.123$ in dimensionless units.

Appendix B

Markovian Quantum Master Equation

The Markovian quantum master equation plays an integral role in the formulation of the Caldeira-Leggett model. In this section, we provide a short derivation with a justification of the most important approximations.

Considering an open quantum system, the system of interest A is weakly coupled to a reservoir B. The Hamiltonian of the system can be expressed as

$$H(t) = H_A + H_B + \hat{H}_I(t), \tag{B.1}$$

where H_A and H_B denote respectively the free Hamiltonian's of systems A and B, and $\hat{H}_I$ represents the interaction between the two systems.

The weak coupling approximation implies that the influence of the system on the reservoir is negligible. Mathematically, this means that the density matrix of B, ρ_B, is approximately time independent. Known as the Born approximation, the total density matrix, $\rho(t)$, can be written as

$$\rho(t) \approx \rho_A(t) \otimes \rho_B, \tag{B.2}$$

where $\rho_A(t)$ is the density matrix of system A. Using the formalism developed in Section 1.3.1, the total density matrix satisfies Eq. (1.28), which in integral form is given by

$$\rho_I(t) = \rho_I(0) - \frac{i}{\hbar} \int_0^t ds [H_I(s), \rho_I(s)]. \tag{B.3}$$

Substituting this expression back into Eq. (1.28), taking the trace over reservoir B and using the Born approximation yields

$$\frac{d}{dt}\rho_A(t) = -\frac{1}{\hbar^2} \int_0^t ds tr_B \{[H_I(t), [H_I(s), \rho_A(s) \otimes \rho_B]]\}, \tag{B.4}$$

where the subscript I for interaction picture on the density matrices was dropped. The above equation is still not Markovian. In the above formulation, the change in $\rho_A(t)$ is determined by its long-term past. A Markov process is a stochastic process characterised by a short-term memory meaning its future probabilities are determined only by its most recent value. Therefore on the right hand side, $\rho_A(s)$ has to be replaced by $\rho_A(t)$. The resulting equation will be local in time, but will still depend on the initial state. By substituting $H_I(s)$ with $H_I(t-s)$ and allowing the upper limit of the integral to go to infinity, $\rho(t)$ will be homogeneous. Physically this is justified if the characteristic time scales over which the system A correlation function decay are much larger than the characteristic time scale of the system B. Under these assumptions, we finally arrive at the Markovian quantum master equation

$$\frac{d}{dt}\rho_A(t) = -\frac{1}{\hbar^2} \int_0^\infty ds tr_B \{[H_I(t), [H_I(t-s), \rho_A(t) \otimes \rho_B]]\}. \tag{B.5}$$

Appendix C

Computational Implementation

The classical and quantum libraries of functions developed for this Master's project can be downloaded from the Github repository:
    https://github.com/kk2714/Masters_Project.git.

C.1 Quantum Harmonic Oscillator

The quantum harmonic oscillator basis results from solving the time independent Schrödinger equation with the following Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 = \hbar\omega\Big(a^\dagger a + \frac{1}{2}\Big), \tag{C.1}$$

where p and q are the position and momentum operators respectively and $a^\dagger$ and a are raising and lowering operators respectively. The mass of the quantum particle is denoted by m and ω is the angular frequency. The energy eigenstates are given by

$$\langle q|n\rangle = \frac{1}{\sqrt{2^n n!}}(\frac{m\omega}{\pi\hbar})^{\frac{1}{4}} \exp\Big\{-\frac{m\omega q^2}{2\hbar}\Big\} H_n(\sqrt{\frac{m\omega}{\hbar}}q), \tag{C.2}$$

where n is an integer, $n \in \mathbb{N}_0$, and $H_n(\cdot)$ denotes the Hermite polynomials

$$H_n(z) = (-1)^n e^{z^2}\frac{d^n}{dz^n}(e^{z^2}). \tag{C.3}$$

The raising and lowering operators, $a^\dagger$ and a respectively, in the position and momentum representation are given by

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(q + \frac{i}{m\omega}p)$$
$$a = \sqrt{\frac{m\omega}{2\hbar}}(q - \frac{i}{m\omega}p) \tag{C.4}$$

with the following properties when operating on energy eigenstates, $|n\rangle$,

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$$
$$a\,|n\rangle = \sqrt{n}\,|n-1\rangle . \tag{C.5}$$

Using the quantum harmonic oscillator basis, we can define the coherent state. The coherent state, $|z\rangle$, is defined as the eigenstate of the following equation

$$a\,|z\rangle = z\,|z\rangle , \tag{C.6}$$

where a is the lowering operator and z is the eigenvalue with $z \in \mathbb{C}$. In the harmonic oscillator basis, the solution of this eigenvalue problem is

$$|z\rangle = e^{-\frac{|z|^2}{2}} \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}} |n\rangle, \tag{C.7}$$

where z is given by

$$z = \sqrt{\frac{m\omega}{2\hbar}}\langle q \rangle + i \frac{1}{\sqrt{2m\omega\hbar}}\langle p \rangle, \tag{C.8}$$

where $\langle \cdot \rangle$ denotes the expectation value. The coherent state plays an important role in quantum dynamics due to it being the minimum uncertainty state.

The quantum harmonic oscillator basis is a natural choice for computational implementation. The energy eigenstates form an orthogonal basis allowing calculations to be carried out in matrix form. An N-dimensional Hilbert space is composed of the eigenstates of the harmonic oscillator, $\{|0\rangle, |1\rangle ... , |N\rangle\}$. For example in this basis, the coherent state would be defined as a matrix in the following way

$$|\psi\rangle = e^{-\frac{|z|^2}{2}} \begin{pmatrix} \frac{z^0}{\sqrt{0!}} \\ \frac{z^1}{\sqrt{1!}} \\ ... \\ \frac{z^N}{\sqrt{N!}} \end{pmatrix} \tag{C.9}$$

with z being chosen based on the initial conditions (q_0, p_0) for the expectation values. Operators are expressed using the lowering and raising operators, a and $a^\dagger$, respectively. These can be easily defined in matrix notation using Eq. (C.5).

The size of the N-dimensional Hilbert space depends on the problem being solved. For the Caldeira-Leggett model, this will depend on the values of T and η. The basis needs to be large enough for lower energy eigenstates of the system to converge both in terms of eigenvalues and matrix elements. For the toy model, it was found that $N = 80$ was an appropriate choice both in terms of CPU and accuracy.

C.2   Numerical Methods

In this section, several numerical schemes will be introduced for modelling the stochastic Schrödinger equation. As quantitative comparisons can be frequently found in literature, e.g. [25], here we will only give a short qualitative comparison between the different schemes in terms of CPU time and accuracy.

The stochastic Schrödinger equation can be re-written in Itô form as

$$|d\psi\rangle = \mu(\psi(t))dt + \sigma(\psi(t))dW_t, \tag{C.10}$$

where we have introduced the diffusion, $\mu(\psi(t))$, and drift, $\sigma(\psi(t))$ terms in the following way

$$\mu(\psi(t)) = -\frac{i}{\hbar}H|\psi\rangle + (\langle L^\dagger \rangle L - \frac{1}{2}L^\dagger L - \frac{1}{2}\langle L^\dagger \rangle\langle L \rangle)|\psi\rangle$$
$$\sigma(\psi(t)) = (L - \langle L \rangle)|\psi\rangle. \tag{C.11}$$

The operators H and L are defined in the following way

$$H = \frac{p^2}{2m} + V(q) + \frac{\gamma}{2}\{p, q\}$$
$$L = \frac{\sqrt{4m\gamma k_b T}}{\hbar}q + i\sqrt{\frac{\gamma}{4mk_b T}}p. \tag{C.12}$$

Using Eq. C.10, we will define the Euler scheme, Heun scheme, fourth-order Runge-Kutta scheme and the Platen scheme used to model Eq. C.10 computationally.

C.2.1 Euler Scheme

The Euler scheme is defined in a similar way as for integration of ordinary differential equations. The scheme is given by

$$\psi_{k+1} = \psi_k + \mu(\psi_k)\Delta t + \sigma(\psi_k)\sqrt{\Delta t}\xi_k, \tag{C.13}$$

where ξ_k are independent Gaussian distributed random variables with mean zero and variance one. The main advantages of using an Euler scheme are easy implementation and reasonable degree of approximation. The Euler scheme is a weak scheme of order 1.

C.2.2 Heun Scheme

The Heun scheme can be seen as an extension of the Euler scheme and is known as a predictor-corrector method. In this scheme, an intermediate step is used to correct overestimating and underestimating the next value. The scheme can be written as

$$\psi_{k+1} = \psi_k + \frac{1}{2}(\mu(\psi_k) + \mu(\tilde{\psi}_k))\Delta t + \sigma(\psi_k)\sqrt{\Delta t}\xi_k \tag{C.14}$$

with

$$\tilde{\psi}_k = \psi_k + \mu(\psi_k)\Delta t + \sigma(\psi_k)\sqrt{\Delta t}\xi_k, \tag{C.15}$$

where ξ_k are independent Gaussian distributed random variables with mean zero and variance one. For ordinary differential equations, the scheme is of weak order 2. Due to the stochasticity, for the stochastic Schrödinger equation this scheme has weak order convergence of 1. Unless the drift term is much greater than the diffusion term, this scheme does not offer any benefits over the Euler scheme. In fact, it is more CPU intensive.

C.2.3 Fourth-order Runge-Kutta Scheme

The fourth order Runge-Kutta scheme can be seen as an extension of the Euler scheme and it involves four additional intermediate steps to avoid overestimating and underestimating. The scheme can be written as

$$\psi_{k+1} = \psi_k + \frac{1}{6}(\psi_k^1 + \psi_k^2 + \psi_k^3 + \psi_k^4)\Delta t + \sigma(\psi_k)\sqrt{\Delta t}\xi_k \tag{C.16}$$

with

$$
\begin{aligned}
\psi_k^1 &= \mu(\psi_k) \\
\psi_k^2 &= \mu(\psi_k + \frac{1}{2}\Delta t\psi_k^1) \\
\psi_k^3 &= \mu(\psi_k + \frac{1}{2}\Delta t\psi_k^2) \\
\psi_k^4 &= \mu(\psi_k + \Delta t\psi_k^3),
\end{aligned}
\tag{C.17}
$$

where ξ_k are independent Gaussian distributed random variables with mean zero and variance one. For ordinary differential equations, the scheme is of weak order 4. Due to the Brownian motion, for the stochastic Schrödinger equation this scheme has weak order convergence of 1. Similarly to the Heun scheme, unless the drift term is much greater than the diffusion term, this scheme does not offer any benefits over the Euler scheme. In fact, it is even more CPU intensive than the Heun scheme.

C.2.4   Platen Scheme

In 1992, Platen proposed a numerical scheme with weak order of convergence equal to 2 for modelling the stochastic Schrödinger equation [26]. The scheme can be written as

$$
\begin{aligned}
\psi_{k+1} = \psi_k &+ \frac{1}{2}(\mu(\tilde{\psi}_k) + \mu(\psi_k)\Delta t \\
&+ \frac{1}{4}(\sigma(\psi_k^+) + \sigma(\psi_k^-) + 2\sigma(\psi_k))\sqrt{\Delta t}\xi_k \\
&+ \frac{1}{4}(\sigma(\psi_k^+) - \sigma(\psi_k^-))(\xi_k^2 - 1)\sqrt{\Delta t}
\end{aligned}
\tag{C.18}
$$

with

$$
\begin{aligned}
\tilde{\psi}_k &= \psi_k + \mu(\psi_k)\Delta t + \sigma(\psi_k)\sqrt{\Delta t}\xi_k \\
\psi_k^\pm &= \psi_k + \mu(\psi_k)\Delta t \pm \sigma(\psi_k)\sqrt{\Delta t},
\end{aligned}
\tag{C.19}
$$

where ξ_k are independent Gaussian distributed random variables with mean zero and variance one. Therefore the Platen scheme offers large benefits in terms of accuracy, but it is more intensive in terms of CPU compared to the Euler and Heun schemes. In situations, where the diffusion term is of the order of or greater than the drift term, the Platen scheme should be used.

Appendix D

Explicit Solution of Lindblad Equation: Superoperator Method

As the Hamiltonian and Lindblad are both time independent operators, we can solve the following Liouville-Neumann equation

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[H,\rho] + L\rho L^{\dagger} - \frac{1}{2}\rho L^{\dagger}L - \frac{1}{2}L^{\dagger}L\rho \tag{D.1}$$

explicitly by working in the Liouville space, $\mathcal{L}_{N\times N}$. The Liouville space is an $N\times N$ dimensional space formed by the Kronecker product of the N-dimensional Hilbert space with itself. By mapping operators from the original Hilbert space onto the Liouville space, $\mathcal{H}_{\mathcal{N}} \mapsto \mathcal{L}_{N\times N}$, we are able to obtain an explicit solution to the problem, which can be implemented computationally.

Components of the Hilbert space can be transformed into the Liouville space in the following way

$$
\begin{aligned}
\mathcal{H}_{\mathcal{N}} &\mapsto \mathcal{L}_{N\times N} \\
|i\rangle\langle j| &\mapsto |i\rangle \otimes |j\rangle \\
\rho = \sum_{i,j} \rho_{ij} |i\rangle\langle j| &\mapsto \sum_{i,j} \rho_{ij} |i\rangle \otimes |j\rangle \\
A|i\rangle\langle j| &\mapsto (A \otimes \mathbb{1})|i\rangle \otimes |j\rangle \\
|i\rangle\langle j|A &\mapsto (\mathbb{1} \otimes A^T)|i\rangle \otimes |j\rangle,
\end{aligned}
\tag{D.2}
$$

where $|i\rangle,|j\rangle$ are orthogonal basis functions belonging to the Hilbert space, $\mathbb{1}$ is the identity operator in the Hilbert space, A is an arbitrary operator in the Hilbert space and $\otimes$ denotes the Kronecker product. To simplify the notation, we can define the following superoperators in the Liouville space

$$
\begin{aligned}
\mathbb{L}(A) &= A \otimes \mathbb{1} \\
\mathbb{R}(A) &= \mathbb{1} \otimes A^T
\end{aligned}
\tag{D.3}
$$

to denote operators acting from the left and right, respectively. Furthermore, in the Liouville space, we have the commutation relation $\mathbb{L}(A)\mathbb{R}(A) = \mathbb{R}(A)\mathbb{L}(A)$.

In order to solve the Lindblad equation from the Caldeirra-Leggett model, we can map it into the Liouville space. The Liouville operator can be decomposed in the following way

$$\mathcal{L} = \mathcal{H} + \mathcal{G}, \tag{D.4}$$

where

$$\mathcal{H} = -\frac{i}{\hbar}(\mathbb{L}(H) - \mathbb{R}(H)), \tag{D.5}$$

and

$$\mathcal{G} = \mathbb{L}(L)\mathbb{R}(L^{\dagger}) - \frac{1}{2}\mathbb{R}(L^{\dagger}L) - \frac{1}{2}\mathbb{L}(L^{\dagger}L). \tag{D.6}$$

The solution to the Liouville-Neumann equation becomes

$$col(\rho_S(t)) = e^{\mathcal{L}t}col(\rho_S(0)), \qquad (D.7)$$

where $\mathcal{L}$ is an $N \times N$ matrix and $col(\rho)$ denotes the result of stacking the columns of the corresponding density matrix, ρ, in left-to-right order on top of one another to get a single column vector of dimension N^2 in the Liouville space. It is worth noting, that this is the exact solution to the problem and can be transformed back into the original Hilbert space.

Appendix E

Husimi Representation Algorithm

The Husimi representation can be used to generate the quasiprobability distribution in the phase-space [24]. In this section, we describe the numerical implementation of this technique rather than its theoretical foundations, which can be found in any standard quantum mechanics textbook.

The algorithm can be defined in the following way:

1. Prepare the wave function, $|\psi\rangle$, whose probability distribution we are interested in.

2. Define the partitioned phase-space (q, p).

3. Define the partitioned phase-space (q', p'). For this partitioning the Δq and Δp spacing can be larger than in the first case. This partitioning will determine the positioning of the coherent states acting as the basis.

4. Generate the set of coherent states, $|\alpha_k\rangle$, with initial conditions corresponding to $(q_i, p_j) \in (q', p')$. The sets of expectation values and variances of position and momentum coordinates should also be stored, i.e. $\{\overline{q_k}\}$, $\{\overline{p_k}\}$, $\{\sigma_{q_k}\}$, $\{\sigma_{p_k}\}$.

5. Compute the following quantities: $\beta_i = |\langle \alpha_i | \psi \rangle|^2$. Renormalise such that $\sum \beta_i = 1$.

6. For each $(q_i, p_j) \in (q, p)$ compute the following quantity:
$P(q_i, p_j) = \sum_k \beta_k P_{\alpha_k}(q_i, p_j) = \sum_k \beta_k \frac{1}{\sigma_{p_k} \sigma_{q_k}} \exp\left\{-\frac{(q_i - \overline{q_k})^2}{2\sigma_{q_k}^2}\right\} \exp\left\{-\frac{(p_j - \overline{p_k})^2}{2\sigma_{p_k}^2}\right\}$

7. Renormalise such that $\sum_{ij} P(q_i, p_j) = 1$. This is the quasi phase-space distribution.

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