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Numerical Simulation of Quantum Spins in a Dissipative Environment

by

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As the candidate's supervisor I have approved this dissertation for submission.

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Signed: . . . . Name: Prof F. Petruccione(co-supervisor) Date: . . . .

Abstract

When modelling real physical systems, one should always consider the influence of the environment. The study of open quantum systems aims precisely at the assessment of the role of the environment in the evolution of these systems. The computational study of these systems is in general a formidable task. However, in many instances one can approximate the environment by means of classical dynamics. For such cases, when the environment is in a thermal state, one can generalize non-Hamiltonian equations of motion to quantum-classical dynamics in order to control the thermodynamic temperature. Such a generalization is achieved within the partial Wigner representation of quantum mechanics, and leads to a quantum-classical evolution of the system. We have studied how to simulate a thermal bath, by means of the least possible number of additional extended variables [1]. This has been achieved upon reformulating the Nosé-Hoover Power (NHP) thermostat in quantum-classical theory. When applied to the dissipative evolution of a quantum spin the NHP thermostat, obtained numerical results in agreement with those obtained using Nosè-Hoover chains. However, since a fewer number of variables are needed to achieve the correct sampling of the canonical distribution at equilibrium, the NHP thermostat promises to be better suited for the simulation of low dimensional open quantum system on discrete grids. Following this the quantum dynamics of a XXZ two-spin chain interacting with multiple bosonic baths have been studied, within the mixed Wigner-Heisenberg representation of quantum mechanics. In particular, we have simulated the dynamics of the reduced density matrix $\rho_{\mathrm{s}}(t)$, along with the time evolution of the quantum entanglement of the two spins via the concurrence $\mathcal{C}\left(\rho\right)$.

Declaration

I, Nkosinathi B. Dlamini, declare that

(i) The research reported in this thesis, except where otherwise indicated, is my original research.

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Publications

Details of contribution to publications that form part and/or include research presented in this thesis:

1. N. Dlamini and A. Sergi, "Quantum Dynamics in Classical Thermal Baths"

   Status: Published in *Computer Physics Communication* (2013).

   Computational work performed by N. Dlamini, paper written by A. Sergi and N. Dlamini.

2. N. Dlamini and A. Sergi, "Entanglement dynamics of a two-spin chain with a time dependent thermal gradient "

   Status: Draft in preparation.

   Computational work performed by N. Dlamini, paper written by A. Sergi and N. Dlamini.

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Conferences and Presentations

Details of the conferences attended while a PhD student and presentations given that include research presented in this thesis:

Conferences and Workshops attended:

- ”Non-equilibrium physics of driven-dissipative many-body systems”, Palm Dune, KZN, 21-25 September 2015
- ”Phase space description of quantum systems”, UKZN-Westville, 5th, 9th, 12th, 19th June 2015
- ”Superconducting Qubits”, UKZN-Westville, 13-17 July 2015
- ”Mini-workshop on Quantum Dynamics and Non-Hermitian Hamiltonians”, UKZN - Pietermaritzburg, 3 - 8 December 2014.
- ”Quantum Simulation and Quantum Walks 2014”, Pumula Beach Hotel, South Coast, KZN, 24 - 28 November 2014.
- ”Quantum Information Processing, Communication and Control 2014”, Alpine Heath, Drakensberg, KZN, 3 - 7 November 2014.
- ”Quantum Information Processing, Communication and Control 2”, Pumula Beach Hotel, South Coast, KZN, 25 - 29 November 2013.”

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Presentations delivered:

- **Title**: Simulating quantum dynamics in classical thermal baths

  Date: 21 November 2013

  Venue: NITheP, University of Stellenbosch, South Africa

- **Title**: Simulating quantum dynamics in classical thermal baths

  Date: 27 November 2013

  Venue: Pumula Beach Hotel, South Coast, KZN

- **Title**: Thermodynamic driving of a quantum two-spin chain in contact with independent thermal baths

  Date: 21 November 2014

  Venue: NITheP, University of Stellenbosch, South Africa

- **Title**: Quantum dynamics of a two-spin chain in bosonic thermal baths

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Contents

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Chapter 1

Introduction

There exists a symbiotic relationship between theoretical and experimental physics. Theoretical physics is based upon mathematical models which are used not only to explain, but also predict natural phenomena. While experimental physics is based upon the use of experimental tools to predict and explain these natural phenomena. Computational physics lies somewhere in between these two approaches and provides a way to perform numerical "experiments" on a computer. Once a particular model has been numerically solved, a comparison may then be made between the experimentally obtained results and those of the numerical simulation. If the predictions of the model agree well with the experimental observations then the model may possibly be used to give new insight into these observations [2]. The relationship which exists between theoretical, experimental and computational physics is illustrated in Fig. 1.1.

In classical physics, Molecular Dynamics (MD) simulation is used to study the dynamics of molecules or atoms from a classical perspective [2, 3]. However, there is no corresponding general method for simulating the quantum dynamics of many body systems [2, 4]. While almost all classical systems can be solved using MD, it fails to successfully simulate systems where quantum effects are important, due to its intrinsically classical treatment of particles. Instead, numerical methods for solving quantum dynamics have to be decided on a system by system basis. This is a consequence of quantum mechanics itself being difficult to implement on a computer due to its complex mathe-

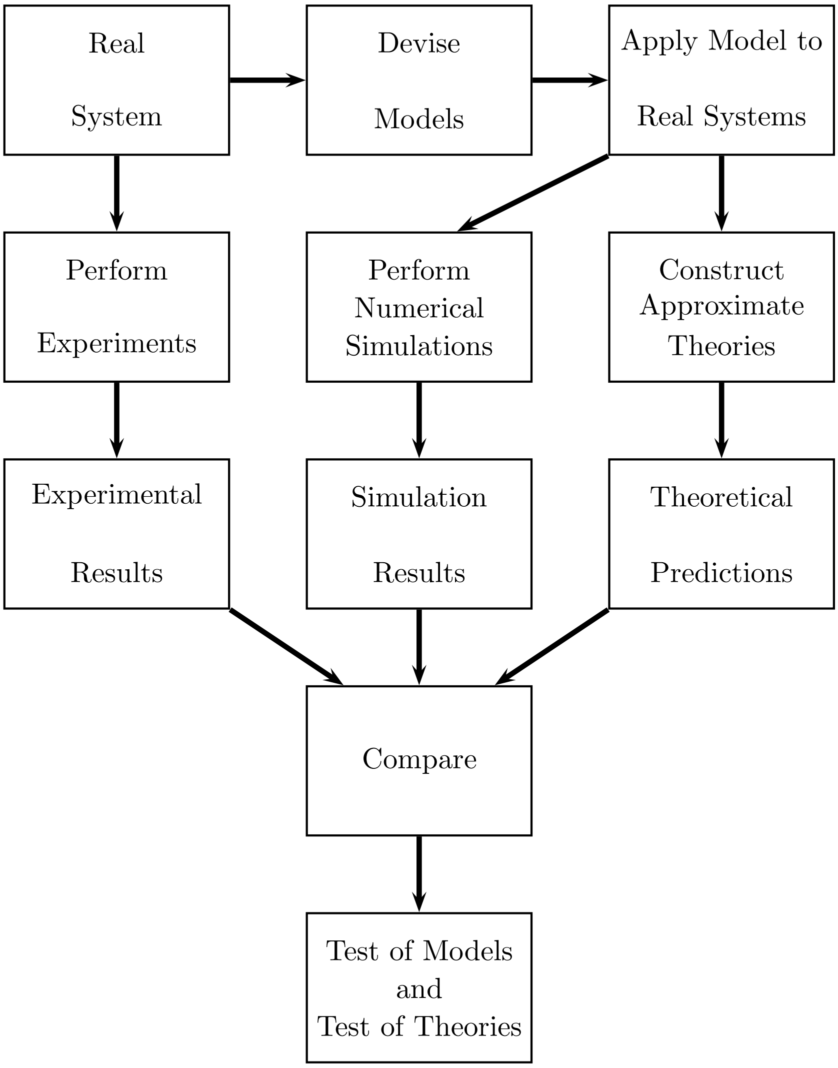

Figure 1.1: Flow chart illustrating the connection between experiment, theory, and computer simulations [2]. The left hand side represents experimental procedure, while the centre branch deals with the processes of computational physics. The right hand outlines the work flow of theoretical physics.

matical nature. This difficulty arises since quantum mechanics is formulated not in terms of functions, as in the case of classical mechanics, but rather in terms of operators which do not necessarily commute [5]. A second reason is that the computational expense rises extremely rapidly with an increase in the number of particles being simulated. As stated in Ref. [5], it is impossible to either store nor calculate the many body wave-function with the numerical precision required, due to the limitations on the available resources. As a result of this severe limitation on the simulation of quantum dynamics, one is forced to resort to clever approximations to simplify the system of study in some way. The development of efficient algorithms for the simulation of quantum dynamics currently forms a large area of research within the field of computational physics.

In using quantum mechanics to describe real physical systems, one should always take into account the influence of the surroundings upon the system. Such systems, where there is an interaction between the quantum system and its environment are known as open quantum systems. These systems are not only of theoretical interest, but also of great practical interest in various research fields, including those of quantum biology [6, 7], quantum optics [8, 9], nano physics [10] and quantum information [11, 12]. The dynamics of these quantum systems are usually formulated by means of influence functionals [13] or master equations [4]. Alternatively, a Hamiltonian approach [14] may be used which requires one to embed the system of interest in a bath comprising a large number of degrees of freedom to calculate the evolution of the total system. To obtain an open system description, the coordinates of the bath are then integrated out. The numerical implementation of this latter technique is generally also computationally expensive. A classical bath can also be considered in order to generate the open dynamics of a quantum subsystem. In this case, it has been recently shown how to formulate master equations which are thermodynamically consistent [15–20]. Within the Hamiltonian approach to dissipation [14], one can obtain a phase-space representation of the quantum bath by performing a partial Wigner transform only over the coordinates coupled to the quantum subsystem [21]. Upon taking a suitable approximation, a combined quantum-classical law of motion for the quantum subsystem coupled to the bath coordinates is obtained [22]. This representation still requires one to calculate the dynamics of the total system and it is also computationally demanding. However, once the classical bath coordinates are represented in phase space through a partial Wigner transform, well established non-Hamiltonian molecular dynamics equations of motion [23–25] become available to represent the thermal bath by means of a minimal number of degrees of freedom. Hence, one can use a non-Hamiltonian bath with few degrees of freedom to numerically simulate on the computer a Hamiltonian bath with many degrees of freedom. This approach has been suggested in Refs. [26, 27].

With this in mind, the first project discussed in this thesis deals with using the so called Nosè-Hoover Power (NHP) thermostat [23]. This thermostat is defined by a set of equations of motion that, using only two additional phase space variables, are able to provide a correct sampling of the canonical distribution function for stiff systems. The Nosè-Hoover Chain (NHC) thermostat [28] is also able to produce chaotic dynamics but it requires at least four additional thermostat variables in phase space, and so does the Bulgac-Kusnezov (BK) thermostat [29–31]. Our final aim is to implement non-Hamiltonian thermostats in quantum-classical dynamics. The NHP thermostat has the nice feature of generating a thermal bath by means of the smallest possible number of degrees of freedom [1]. Because of this, it was chosen to be generalized to the quantum-classical case and applied to study the relaxation dynamics of an excited spin situated in a classical-like thermal bath

Having completed this, a second study was undertaken where the dynamics of a simple spin chain comprising two spins each coupled to independent bosonic baths at various temperatures was studied. The system was constructed in such a way that the temperature of each bath may be defined independently. Doing this allows one to study non-equilibrium situations. Systems of this nature are of great interest within the field of quantum information [32–34]. Rather than using the master equation approach [34] to simulate the dynamics of this system, a mixed Wigner-Heisenberg representation of the dynamics has been used. The evolution in time of the system's reduced density matrix, along with the entanglement dynamics of the minimal chain have been calculated. It should be noted that the total system dynamics are unitary and numerically exact for the class of Hamiltonian under study. As such, for the work presented here there is no need for one to make use of either the Markovian or rotating wave approximation.

This thesis is structured as follows: In Chapter 2 a discussion on classical dynamics and its underlying mathematical structure is presented. In particular Hamiltonian, and non-Hamiltonian theories are introduced before the general algebraic bracket structure underlying the dynamics is introduced. Finally in this chapter, constant temperature dynamics are discussed along with the introduction of some non-Hamiltonian thermostatting schemes. In Chapter 3 a brief overview of quantum dynamics is presented, beginning with a general summary of quantum statistical mechanics. This is followed by a summary of the quantum dynamics of both closed and open quantum systems. During the latter, the phase-space formulation of quantum mechanics is introduced and discussed. This chapter ends with a discussion on correlations and entanglement. In Chapter 4 a discussion on how to model and numerically simulate the quantum dynamics of systems situated in classical-like thermal baths is presented. Following this, the adiabatic basis is introduced along with a discussion on how to numerically implement the dynamics via surface-hopping algorithms. Two thermostatting schemes are then extended to the quantum-classical case, and applied to the study of the spin boson model. In Chapter 5 the numerical study of a two-spin chain, where each spin is coupled to its own independent thermal bath is presented. In particular, the reduced density matrix and entanglement dynamics are studied with the latter done via the concurrence. In Chapter 6 a summary of the work done in this thesis is given along with some conclusions and perspectives regarding possible future studies.

Chapter 2

Classical Dynamics

This chapter contains a discussion on classical dynamics and its underlying mathematical structure. It begins with the introduction of Hamiltonian and non-Hamiltonian theories. This is followed by an illustration of the general algebraic bracket structure which underlies non-Hamiltonian dynamics. Finally, three extended system thermostat schemes are introduced and discussed.

2.1 Hamiltonian Theory

For the work presented in this chapter a brief sketch of what defines a Hamiltonian algebra is presented. Such algebras are also commonly referred to as Lie algebras [3]. Following the prescription outlined in Ref. [5], it will be shown how through the relaxation of only one of the conditions defining these algebras it becomes possible to generalise them and obtain non-Hamiltonian algebras. To this end one begins by considering an arbitrary mathematical space $\mathcal{G}$ comprised of mathematical objects $(u, v, w, \cdots)$. These objects may in general represent functions of phase-space, in which case the algebra in question is defined in terms of Poison brackets, or they may represent Hermitian quantum operators. For the latter case the algebra is then defined in terms of the commutator. An algebraic closed operation may be defined on pairs of these elements, in terms of a generic bracket as [5]:

$$\{u, v\} = w \ , \tag{2.1}$$

where w belongs to $\mathcal{G}$ for any arbitrary u and v. A Lie algebra for such a mathematical space is then one which has the following properties [3]:

$$\{u, v\} = -\{v, u\} \, , \tag{2.2}$$

$$\{u + v, w\} = \{u, w\} + \{v, w\} \, , \tag{2.3}$$

$$\{\lambda u, v\} = \lambda \{u, v\} \, , \tag{2.4}$$

where λ is a complex number which does not belong to the space $\mathcal{G}$. In order for an algebra to be considered a Lie algebra there is a further, less obvious property which needs to be satisfied. This property is known as the Jacobi relation and is given by

$$\mathcal{J} = \{u, \{v, w\}\} + \{v, \{w, u\}\} + \{w, \{u, v\}\} = 0 \ . \tag{2.5}$$

In Eqns. (2.1) to (2.5), $\{\cdots, \cdots\}$ has been used to denote a generic bracket whose algebra one is interested in. This bracket may either be classical or quantum in its nature, since there is a similarity which exists within the underlying mathematical structure of the bracket formulation of both classical and quantum mechanics [35]. Classical theory may be defined through the use of the Poisson bracket, while quantum theory is defined through the use of the commutator. In order for any bracket algebra to be considered Hamiltonian, it must satisfy all four of these properties; in other words, it must be a Lie algebra. The antisymmetric nature of the generic bracket shown by Eqn. (2.2) plays a role in defining its time evolution (see Appendix A.1), while Eqns. (2.3) and (2.4) show that such a bracket is a linear operator with respect to complex numbers, λ, along with other elements of its own mathematical space respectively. If the elements of the mathematical space are time independent, then any bracket composed of these conserved elements will be conserved.

Consider an element of the space, H, where H is usually taken to be the Hamiltonian. Then the equations of motion may be defined as [5]

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \{u, H\} \, . \tag{2.6}$$

Due to the antisymmetric nature of the bracket, it can easily be shown that Eqn. (2.6) has the implication that H is a constant of motion [3]. Similarly, if one considers two different elements u and v of a mathematical space, whose bracket algebra is Hamiltonian, then these two elements will also be constants of motion provided that their equations of motion satisfy the following,

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \{u, H\} = 0 \;, \qquad \frac{\mathrm{d}v}{\mathrm{d}t} = \{v, H\} = 0 \;. \tag{2.7}$$

A bracket of these two elements, $\{u, v\}$ is then also a constant of motion [3]:

$$\{\{u, v\}\,, H\} = 0 \;. \tag{2.8}$$

This is implied by Eqn. (2.7), provided that the theory is invariant under time translation. Since Hamiltonian algebras obey Eqn. (2.5), they are invariant under time translation. A full derivation of the time invariance property for such algebras may be found in Appendix A.1.

2.2 Non-Hamiltonian Theory

A non-Hamiltonian theory is one which satisfies the properties illustrated by Eqns. (2.2) to (2.4), but does not satisfy the Jacobi relation, namely,

$$\mathcal{J} = \{u, \{v, w\}\} + \{v, \{w, u\}\} + \{w, \{u, v\}\} \neq 0 \;. \tag{2.9}$$

As shown in Appendix A.1, this violation results in the algebra associated with such brackets no longer having the property of being invariant under time translation. This often leads to problems when one is interested in studying the non-equilibrium statistical mechanics of a Hamiltonian system. One may be inclined to ask why one would want to use theories of this type if this is the case. It turns out that the advantages of using a non-Hamiltonian approach only start to become apparent when one looks at systems which contain many degrees of freedom. Such a situation may arise, for example, if one wishes to simulate the dynamics of some system of interest interacting with its environment, where the role of the environment is to constrain the system's temperature. To successfully perform such a task using Hamiltonian theories, one would require an infinite number of degrees of freedom. However it is not possible to perform such a calculation, even classically, due to the lack of computational resources [5]. A consequence of this is that the results of calculations performed at constant energy, will differ from those performed at constant temperature,for Hamiltonian dynamics [36]. However, if one makes use of non-Hamiltonian theories, it becomes possible to simulate an infinite thermal bath through the use of only a few degrees of freedom and achieve the desired result [35].

Another example where non-Hamiltonian theory plays a crucial role is in the simulation of quantum systems, where it is virtually impossible to perform a full quantum mechanical simulation of a many body interacting system on a computer. The difficulty in this case arises from computational limitations in terms of storing all the information contained within the system [5]. However, through the use of a non-Hamiltonian approach, it is possible to perform such simulations in the limit of certain approximations [37–40].

2.3 General Bracket Formulation of Dynamics

In the previous sections, both Hamiltonian and non-Hamiltonian theories have been defined. In this section the generalised formalism which is used to express the equations of motion in phase space is introduced. These equations conserve some chosen time-independent Hamiltonian, H. To introduce this bracket formulation, one begins by introducing an antisymmetric matrix

$$\mathcal{B}_{jk} = -\mathcal{B}_{kj} \qquad j,k = 1, 2N \ ,$$

where $2N$ represents the dimension of the phase space. This matrix is responsible for the interaction which occurs between the system and environmental degrees of freedom. The generalised non-Hamiltonian bracket may then be defined as [41]

$$\{a,b\}_{\mathcal{B}} = \sum_{j,k=1}^{2N} \frac{\partial a}{\partial X_j} \mathcal{B}_{jk} \frac{\partial b}{\partial X_k} \ , \tag{2.10}$$

where $X = (R_1, R_2, \cdots, R_N, P_1, P_2, \cdots, P_N)$ represents the phase-space point, and a and b represent two phase-space functions. This allows one to express the equations of motion for the entire system as

$$\dot{X} = \{X, H\}_{\mathcal{B}} = \sum_{jk} \frac{\partial X}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \ , \tag{2.11}$$

while those of the components of X, may be expressed as

$$\dot{X}_j = \sum_k \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \ , \tag{2.12}$$

where $X_j = (R_j, P_j)$. If the antisymmetric matrix is given by

$$\mathcal{B}^c = \left(\begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \right) \ , \tag{2.13}$$

then Eqn. (2.11) simply produces the canonical equations of motion for a Hamiltonian system. These equations correspond to a canonical transformation of X [3]. However, if a non canonical transformation is applied to X, then the form of the equations of motion is still conserved, while the elements of the matrix $\mathcal{B}$ are then defined in terms of complex phase-space functions. In this case, the matrix $\mathcal{B}$ loses its canonical form, but remains antisymmetric [1]. A consequence of this antisymmetry is that any phase-space flow which is defined by Eqn. (2.11) for a time independent Hamiltonian will be a constant of motion [41]. This can easily be verified by taking the total time derivative of H,

$$\begin{aligned} \frac{\mathrm{d}H}{\mathrm{d}t} &= \{H, H\}_{\mathcal{B}} \\ &= \sum_{jk} \frac{\partial H}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \\ &= 0 \ . \end{aligned} \tag{2.14}$$

The derivative is equal to zero since it is equivalent to taking the trace of the product of the antisymmetric matrix $\mathcal{B}_{jk}$ with the symmetric one $\partial H/\partial X_j \partial H/\partial X_k$. If $\mathcal{B}$ is antisymmetric then Eqn. (2.14) is always valid. This means that if one wishes to define a non-Hamiltonian flow which possesses a conserved energy, then one need only require that some general matrix $\mathcal{B}$ be antisymmetric [1]. This approach has been used as a way to define conservative non-Hamiltonian phase-space flows [1, 41].

The flux in phase space will be Hamiltonian if $\mathcal{B}$ has the property

$$\sum_{n=1}^{2N} \mathcal{B}_{in} \frac{\partial \mathcal{B}_{jk}}{\partial X_n} + \mathcal{B}_{kn} \frac{\partial \mathcal{B}_{ij}}{\partial X_n} + \mathcal{B}_{jn} \frac{\partial \mathcal{B}_{ki}}{\partial X_n} = 0 \ , \tag{2.15}$$

for any given choice of i, j and k [1, 42]. Moreover, if $\mathcal{B}$ is antisymmetric and Eqn. (2.15) holds, then Eqn. (2.11) produces non-canonical Hamiltonian flows in phase space [42, 43]. However, if Eqn. (2.15) does not hold, then the phase-space flow described by Eqn. (2.11) produces non-Hamiltonian phase-space-flows [1]. If the flows are non-Hamiltonian, then one may define the phase-space compressibility as [44]

$$\begin{aligned}\kappa &= \nabla \dot{X} \\ &= \sum_j \sum_k \frac{\partial}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \ .\end{aligned} \tag{2.16}$$

In general this will be non-zero for non-Hamiltonian dynamics, although there are a few exceptions [45]. A consequence of the compressibility being non-zero is that the phase-space measure, $\mathrm{d}X$, is no longer invariant [46]. To see this, one needs to consider the Jacobian of the transformation, from some initial phase space point, X_0, to a time evolved point, X_t, given by [44]

$$J\left(X_t; X_0\right) = \frac{\partial X_t}{\partial X_0} \ . \tag{2.17}$$

The Jacobian of the transformation, $J\left(X_t; X_0\right)$ satisfies the evolution equation [46]

$$\frac{\mathrm{d}}{\mathrm{d}t} J\left(X_t; X_0\right) = \kappa \ J\left(X_t; X_0\right) \ , \tag{2.18}$$

with the initial condition that $J(0) = 1$. Considering this equation of motion, it is clear that $J = 1$ for all time, if and only if $\kappa = 0$. Therefore, if the system compressibility is non-zero, the corresponding Jacobian of transformation will not be unity. Rearranging Eqn. (2.17) allows one to express the measure transformation as

$$\mathrm{d}X_t = J\left(X_t; X_0\right) \ \mathrm{d}X_0 \ , \tag{2.19}$$

clearly if $J \neq 1$, then $\mathrm{d}X_t \neq \mathrm{d}X_0$, meaning that the measure is not preserved. A consequence of the phase space measure not being conserved is that the dynamics no longer sample phase space uniformly. However, there are several ways to overcome this. One way is to make use of the fact that one is free to choose the form of both H and $\mathcal{B}$ independently, when setting up the systems equations of motion. Doing this makes it possible to obtain a desired compressibility. This is achieved through the freedom one has in defining the antisymmetric matrix $\mathcal{B}$ [1]. This is equivalent to essentially designing conservative non-Hamiltonian equations of motion. Such equations possess a controlled statistical weighting of the phase space, which assists them in sampling the phase space uniformly [1, 47].

2.4 Constant Temperature Dynamics

Real life experiments are often performed in a controlled environment under isothermal conditions [5]. These conditions usually fall under the canonical ensemble. Within this ensemble the number of particles (N), the volume (V) and system temperature (T) are kept constant. The system itself is not isolated, and is allowed to exchange energy with a heat bath. However the total energy of the bath and system is fixed, while the absolute temperature T, is defined by the heat bath. As stated previously, through the use of non-Hamiltonian dynamics, it becomes possible to mimic, for the purpose of simulation, an infinite thermal bath on the computer through the use of only a few degrees of freedom [35, 37–40].

There are several different methods which may be used to control the temperature of the system during the simulation of its dynamics. A particularly important method is the method of extended systems. Within this method, additional degrees of freedom are added to the system Hamiltonian. Schemes which follow this method are typically known as thermostat schemes. For the work presented here, we will be focusing on the Nosé-Hoover Chain and Nosé-Hoover Power thermostat schemes. An overview of these schemes is given in the following sections. The Nosé-Hoover thermostat has been included for the sake of completeness, and is the starting point of this overview.

2.4.1 Nosé-Hoover Thermostat

The Nosé-Hoover (NH) thermostat was first introduced by S. Nosé in 1984 [48–50]. An equivalent way to present it may be found in [1], where its extended system Hamiltonian is given by

$$H^{\mathrm{NH}} = H_{\mathrm{c}} + \frac{P_\eta^2}{2M_\eta} + g k_{\mathrm{B}} T \eta \ . \tag{2.20}$$

In Eqn. (2.20) H_{c} represents the Hamiltonian which describes some classical system of interest. H_{c} is defined as,

$$H_{\mathrm{c}} = \frac{P^2}{2M} + V\left(R\right) \ , \tag{2.21}$$

where R and P represent the system coordinates and momenta, respectively, while M and $V\left(R\right)$ represent the mass and interaction potential of the system respectively. In Eqn. (2.20), η represents the fictitious thermostat variable, P_η its associated momentum, while M_η is its associated mass which controls the dynamical properties of the thermostat. The Boltzmann constant is represented by k_{B} , T is the absolute temperature of the thermal bath, and g is a constant that is equal to the number of degrees of freedom associated with the system. The non-Hamiltonian equation of motion for this extended system may be expressed, by means of a generalized bracket, as

$$\dot{X} = \left\{X, H^{\mathrm{NH}}\right\}_{\mathcal{B}^{\mathrm{NH}}} = \sum_{j\,k} \frac{\partial X}{\partial X_j} \mathcal{B}^{\mathrm{NH}}_{j\,k} \frac{\partial H^{\mathrm{NH}}}{\partial X_k} \ . \tag{2.22}$$

Here the antisymmetric matrix, $\mathcal{B}^{\mathrm{NH}}$ is

$$\mathcal{B}^{\mathrm{NH}} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ 0 & -1 & P & 0 \end{bmatrix} , \tag{2.23}$$

while the phase-space point of the extended system is $X = (R, \eta, P, P_\eta)$. The antisymmetric matrix $\mathcal{B}^{\mathrm{NH}}$, is responsible for the interaction which occurs between the system and environmental degrees of freedom. The phase-space compressibility, associated with this scheme, is given by

$$\begin{aligned} \kappa &= \sum_j \sum_k \frac{\partial \mathcal{B}^{\mathrm{NH}}_{jk}}{\partial X_j} \frac{\partial H^{\mathrm{NH}}}{\partial X_k} \\ &= -g \frac{P_\eta}{M_\eta} \ . \end{aligned}$$

One of the main problems with the NH thermostat is that it does not provide an ergordic sampling of phase-space, even for very long simulation times [51]. Its non-ergordic behaviour was first discovered by Hoover [50]. As a way to overcome this problem Martyna *et al.* [28] proposed a scheme in which the NH thermostat is coupled to a second NH thermostat, or if required an entire chain of NH thermostats. This generalization of the original NH method solved the problem of ergodicity, and came to be known as the Nosé-Hoover Chain (NHC) thermostat scheme.

2.4.2 Nosé-Hoover Chain Thermostat

As stated in the previous section, the NHC thermostat scheme may be formulated using a chain of N thermostats, however, for the work presented here only chains comprised of two thermostats will be considered. Doing this enables one to simplify the algebra involved, along with allowing both the antisymmetric matrix and equations of motion associated with this thermostat scheme to be explicitly written. It should be noted, however, that an extension to chains comprised of more that two thermostats can readily be made. The extended system Hamiltonian for the simplified version of the NHC thermostat is given by

$$H^{\mathrm{NHC}} = H_{\mathrm{c}} + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P_{\eta_2}^2}{2M_{\eta_2}} + g k_{\mathrm{B}} T \eta_1 + k_{\mathrm{B}} T \eta_2 \ . \tag{2.24}$$

In Eqn. (2.24) H_{c} represents the Hamiltonian that describes a classical system of physical interest, and is defined by Eqn. (2.21). The fictitious thermostat variables are represented by η_1 and η_2, and have momentum P_{η_1} and P_{η_2} associated with them, respectively. The thermostat masses are represented by M_{η_1} and M_{η_2}, these control the dynamical properties of the thermostats. The Boltzmann constant is represented by k_{B}, T represents the absolute temperature of the thermal bath, and g is a constant that is equal to the number of degrees of freedom associated with the system.

By making use of Eqn. (2.11), the equations of motion for this extended system may be expressed by means of a generalised bracket as

$$\dot{X} = \{X, H^{\mathrm{NHC}}\}_{\mathcal{B}^{\mathrm{NHC}}} = \sum_{jk} \frac{\partial X}{\partial X_j} \mathcal{B}_{jk}^{\mathrm{NHC}} \frac{\partial H^{\mathrm{NHC}}}{\partial X_k} \ . \tag{2.25}$$

Here the antisymmetric matrix $\mathcal{B}^{\rm NHC}$ reads

$$\mathcal{B}^{\rm NHC} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -P & 0 \\ 0 & -1 & 0 & P & 0 & -P_{\eta_1} \\ 0 & 0 & -1 & 0 & P_{\eta_1} & 0 \end{bmatrix} , \tag{2.26}$$

while the phase-space point of the extended system is $X = (R, \eta_1, \eta_2, P, P_{\eta_1}, P_{\eta_2})$. The phase-space compressibility associated with this scheme is given by

$$\begin{aligned} \kappa &= \sum_j \sum_k \frac{\partial \mathcal{B}_{jk}^{\rm NHC}}{\partial X_j} \frac{\partial H^{\rm NHC}}{\partial X_k} \\ &= -g \frac{P_{\eta_1}}{M_{\eta_1}} - \frac{P_{\eta_2}}{M_{\eta_2}} \ . \end{aligned}$$

2.4.3 Nosé-Hoover Power Thermostat

The NHC thermostat scheme achieves an ergordic sampling of phase space by changing the dimensionality of the extended system. However, Sergi *et al.* [1], found another way to overcome the ergodicity problem of the NH thermostat without having to extend the dimensionality of the extended system. This was achieved through a modification of the NH thermostat's equations of motion and lead to the so called Nosé-Hoover Power (NHP) thermostat. The NHP extended system Hamiltonian is given by

$$H^{\rm NHP} = H_{\rm c} + \frac{P_\eta^2}{2M_\eta} + g k_b T \eta \ , \tag{2.27}$$

where $H_{\rm c}$ again represents the Hamiltonian that describes a classical system of physical interest, and is defined by Eqn. (2.21). In Eqn. (2.27), η represents the fictitious thermostat variable, P_η its associated momentum, while M_η is its associated mass which controls the dynamical properties of the thermostat. The Boltzmann constant is represented by $k_{\rm B}$, T is the absolute temperature of the thermal bath, and g is a constant that is equal to the number of degrees of freedom associated with the system. The non-Hamiltonian equations of motion for this extended system may be expressed by means of a generalised bracket as,

$$\dot{X} = \{X, H^{\mathrm{NHP}}\}_{\mathcal{B}^{\mathrm{NHP}}} = \sum_{j\,k} \frac{\partial X}{\partial X_j} \mathcal{B}^{\mathrm{NHP}}_{j\,k} \frac{\partial H^{\mathrm{NHP}}}{\partial X_k} \,. \tag{2.28}$$

Here the antisymmetric matrix $\mathcal{B}^{\mathrm{NHP}}$ is given by

$$\mathcal{B}^{\mathrm{NHP}} = \left[\begin{array}{cccc} 0 & 0 & 1 & \tau P/M \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ -\tau P/M & -1 & P & 0 \end{array} \right] , \tag{2.29}$$

while the phase-space point of the extended system is $X = (R, \eta, P, P_\eta)$. The phase-space compressibility associated with this scheme is given by

$$\begin{aligned} \kappa &= \sum_j \sum_k \frac{\partial \mathcal{B}^{\mathrm{NHP}}_{jk}}{\partial X_j} \frac{\partial H^{\mathrm{NHP}}}{\partial X_k} \\ &= -g \frac{P_\eta}{M_\eta} \,. \end{aligned}$$

For this scheme, the NH antisymmetric matrix has been modified through the introduction of two non-zero elements, $\mathcal{B}^{\mathrm{NHP}}_{41} = \tau P/M$ and $\mathcal{B}^{\mathrm{NHP}}_{14} = -\tau P/M$, where τ is a time dimensional parameter. These two elements contribute to the driving of the dynamics of η. Indeed, if one sets τ equal to zero, then one recovers the standard NH thermostat scheme. Above a threshold value of $\tau = 0.5$, in scaled units (see Sec. 4.3.3), the system becomes chaotic and provides an ergordic sampling of phase space [1, 52]

Chapter 3

Quantum Dynamics

This chapter contains a brief overview of quantum dynamics. It begins with a general summary of quantum statistical mechanics, followed by a discussion regarding the quantum dynamics of both closed and open quantum systems. During the latter, the phase-space formulation of quantum mechanics is introduced and discussed. This chapter ends with a discussion on correlations and entanglement.

3.1 Quantum Statistical Mechanics

Quantum mechanics is an intrinsically statistical theory where the statistics enter the theory in two ways [53]. Firstly, due to the statistical interpretation of the wave function. The second way is a consequence of the incomplete knowledge one has about the dynamical state of the system, as demonstrated by Heisenberg's uncertainty principle [54]. We refer to the quantum state described by a single state vector, $|\psi\rangle$ with unit length ($\langle\psi\,|\,\psi\rangle = 1$) in some complex Hilbert space as a pure state and consider this to contain the maximum available information about the system. It should be noted that for the work presented in this thesis, $|\psi\rangle$ will be used to represent only the state of the spin system under study. As such the complex Hilbert space will have a finite dimensionality. For a system in a pure state, the state vector may be expressed in an orthonormal basis $|\phi_j\rangle$ as

$$|\psi\rangle = \sum_j c_j\,|\phi_j\rangle \ , \tag{3.1}$$

where the c_j are constant coefficients defined by $c_j = \langle \phi_j \mid \psi \rangle$ with $\sum_j |c_j|^2 = 1$. In this notation the expectation value of an arbitrary observable is given by

$$\begin{aligned}
\bar{A} = \langle A \rangle &= \langle \psi \mid A \mid \psi \rangle \\
&= \sum_k c_k^* \left\langle \phi_k \,\middle|\, A \sum_j c_j \,\middle|\, \phi_j \right\rangle \\
&= \sum_j \sum_k c_j c_k^* \langle \phi_k \mid A \mid \phi_j \rangle \\
&= \sum_j \sum_k c_j c_k^* A_{kj} \, . \qquad (3.2)
\end{aligned}$$

The statistical description which has been presented, for an arbitrary observable above, applies to systems in a pure state. However, in reality one often has less information about a quantum system than the maximally possible information contained within the state vector. For such cases one can no longer use Eqn. (3.2) to calculate the observable averages. To see this, consider an arbitrary two level system whose exact state is unknown. Since the system is a two level system it will be found in one of two states which may be denoted as $|\psi\rangle$ and $|\phi\rangle$. Each of these states will have some probability associated with it, which gives the likelihood of finding the system in that state, these probabilities may be denoted as P_ψ and P_ϕ, respectively. Such a mixed state cannot be represented by Eqn. (3.2), since the summation which appears on the right hand side simply produces another pure state rather than the mixed state of the system [55]. It therefore becomes necessary to consider situations where a system is described not by a single state vector, but by an ensemble of state vectors, $\{|\psi\rangle_1, |\psi\rangle_2, ..., |\psi\rangle_n\}$, having a probability distribution, $\{\gamma_1, \gamma_2, ..., \gamma_n\}$, defined over the entire ensemble. A system described by such an ensemble of states is said to be in a mixed state.

To calculate the expectation value of a quantum observable in a mixed state, one is required to add an associated weighting to each of the systems possible states. These weights are given by the probabilities associated with each state [56]. The observable average given by Eqn. (3.2) is modified by these probabilities to produce a weighted average,

$$\langle A \rangle = \sum_i \gamma_i \bar{A}_i \ , \tag{3.3}$$

where γ_i represents the probability that the system is in the i-th state. Since these terms represent probabilities, one requires that all γ_i terms must be non-negative, $\gamma_i \geq 0$, along with being normalised, $\sum_i \gamma_i = 1$. The average value of the observable in the i-th state is denoted by

$$\bar{A}_i = \langle \psi_i \,|\, A \,|\, \psi_i \rangle \ . \tag{3.4}$$

Substituting this into Eqn. (3.3) allows one to write down the average value for an observable of a mixed state as,

$$\langle A \rangle = \sum_i \gamma_i \langle \psi_i \,|\, A \,|\, \psi_i \rangle \,. \tag{3.5}$$

This expression motivates the introduction of the density operator associated with the mixed state [57],

$$\rho = \sum_i \gamma_i \, |\psi_i\rangle \langle \psi_i| \,. \tag{3.6}$$

The corresponding matrix defined by reference to an orthogonal basis is called the density matrix,

$$\begin{aligned} \rho_{jk} &= \sum_i \gamma_i \langle \phi_j \,|\, \psi_i \rangle \langle \psi_i \,|\, \phi_k \rangle \\ &= \langle \phi_j \,|\, \rho \,|\, \phi_k \rangle \,. \end{aligned} \tag{3.7}$$

An important point to note here is that all the information about the mixed state is contained within the density operator of the state, since the expectation value of any observable may be expressed in terms of ρ as

$$\begin{aligned} \langle A \rangle &= \sum_i \gamma_i \sum_{jk} \langle \psi_i \,|\, \phi_j \rangle \langle \phi_j \,|\, A \,|\, \phi_k \rangle \langle \phi_k \,|\, \psi_i \rangle \\ &= \sum_i \gamma_i \sum_k \langle \phi_k \,|\, \psi_i \rangle \langle \psi_i \,|\, A \,|\, \phi_k \rangle \\ &= \sum_k \langle \phi_k \,|\, \rho A \,|\, \phi_k \rangle \,. \end{aligned} \tag{3.8}$$

The summation which appears in Eqn. (3.8) is over all the diagonal elements of the density matrix. It is also known as the trace, and is denoted as

$$\langle A \rangle = \mathrm{Tr}\left(\rho A\right) = \mathrm{Tr}\left(A\rho\right), \tag{3.9}$$

since the trace is invariant under cyclic permutations [57].

The density matrix has several important properties, that play a crucial role in its use for the quantum mechanical description of mixed states. The first of these properties is that the density matrix is normalised, $\mathrm{Tr}\left(\rho\right) = 1$. It is also Hermitian, $\left(\rho_{kj}\right)^* = \rho_{jk}$. Another important property of the density matrix is that of positivity,

$$\langle \chi \,|\, \rho \,|\, \chi \rangle \geq 0 \;\forall \, |\chi\rangle \,,$$

this condition implies that $\gamma_i \geq 0$, in other words one has non-zero eigenvalues. The diagonal elements of the density ρ_{jj} give the probability that the system is in state j [58]. While the off diagonal elements ρ_{jk} may be both positive or negative [57], consequently, these elements may not be interpreted as probabilities [58]. These elements are linked to certain quantum mechanical effects which have no classical analogue, such effects arise due to the wave like properties of matter [36]. These elements are also related to the phase correlations which exist between states j and k. For pure states the density operator is simply the projection operator on a single state

$$\rho = |\psi\rangle \langle\psi| \,. \tag{3.10}$$

This implies that $\rho^2 = \rho$. In this case $\mathrm{Tr}\left(\rho^2\right) = 1$, while for all mixed states we have $\mathrm{Tr}\left(\rho^2\right) < 1$. A mixed state described by the density operator given by Eqn. (3.6) is often referred to as an incoherent mixture of states $|\psi_i\rangle$. While a coherent mixture is instead a superposition of the states

$$|\psi\rangle = \sum_i c_i \,|\psi_i\rangle \tag{3.11}$$

which then represents a pure state.

3.2 Time Evolution in Closed Quantum Systems

3.2.1 Schrödinger Representation

The first quantum evolution equation that describes the behaviour of an isolated or closed quantum system, was obtained in 1926 by Erwin Schrödinger [59]. According to this equation, if the system is in some pure state $|\psi(t)\rangle \in \mathcal{H}$ at time t, where $\mathcal{H}$ denotes the Hilbert space of the system, then this state evolves in time according to the Schrödinger equation,

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = -\frac{\mathrm{i}}{\hbar}H(t)|\psi(t)\rangle\ , \tag{3.12}$$

where $H(t)$ denotes the Hamiltonian of the system. An important property of this equation is that it preserves the norm of the states [4, 60],

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)\,|\,\psi(t)\rangle &= \left(\frac{\mathrm{d}\langle\psi(t)|}{\mathrm{d}t}\right)|\psi(t)\rangle + \langle\psi(t)|\left(\frac{\mathrm{d}|\psi(t)\rangle}{\mathrm{d}t}\right)\\ &= \mathrm{i}\left\langle\psi(t)\,\middle|\,H^{\dagger}(t)\,\middle|\,\psi(t)\right\rangle - \mathrm{i}\langle\psi(t)\,|\,H(t)\,|\,\psi(t)\rangle\\ &= 0\ ,\end{aligned} \tag{3.13}$$

since the Hamiltonian is self-adjoint, $H^{\dagger}(t) = H(t)$. Due to the fact that the Schrödinger equation is linear, its solution may be represented in terms of a time evolution operator $U(t,t_0)$. This operator transforms the state $|\psi(t_0)\rangle$ at some initial time to the state $|\psi(t)\rangle$ at time t

$$|\psi(t)\rangle = U(t,t_0)\,|\psi(t_0)\rangle\,. \tag{3.14}$$

One can obtain an operator equation for the time evolution operator by substituting Eqn. (3.14) into Eqn. (3.12)

$$\frac{\partial}{\partial t}U(t,t_0) = -\frac{\mathrm{i}}{\hbar}H(t)\,U(t,t_0)\,, \tag{3.15}$$

which is subject to the initial condition $U(t_0,t_0) = \mathcal{I}$. The time evolution operator, $U(t,t_0)$ is a unitary operator since

$$U^{\dagger}(t,t_0)\,U(t,t_0) = U(t,t_0)\,U^{\dagger}(t,t_0) = \mathcal{I}, \tag{3.16}$$

where $\mathcal{I}$ represents the identity operator. In general, the form of $U(t, t_0)$ depends on the properties of the Hamiltonian under consideration. In the case of a closed physical system, the Hamiltonian H is independent of time [4, 61], and Eqn. (3.14) may be integrated to obtain

$$U(t, t_0) = \mathrm{e}^{-\mathrm{i}(t-t_0)H/\hbar} \, . \tag{3.17}$$

On the other hand, if the system is in a mixed state, then the quantum statistical ensemble is characterized through the use of density matrix. In order to derive an equation of motion for the density matrix, one assumes that the initial state of the system at some initial time, t_0, is given by

$$\rho(t_0) = \sum_i \gamma_i \left|\psi_i(t_0)\right\rangle \left\langle\psi_i(t_0)\right| \tag{3.18}$$

where the γ_i are positive weights, while the $\left|\psi_i(t_0)\right\rangle$ are normalized state vectors which evolve in time according to the Schrödinger equation. As such the state of the system at some future time, t, is given by

$$\begin{aligned} \rho(t) &= \sum_i \gamma_i U(t, t_0) \left|\psi_i(t_0)\right\rangle \left\langle\psi_i(t_0)\right| U^\dagger(t, t_0) \\ &= U(t, t_0)\, \rho(t_0)\, U^\dagger(t, t_0) \, . \end{aligned}$$

To obtain an equation of motion for the density matrix one then differentiates this equation with respect to time,

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = -\mathrm{i}\left[H(t), \rho(t)\right] \, . \tag{3.19}$$

Equation (3.19) is known as the Liouville-von Neumann equation or the von Neumann equation. It is often not written in the form above, but rather in one that is similar to the classical Liouville equation [61],

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = \mathcal{L}\rho(t) \, , \tag{3.20}$$

where $\mathcal{L}$ is the Liouville super-operator which is defined via the condition that $\mathcal{L}[\cdots] = -\mathrm{i}\left[H(t), \cdots\right]$.

3.2.2 Heisenberg Representation

An equivalent description of the quantum dynamics may be obtained by transferring the time dependence from the states to the operators in the Hilbert space such that $A = A(t)$. This leads to the so called Heisenberg formulation of quantum mechanics. This formulation was developed in 1925 by W. Heisenberg [62]. It is also known as the matrix formulation of quantum mechanics. Within this formulation all operators are represented by $N \times N$ matrices where N is the number of basis states required to form a complete basis set for the system, while the quantum states of the system are represented by vectors having dimension $N \times 1$ [55]. The operators in both the formulations discussed here are related through the canonical transformation [4]

$$A_{\mathrm{H}}(t) = U^{\dagger}(t, t_0)\, A(t)\, U(t, t_0) \tag{3.21}$$

where the subscript H has been used to denote the Heisenberg picture operators. The Heisenberg formulation is equivalent to that of Schrödinger. This equivalence may be seen by the fact that the expectation value of an arbitrary observable, $\chi(t)$, is the same in both pictures,

$$\langle \chi(t) \rangle = \mathrm{Tr}\left\{\chi(t)\, \rho(t)\right\} \tag{3.22}$$

$$= \mathrm{Tr}\left\{\chi_{\mathrm{H}}(t)\, \rho_{\mathrm{H}}(t_0)\right\} \tag{3.23}$$

where $\rho_{\mathrm{H}}(t_0)$ is the fixed density matrix found in the Heisenberg formulation [60]. The equation of motion for a Heisenberg picture operator $A_{\mathrm{H}}(t)$ is obtained by differentiating both sides of the canonical transformation [Eqn. (3.21)] with respect to time

$$\frac{\mathrm{d}}{\mathrm{d}t} A_{\mathrm{H}}(t) = \frac{\mathrm{i}}{\hbar}\left[H_{\mathrm{H}}(t), A_{\mathrm{H}}(t)\right] + \frac{\partial A_{\mathrm{H}}(t)}{\partial t}\,, \tag{3.24}$$

where $H_{\mathrm{H}}(t)$ represents the Hamiltonian in the Heisenberg picture. The partial derivative which appears on the right hand side of Eqn. (3.24) is taken with respect to the explicit time dependence found in the operator. For the case where $\frac{\mathrm{d}A_{\mathrm{H}}(t)}{\mathrm{d}t} = 0$, then $A_{\mathrm{H}}(t)$ is a constant of motion. For the special case where A_{H} is chosen to be the Hamiltonian of a closed system, $A_{\mathrm{H}} = H$, then $\frac{\partial H(t)}{\partial t} = 0$ and the time evolution operator has the form given by Eqn. (3.17) [4]. As such, it follows that the Heisenberg formulation Hamiltonian is a constant of motion, $\frac{\mathrm{d}}{\mathrm{d}t}H_{\mathrm{H}} = 0$. Therefore if the operators carry no explicit time dependence and the system is isolated, the Heisenberg equation of motion reduces to

$$\frac{\mathrm{d}}{\mathrm{d}t}A_{\mathrm{H}} = \frac{\mathrm{i}}{\hbar}\left[H_{\mathrm{H}}\left(t\right), A_{\mathrm{H}}\left(t\right)\right]. \tag{3.25}$$

	Schrödinger Picture	Heisenberg Picture
Ket state	$\lvert\psi\left(t\right)\rangle = U\left(t, t_0\right)\lvert\psi\left(t_0\right)\rangle$	$\lvert\psi_0\rangle$
Operator	constant	$A_{\mathrm{H}}\left(t\right) = U^{\dagger}\left(t, t_0\right)A\left(t\right)U\left(t, t_0\right)$
Density Matrix	$\rho\left(t\right) = U\left(t, t_0\right)\rho\left(t_0\right)U^{\dagger}\left(t, t_0\right)$	$\rho\left(0\right)$

Table 3.1: A summary comparison of the evolution of the ket state $\lvert\psi\left(t\right)\rangle$, an arbritary observable $A_{\mathrm{H}}\left(t\right)$ and the density matrix $\rho\left(t\right)$ within the Scrödinger and Heisenberg representations of quantum mechanics. The time evolution operator is defined as $U\left(t, t_0\right) = \mathrm{e}^{-\mathrm{i}\left(t-t_0\right)H/\hbar}$.

3.3 Time Evolution in Open Quantum Systems

An open quantum system is, in general, comprised of some quantum system, S, coupled to another quantum system, B, which represents the environment. S represents a subsystem of the combined total system S + B. This combined system is assumed to be a closed system which follows Hamiltonian dynamics [4]. The dynamics of S due to the Hamiltonian evolution of the system are referred to as reduced system dynamics, while S is called the reduced system. Let $\mathcal{H}_{\mathrm{S}}$ be the Hilbert space of the reduced system while $\mathcal{H}_{\mathrm{B}}$ is that of the environment. The Hilbert space of the total system is then given by,

$$\mathcal{H} = \mathcal{H}_{\mathrm{S}} \otimes \mathcal{H}_{\mathrm{B}}, \tag{3.26}$$

while the total Hamiltonian has the form

$$H = H_{\mathrm{S}} + H_{\mathrm{B}} + H_{\mathrm{SB}}, \tag{3.27}$$

where H_{S} is the Hamiltonian of the subsystem S, H_{B} is the Hamiltonian of the environment B, and H_{SB} is the Hamiltonian which describes the interaction between the subsystem and environment. A schematic representation of such a system is shown in Fig. 3.1. The

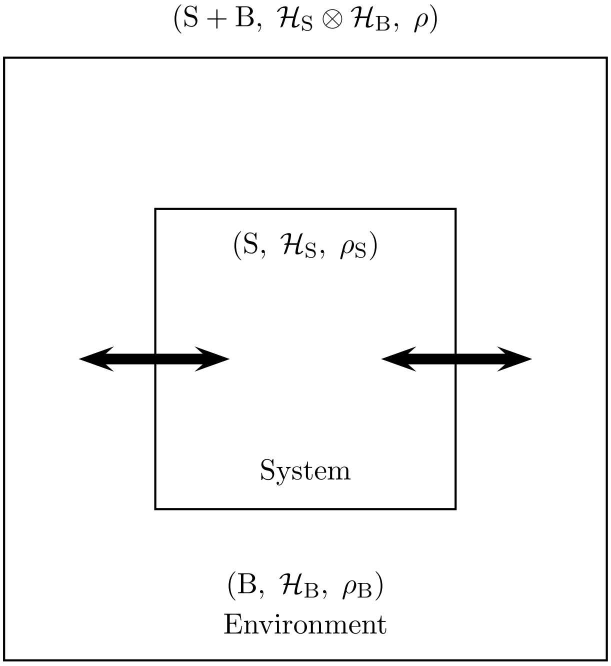

Figure 3.1: Schematic representation of an open quantum system [4]. The system and environment are coupled to each other and are free to exchange energy as denoted by the black arrows. Due to this interaction it is no longer possible to use unitary Hamiltonian dynamics to represent state changes in the system.

reduced density matrix $\rho_{\mathrm{S}}(t)$ is obtained from the density matrix of the total system by taking a partial trace over the environment degrees of freedom. Since the total system evolves via unitary Hamiltonian dynamics one has that,

$$\rho_{\mathrm{S}}(t) = \mathrm{Tr}_{\mathrm{B}} \left\{ U(t, t_0)\ \rho\, U^{\dagger}(t, t_0) \right\}, \tag{3.28}$$

where $U(t, t_0)$ is the time-evolution operator of the total system [60]. The equation of motion is obtained by taking the partial trace over the environment of both sides of the von Neumann equation for the total system

$$\frac{\mathrm{d}}{\mathrm{d}t} \rho_{\mathrm{S}}(t) = -\frac{\mathrm{i}}{\hbar} \mathrm{Tr}_{\mathrm{B}} \left[H(t), \rho(t) \right]. \tag{3.29}$$

The main reason for the study of open quantum systems is that in many physically important situations a complete mathematical model of the coupled systems dynamics is much too complicated to solve. Some examples of such situations may be found in the fields of quantum biology [6, 7], quantum communication [11, 12] and nano physics [10]. The environment may contain an infinite number of degrees of freedom, in which case an exact treatment of the problem requires one to solve an infinite number of coupled equations of motion. This makes it often impossible to perform full quantum simulations on a computer [5]. Another common problem is that the environmental degrees of freedom are neither controllable nor exactly known. As such, one is forced to develop a simpler description in a reduced state which is formed by a restricted set of physically relevant variables. This is achieved through the use of various analytical methods and techniques. One of the most common techniques used to simulate the dynamics of such systems is that of master equations [4]. However, for the work presented here a mixed Wigner-Heisenberg formulation of the dynamics has been used. This representation is achieved through use of the partial Wigner transform, which allows one to treat the environmental degrees of freedom in terms of phase-space functions. This phase-space representation of the environment and the partial Wigner transform are discussed in the following section.

3.3.1 Phase-Space Representation of Quantum Mechanics

If one wishes to obtain a classical-like description of quantum mechanics, then one is required to describe the quantum system of interest in phase space [57]. However, since one can not simultaneously have well defined knowledge about the position and momentum for quantum systems, it is then impossible to define true phase-space probability-distribution-functions for quantum systems. It is, however, possible to obtain quasiprobability distribution-functions for such systems. These functions are of great use in the study of quantum systems [63], as they provide insights into the connections which exist between classical and quantum mechanics. They achieve this by expressing the system's quantum averages in a form that is very similar to that used to display classical averages.

Of the many attempts to produce useful quasiprobability distribution-functions, one of the earliest and most successful was by E. Wigner [64].

3.3.2 Wigner Representation of Quantum Mechanics

Since the Wigner transform is a special case of the more general Weyl transform, a discussion of the Weyl transform is required, before the Wigner transform is introduced. The Weyl transform, for the density matrix in the position basis, reads [65]

$$\tilde{\rho}\,(x,p) = \int \mathrm{d}y \; \mathrm{e}^{-\mathrm{i}py/\hbar} \left\langle x + y/2 \,|\, \rho \,|\, x - y/2 \right\rangle , \tag{3.30}$$

where the tilde has been used as a means to denote the Weyl transform. This transform may also be expressed in the momentum basis as

$$\tilde{\rho}\,(x,p) = \int \mathrm{d}y \; \mathrm{e}^{\mathrm{i}xy/\hbar} \left\langle p + y/2 \,|\, \rho \,|\, p - y/2 \right\rangle . \tag{3.31}$$

From its definition, one sees that the Weyl transform provides a way to represent an operator as a function of phase-space. When this transform was first introduced by Weyl [66], it showed for the first time that quantum mechanics could be described through not only the use of operators, but also functions [63]. An important property of this transform, which plays a crucial role when it comes to calculating expectation values in the Wigner representation, is that the trace of two arbitrary operators A and B is equivalent to the integral over phase space of the product of their Weyl transforms [65],

$$\mathrm{Tr}\,(AB) = \frac{1}{h} \int \int \mathrm{d}x \; \mathrm{d}p \; \tilde{A}\,(x,p)\, \tilde{B}\,(x,p) \,. \tag{3.32}$$

The Wigner function itself is then defined for a single particle, as the Weyl transform of the density matrix divided by Planck's constant, h [63–65]

$$\mathrm{W}\,(x,p) = \frac{\tilde{\rho}\,(x,p)}{h}. \tag{3.33}$$

It may be expressed in both the position and momentum basis as

$$\mathrm{W}\,(x,p) = \frac{1}{h} \int \mathrm{d}y \; \mathrm{e}^{-\mathrm{i}py/\hbar} \left\langle x + y/2 \,|\, \rho \,|\, x - y/2 \right\rangle \tag{3.34}$$

and

$$\mathrm{W}\left(x,p\right)=\frac{1}{h}\int\mathrm{d}y\;\mathrm{e}^{\mathrm{i}xy/\hbar}\left\langle p+y/2\,|\,\rho\,|\,p-y/2\right\rangle, \tag{3.35}$$

respectively. Making use of Eqn. (3.32), the expectation values within this representation may be expressed as

$$\begin{aligned}\langle A\rangle &= \mathrm{Tr}\left(\rho A\right)\\ &= \frac{1}{h}\int\int\mathrm{d}x\;\mathrm{d}p\;\tilde{\rho}\left(x,p\right)\tilde{A}\left(x,p\right)\\ &= \int\int\mathrm{d}x\;\mathrm{d}p\;\mathrm{W}\left(x,p\right)\tilde{A}\left(x,p\right).\end{aligned} \tag{3.36}$$

The last line of Eqn. (3.36) shows how the Wigner function may be interpreted as a phase-space probability-density which characterises some physical quantity, where this quantity is represented by the Weyl transform of the observable [65]. However, before the Wigner function may be called a probability-distribution function, one needs to make sure that it satisfies both the normalisability and non-negativity conditions. As it turns out, the Wigner transform satisfies the normalisability condition, however, it fails to satisfy the non-negativity condition. To see this violation of the non-negativity condition, one needs to consider two orthogonal sates of a system $|\psi\rangle$ and $|\phi\rangle$ each having a corresponding density matrix ρ_ψ and ρ_ϕ respectively, such that

$$\begin{aligned}\mathrm{Tr}\left(\rho_\psi\rho_\phi\right) &= \frac{1}{h}\int\int\mathrm{d}x\;\mathrm{d}p\;\mathrm{W}_\psi\left(x,p\right)\mathrm{W}_\phi\left(x,p\right)\\ &= \left|\langle\psi|\phi\rangle\right|^2\;.\end{aligned} \tag{3.37}$$

However since the states $|\psi\rangle$ and $|\phi\rangle$ are orthogonal this amounts to

$$\frac{1}{h}\int\int\mathrm{d}x\;\mathrm{d}p\;\mathrm{W}_\psi\left(x,p\right)\mathrm{W}_\phi\left(x,p\right)=0\;. \tag{3.38}$$

The only way that this integral is equal zero is if either W_ψ, W_ϕ or both of them take on negative values for some region in phase space. As such, the Wigner function can not be a probability-distribution function, and is classified as a quasiprobability-distribution function. A final important property of the Wigner function, required for the work presented in the following sections, is that the Wigner transform for the product of two arbitrary operators is given by [22, 67]

$$(AB)_{\mathrm{W}} = A_{\mathrm{W}}(R,P)\ \mathrm{e}^{\frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}^c_{ij} \overrightarrow{\partial}_j}\ B_{\mathrm{W}}(R,P)\ . \tag{3.39}$$

where $\partial_i = \frac{\partial}{\partial X_i}$, and the overhead arrows represent the directions in which these operators act. This identity is important as the commutator which appears in the Heisenberg equation of motion contains a product of two operators. One thus requires the Wigner transform of an operator product, if one wants to use this equation within this representation.

3.3.3 Partial Wigner Representation of Quantum Mechanics

As stated earlier, if one is interested in calculating the dynamics of some system comprised of a quantum subsystem in contact with a thermal bath, it is usually impossible to obtain a fully quantum mechanical solution for its evolution. However, if one is not interested in how the bath degrees of freedom evolve, then one may use the quantum-classical approximation to simulate the dynamics of this system. In this approximation, part of the system is treated classically while its remainder is subject to a quantum mechanical treatment. This is achieved by representing the degrees of freedom belonging to the quantum subsystem in a suitable set of basis states, while the classical phase-space degrees of freedom are used to represent the bath [40].

To obtain this representation of the system, one makes use of the partial Wigner transform. This transform corresponds to simply applying the Weyl transform over only the bath coordinates of the system. This has the effect of converting the system's Hamiltonian from a fully quantum mechanical operator to an operator of both the Hilbert space of the quantum subsystem, as well as a function of the classical phase-space variables [55, 65].

If the bath is comprised of N degrees of freedom, then the partial Wigner transform for the density matrix is given by [63]

$$\rho_{\mathrm{W}}(R,P) = \frac{1}{(2\pi\hbar)^{3N}} \int \mathrm{d}z\ \mathrm{e}^{\mathrm{i}P\cdot z/\hbar} \left\langle R - z/2 \,\middle|\, \rho \,\middle|\, R + z/2 \right\rangle\ , \tag{3.40}$$

where W is now used to denote the partial Wigner transform. It should be noted that all of the variables are now interpreted as vectors with dimension $3N$, since the bath contains

N degrees of freedom [40]. For an arbitrary operator of the system, A, the partial Wigner transform is

$$A_{\mathrm{W}}\left(R,P\right) = \int \mathrm{d}z \; \mathrm{e}^{\mathrm{i}P\cdot z/\hbar} \left\langle R - z/2 \,|\, A \,|\, R + z/2 \right\rangle \; . \tag{3.41}$$

In this transformed representation, A_W becomes an operator on both the quantum subsystem's Hilbert space and the bath's phase space. The properties of the Wigner function defined in the previous section are still valid for the partial Wigner transform representation. However, the system's dynamics will now evolve according to some quantum-classical equation of motion.

3.4 Correlations and Entanglement

It is well known that quantum systems display certain properties and characteristics which have no classical analogue. Examples of such properties include but are not limited to the superposition of quantum states and tunnelling. These properties are examples of effects that may be observed in quantum systems comprised of a single particle. These single particle effects are, however, not the only distinctions which exist between classical and quantum systems. Indeed, there are even more differences which arise in composite quantum systems. That is systems which are made up of at least two subsystems. The correlations which exist between these subsystems give rise to another distinction between classical and quantum systems. While correlations in classical systems can always be described in terms of classical probabilities, this is not always true for quantum systems. These non-classical correlations lead to apparent paradoxes in the theory like the famous EPR paradox [68]. These correlations are often referred to as entanglement, while states which display such correlations are referred to as entangled states. Entanglement is considered to be one of the clearest marks of the difference between classical and quantum physics [69].

3.4.1 Composite Systems

Composite quantum systems may be defined as systems which may be "naturally" split into two or more subsystems, where each subsystem is itself a quantum system. Here the word "naturally" simply implies that the decomposition is given in an obvious way which is determined by the physical situation under study. A typical example is that of a string of ions, where each ion may be regarded as a subsystem while the entire string forms the composite system. The Hilbert space of such a system is given by the tensor product of the spaces corresponding to each of the subsystems

$$\mathcal{H} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} \otimes \cdots \otimes \mathcal{H}^{(N)} \ . \tag{3.42}$$

Such systems are generally referred to as multipartite systems. For the work presented here we have chosen to focus on finite-dimensional bipartite systems. These are systems comprised of two distinct subsystems $S^{(1)}$ and $S^{(2)}$, described by the Hilbert space

$$\mathcal{H} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} \ . \tag{3.43}$$

It should be noted that many of the concepts and ideas which are presented here with respect to these bipartite systems can be readily generalized and extended to the case of a multipartite system.

Taking a fixed orthonormal basis $\left\{\left|\psi_i^{(1)}\right\rangle\right\}$ of $\mathcal{H}^{(1)}$ and a basis of $\left\{\left|\phi_j^{(2)}\right\rangle\right\}$ of $\mathcal{H}^{(2)}$, one may express the Hilbert space basis as,

$$\left|\psi_i^{(1)}, \phi_j^{(2)}\right\rangle = \left|\psi_i^{(1)}\right\rangle \otimes \left|\phi_j^{(2)}\right\rangle \ . \tag{3.44}$$

This allows one to express a general state in $\mathcal{H}$ as,

$$|\chi\rangle = \sum_{ij} c_{ij} \left|\psi_i^{(1)}\right\rangle \otimes \left|\phi_j^{(2)}\right\rangle \ . \tag{3.45}$$

The observables of $S^{(1)}$ and $S^{(2)}$ define commuting observables for the total subsystem. To show this, one needs to consider their action on the basis vectors given by Eqn. (3.44). By letting $A^{(1)}$ be an observable of $S^{(1)}$, and $A^{(2)}$ be an observable of $S^{(2)}$, one then has that

$$A^{(1)} \left|\psi_i^{(1)}, \phi_j^{(2)}\right\rangle = \sum_k A_{ki}^{(1)} \left|\psi_k^{(1)}, \phi_j^{(2)}\right\rangle \tag{3.46}$$

and

$$A^{(2)}\left|\psi_i^{(1)},\phi_j^{(2)}\right\rangle=\sum_{\beta}A_{\beta j}^{(1)}\left|\psi_i^{(1)},\phi_\beta^{(2)}\right\rangle \tag{3.47}$$

from which

$$\begin{aligned}A^{(1)}A^{(2)}\left|\psi_i^{(1)},\phi_j^{(2)}\right\rangle&=\sum_{k\beta}A_{ki}^{(1)}A_{\beta j}^{(2)}\left|\psi_k^{(1)},\phi_\beta^{(2)}\right\rangle\\&=A^{(2)}A^{(1)}\left|\psi_i^{(1)},\phi_j^{(2)}\right\rangle\ .\end{aligned} \tag{3.48}$$

The expectation values of observables acting only on $S^{(1)}$ are determined through the use of the reduced density matrix of $S^{(1)}$. This reduced density matrix is obtained by taking the partial trace with respect to the coordinates of $S^{(2)}$

$$\rho^{(1)}=\mathrm{Tr}^{(2)}\left(\rho\right)\ . \tag{3.49}$$

The expectation values of these observables are then determined through the use of the partial trace as

$$\langle A\rangle=\mathrm{Tr}^{(1)}\left\{A^{(1)}\rho^{(1)}\right\}\ . \tag{3.50}$$

while

$$\langle A\rangle=\mathrm{Tr}^{(2)}\left\{A^{(2)}\rho^{(2)}\right\}\ , \tag{3.51}$$

for the observables of $S^{(2)}$.

3.4.2 Entanglement

Consider some arbitrary state, $|\Psi\rangle$, which may be written as

$$|\Psi\rangle=\left|\psi^{(1)}\right\rangle\otimes\left|\phi^{(2)}\right\rangle\ , \tag{3.52}$$

where $|\psi^{(1)}\rangle$ and $|\phi^{(2)}\rangle$ are pure states. States of the form $|\Psi\rangle$ are called product or unentangled (separable) states. However, if there exists no $|\psi^{(1)}\rangle\in\mathcal{H}^{(1)}$, and $\left|\phi^{(2)}\right\rangle\in\mathcal{H}^{(2)}$ such that Eqn. (3.52) is true, then $|\Psi\rangle$ is said to be entangled (inseparable).

Similarly to the case of pure states, mixed product states

$$\rho=\rho^{(1)}\otimes\rho^{(2)} \tag{3.53}$$

do not exhibit correlations. However, a convex sum of different product states

$$\rho = \sum_i p_i \, \rho_i^{(1)} \otimes \rho_i^{(2)} \tag{3.54}$$

with $p_i > 0$ and $\sum_i p_i = 1$, will in general yield correlated measurement results. These correlations can be described in terms of classical probabilities, p_i, and are therefore considered classical in their nature [60]. States of the form given by Eqn. (3.54) are known as separable mixed states. Mixed entangled states are defined by the non existence of a decomposition into product states [60, 70]. In other words, a mixed state ρ is entangled if there are no local states $\rho_i^{(1)}$, $\rho_i^{(2)}$, along with non-negative weights p_i, such that ρ may be expressed as described by Eqn. (3.54). These entangled states imply the existence of quantum correlations of measurements on different subsystems which can no longer be described in terms of only classical probabilities. The definitions of separable and entangled states given above may appear simple at first sight, however, in general, finding out whether or not a mixed state is entangled is a difficult task. This is due to the fact that separability is defined via the existence of a decomposition of a state into product states in the case of pure states [Eqn. (3.52)], or into a convex sum of tensor products [Eqn. (3.54)] for mixed states. Therefore, to show that a given state is separable, one is required to look for such decompositions of the state. Once such a decomposition is found, then one knows that the given state is separable. However, a failure to find such a decomposition can have two different reasons: either that state is indeed entangled and there is no decomposition into product states, or the state is actually separable, but the appropriate decomposition could not be found. As it is not the aim of this work to give an exhaustive review of the field of entanglement measures, we will not go into further details regarding the technical details of these measures except to introduce the measures that we have used for the work done here in the following sections. If the reader wishes to read more about this topic, a comprehensive review of entanglement measures may be found in the available literature [70–73].

3.4.3 Entanglement Measures

Entanglement measures provide a way to quantify the degree of entanglement present within a quantum state. The first of these measures under consideration here is the von Neumann entropy. This measure is an important entropy function, in the fields of quantum statistical mechanics and thermodynamics [4]. It is defined as

$$S\left(\rho\right) = \mathrm{Tr}\left(\rho \ln \rho\right), \tag{3.55}$$

where ρ is the state of some quantum statistical ensemble. It should be noted that in the definition given by Eqn. (3.55) the Boltzmann constant has been set equal to one. This means that the temperatures are measured in terms of energies. This convention has been used for the remainder of this thesis. Through the use of Eqn. (3.6) we can rewrite Eqn. (3.55) as

$$S\left(\rho\right) = -\sum_i \gamma_i \ln \gamma_i, \tag{3.56}$$

where it is understood that $0 \cdot \ln 0 \equiv 0$ [4]. The von Neumann entropy has, amongst others, the following important properties [4, 74]: For all density matrices one has that

$$S\left(\rho\right) \geq 0,$$

where the equality holds if and only if ρ represents a pure state. For a finite dimensional Hilbert space the entropy has an upper bound given by

$$S\left(\rho\right) \leq \ln D,$$

where $D < \infty$ is the dimension of Hilbert space. The equality sign on the upper bound holds if and only if ρ represents a completely mixed state. For a composite system $S\left(\rho\right)$ obeys the subadditivity condition

$$S\left(\rho\right) \leq S\left(\rho^{(1)}\right) + S\left(\rho^{(2)}\right),$$

where the equality sign holds if and only if the total density matrix describes an uncorrelated state. $S\left(\rho\right)$ is invariant with respect to unitary transformations of the density matrix operator,

$$S\left(U\rho U^{\dagger}\right) = S\left(\rho\right).$$

Although these properties have not been proved here, their proofs can be readily found in the available literature [74–76]. If ρ represents a pure state then the von Neumann entropies of the subsystems are equal to each other,

$$S\left(\rho^{(1)}\right) = S\left(\rho^{(2)}\right) = -\sum_i |\gamma_i| \ln |\gamma_i| \tag{3.57}$$

where the γ_i terms are used to denote the eigenvalues of either $S\left(\rho^{(1)}\right)$ or $S\left(\rho^{(2)}\right)$, which are equal. This equality of the eigenvalues can be readily shown through the application of the Schmidt decomposition [4]. The trace purity, Γ, of the system is defined as

$$\Gamma = \mathrm{Tr}\left(\rho^2\right). \tag{3.58}$$

The purity has amongst others the following important properties [77]: For finite dimensional systems, the purity has has a lower bound given by

$$\Gamma\left(\rho\right) \geq \frac{1}{D},$$

where $D < \infty$ is the dimensionality of the Hilbert space. It is bounded from above

$$\Gamma\left(\rho\right) \leq 1 \ .$$

For certain situations, it is useful to make use of the linear entropy rather than the von Neumann entropy. The linear entropy, $S_{\mathrm{L}}\left(\rho\right)$, which is related to the trace purity is defined as

$$S_{\mathrm{L}}\left(\rho\right) = \mathrm{Tr}\{\rho - \rho^2\} = 1 - \Gamma \tag{3.59}$$

The lower bound of $S_{\mathrm{L}}\left(\rho\right)$ is given by

$$S_{\mathrm{L}}\left(\rho\right) \geq 0 \ ,$$

where the equality only holds if and only if ρ is a pure state, while the upper bound for a D-dimensional Hilbert space is given by [4]

$$S_{\mathrm{L}}\left(\rho\right) \leq 1 - \frac{1}{D}.$$

The equality in the upper bound is attained for the case of a completely mixed state. The final entanglement measure of interest is the concurrence, $\mathcal{C}\left(\rho\right)$, of the system. To define this measure, it is necessary to begin by introducing the spin-flip operator [78–80],

$$\xi = \left(\sigma_{\mathrm{y}} \otimes \sigma_{\mathrm{y}}\right), \tag{3.60}$$

where σ_{y} is the Pauli spin matrix. The spin-flipped density matrix is defined to be [78–81]

$$\tilde{\rho} = \xi \rho^{*} \xi, \tag{3.61}$$

with the complex conjugate also taken in the standard basis. Since ρ and $\tilde{\rho}$ are both positive operators, their product $\rho\tilde{\rho}$, which is non-Hermitian, has only real and non-negative eigenvalues. The concurrence of ρ may then be defined as [78–82]

$$\mathcal{C}\left(\rho\right) = \max\ \left\{0, \lambda_1 - \lambda_2 - \lambda_3 - \lambda_4\right\}, \tag{3.62}$$

where the λ_i's are the square roots of the eigenvalues obtained from the matrix $\rho\tilde{\rho}$ in decreasing order. The concurrence has a minimum value of $\mathcal{C}\left(\rho\right) = 0$ and a maximum value of $\mathcal{C}\left(\rho\right) = 1$ which correspond to an unentangled and completely entangled state, respectively. The concurrence on an arbitrary ρ is related to the entanglement of formation by the function [78, 83]

$$\begin{aligned} E_f\left(\rho\right) &= \epsilon\left[\mathcal{C}\left(\rho\right)\right] \\ &= h\left[\frac{1+\sqrt{1-\mathcal{C}^2\left(\rho\right)}}{2}\right]. \end{aligned} \tag{3.63}$$

The binary entropy function $h\left(x\right)$ is given by $h\left(x\right) = -x\ \log\left(x\right) - \left(1-x\right)\log\left(1-x\right)$. While the concurrence is often regarded as an entanglement measure in its own right [80], it should be noted that it is only the entanglement of formation that is an entanglement measure, while the concurrence is regarded as an entanglement measure through its relation to the entanglement of formation [82].

Chapter 4

Quantum Dynamics in Classical-like Thermal Baths

This chapter contains a discussion on how to model and numerically simulate the quantum dynamics of systems situated in classical-like thermal baths. This includes the introduction of the adiabatic basis, as well as a discussion on how to numerically implement the dynamics via surface-hopping algorithms. The NHC and NHP thermostating schemes are then extended to the quantum-classical case, and applied to the study of the spin boson model.

4.1 The Quantum-Classical Liouville Equation

We now proceed to study the Liouville quantum-classical representation of the dynamics. This approach is extremely useful when one is considering the dynamics of a system that can easily be spilt into two parts, namely, a small quantum subsystem and a larger environment or bath, comprised of slower, heavier particles. It has the advantage of allowing one to treat the subsystem degrees of freedom in a fully quantum way, while the environmental degrees of freedom are represented in terms of functions of phase space. To achieve this mixed representation of the dynamics, it becomes necessary to make use of the Partial Wigner Transform which was introduced in Sec. 3.3.3. To this end, one begins by considering a system whose total Hamiltonian operator is of the form given by Eqn. (3.27), namely,

$$\hat{H}\left(\hat{R},\hat{P}\right)=\hat{H}_{\rm S}+\hat{H}_{\rm B}\left(\hat{R},\hat{P}\right)+\hat{H}_{\rm SB}\left(\hat{R}\right), \tag{4.1}$$

where $\hat{R}$ and $\hat{P}$ are the conjugate position and momentum operators. For such a system, the Heisenberg equation of motion for some arbitrary operator $\hat{\chi}$, is given by

$$\begin{aligned}\frac{\partial\hat{\chi}}{\partial t}&=\frac{\rm i}{\hbar}\left[\hat{H},\hat{\chi}\right]\\&=\frac{\rm i}{\hbar}\left(\hat{H}\hat{\chi}-\hat{\chi}\hat{H}\right).\end{aligned} \tag{4.2}$$

To obtain a mixed quantum-classical representation of the dynamics one applies the Partial Wigner Transform to the bath degrees of freedom. This results in a partially transformed total system Hamiltonian operator of the form

$$\hat{H}_{\rm W}\left(X\right)=\hat{H}_{\rm W,S}+\hat{H}_{\rm W,B}\left(X\right)+\hat{H}_{\rm W,SB}\left(\hat{R}\right). \tag{4.3}$$

Making use of the identity given by Eqn. (3.39), allows one to write Eqn. (4.2) as

$$\frac{\partial\hat{\chi}_W}{\partial t}=\frac{\rm i}{\hbar}\left(\hat{H}_W\,{\rm e}^{\frac{{\rm i}\hbar}{2}\overleftarrow{\partial}_i\mathcal{B}^c_{ij}\overrightarrow{\partial}_j}\hat{\chi}_W-\hat{\chi}_W\,{\rm e}^{\frac{{\rm i}\hbar}{2}\overleftarrow{\partial}_i\mathcal{B}^c_{ij}\overrightarrow{\partial}_j}\hat{H}_W\right), \tag{4.4}$$

where $\partial_i=\frac{\partial}{\partial X_i}$, and the overhead arrows represent the directions in which these operators act. In general, solving Eqn. (4.4) is a formidable task, which makes it difficult to simulate the dynamics numerically. For this reason, it becomes necessary to apply the quantum-classical approximation to Eqn. (4.4). This approximation works by taking a linear expansion of the exponential terms which appear in the equation of motion and ignoring all the higher order quantum correction terms to the evolution of the bath degrees of freedom. Doing this yields

$$\frac{\partial\hat{\chi}}{\partial t}=\frac{\rm i}{\hbar}\left[\hat{H}_W\left(1+\frac{{\rm i}\hbar}{2}\overleftarrow{\partial}_i\mathcal{B}^c_{ij}\overrightarrow{\partial}_j\right)\hat{\chi}_W-\hat{\chi}_W\left(1+\frac{{\rm i}\hbar}{2}\overleftarrow{\partial}_i\mathcal{B}^c_{ij}\overrightarrow{\partial}_j\right)\hat{H}_W\right]. \tag{4.5}$$

The form of the evolution equation given by Eqn. (4.5) is far easier to solve than that of Eqn. (4.4). This makes it easier to implement in numerical simulations. While ignoring all the higher order terms in the expansion may seem drastic, it should be noted that for certain cases Eqn. (4.5) is exact. Such cases arise if the bath Hamiltonian, $\hat{H}_{\mathrm{W,B}}$, is at most quadratic in R and P while the interaction Hamiltonian is of the form

$$\hat{H}_{\mathrm{W,SB}} = V_{\mathrm{B}}\left(R\right) \otimes H'_{\mathrm{S}}. \tag{4.6}$$

Here $V_{\mathrm{B}}\left(R\right)$ represents the bath potential, and only depends on the positions of the bath degrees of freedom, while H'_{S} acts only on the Hilbert space of the subsystem [84]. The reason that Eqn. (4.5) is exact for this class of Hamiltonians is that all the higher order terms of the expansion go to zero when acted upon $\hat{H}_{\mathrm{W,B}}$ and $\hat{H}_{\mathrm{W,SB}}$ [84]. The simplified equation of motion is also known as the quantum-classical Liouville equation of motion, it may be further simplified to obtain

$$\begin{aligned}\frac{\partial\hat{\chi}}{\partial t} &= \frac{\mathrm{i}}{\hbar}\left[\hat{H}_W, \hat{\chi}_W\right] - \frac{1}{2}\left\{\hat{H}_W, \hat{\chi}_W\right\} + \frac{1}{2}\left\{\hat{\chi}_W, \hat{H}_W\right\} \\ &= \left(\hat{H}_W, \hat{\chi}_W\right)_{\mathrm{QC}} \\ &= \mathrm{i}\mathcal{L}\hat{\chi}_W. \end{aligned} \tag{4.7}$$

In the above, the quantum-classical bracket $\left(\hat{H}_W, \hat{\chi}_W\right)_{\mathrm{QC}}$ has been introduced. This bracket is comprised of a combination of the quantum commutator and classical Poisson brackets. In the final line, the quantum-classical Liouville super-operator, $\mathrm{i}\mathcal{L}$, has also been introduced. It is possible to express this quantum-classical equation of motion, not in bracket form, but rather through the use of matrices. In its matrix form the quantum-classical Liouville equation of motion is [5, 35, 37, 38]

$$\frac{\partial\hat{\chi}}{\partial t} = \frac{\mathrm{i}}{\hbar}\begin{bmatrix} \hat{H}_W & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D}_{\mathrm{lin}} \cdot \begin{bmatrix} \hat{H}_W \\ \hat{\chi}_W \end{bmatrix}, \tag{4.8}$$

where the antisymmetric matrix super-operator is given by

$$\mathcal{D}_{\mathrm{lin}} = \begin{bmatrix} 0 & 1 + \frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}^c_{ij} \overrightarrow{\partial}_j \\ -\left(1 + \frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) & 0 \end{bmatrix}. \tag{4.9}$$

Since $\mathcal{D}_{\mathrm{lin}}$ is antisymmetric, the Hamiltonian operator $\hat{H}_{\mathrm{W}}$ is still a constant of motion [35]. The equivalence of the two forms of the evolution equation given by Eqns. (4.7) and (4.8) is explicitly shown in Appendix A.2. The von-Neumann equation is converted into the partial Wigner representation in exactly the same manner as that of the Heisenberg equation, due to the mathematical form of the two equations being identical apart from a difference in sign. The evolution equation for the density matrix, $\hat{\rho}$, in the partial Wigner representation is therefore given by:

$$\begin{aligned}\frac{\partial\hat{\rho}}{\partial t} &= -\frac{\mathrm{i}}{\hbar}\left[\hat{H}_W,\hat{\rho}_W\right] - \frac{1}{2}\left\{\hat{H}_W,\hat{\rho}_W\right\} + \frac{1}{2}\left\{\hat{\rho}_W,\hat{H}_W\right\} \\ &= -\left(\hat{H}_W,\hat{\rho}_W\right)_{\mathrm{QC}} \\ &= -\mathrm{i}\mathcal{L}\hat{\rho}_W \,. \end{aligned} \tag{4.10}$$

For a time independent Hamiltonian, Eqns. (4.7) and (4.10) have the following formal solutions [40]

$$\hat{\chi}_W\left(R,P,t\right) = e^{\mathrm{i}\mathcal{L}t}\hat{\chi}_W\left(R,P,0\right), \tag{4.11}$$

and

$$\hat{\rho}_W\left(R,P,t\right) = e^{-\mathrm{i}\mathcal{L}t}\hat{\rho}_W\left(R,P,0\right). \tag{4.12}$$

These formal solutions are an abstract quantity with regards to the quantum subsystem's degrees of freedom. To obtain a numerical integration scheme for the system dynamics, one must first represent the system within some basis, which spans the Hilbert space of the quantum subsystem. For a set of basis vectors $|\alpha\rangle$, which satisfy this condition, the solutions may then be expressed within that particular basis as [5, 40]

$$\chi_W^{\alpha\alpha'}\left(R,P,t\right) = \sum_{\beta\beta'}\left(\mathrm{e}^{\mathrm{i}\mathcal{L}t}\right)_{\alpha\alpha',\beta\beta'}\chi_W^{\beta\beta'}\left(R,P,0\right), \tag{4.13}$$

and

$$\rho_W^{\alpha\alpha'}\left(R,P,t\right) = \sum_{\beta\beta'}\left(\mathrm{e}^{-\mathrm{i}\mathcal{L}t}\right)_{\alpha\alpha',\beta\beta'}\rho_W^{\beta\beta'}\left(R,P,0\right). \tag{4.14}$$

In general, one is able to choose any basis one likes to work in, provided that the chosen basis spans the Hilbert space of the quantum subsystem. The most convenient basis for solving a problem is usually determined by two key factors, namely, the type of algorithm one is going to use to perform the numerical calculations, as well as the system being studied. For the work performed here, the adiabatic basis was used, as this has been shown to be a good basis to use in the simulation of quantum-classical systems via surface hopping trajectories [22], since the quantum-classical Liouville operator naturally splits into two parts when represented in this basis. The first part is responsible for the purely adiabatic dynamics, while the second part accounts for any non-adiabatic transitions which may occur in the subsystem as well as the subsequent changes in the bath energy. It is this convenient splitting of terms which makes this basis a suitable choice for use with surface hopping algorithms [40, 85].

4.1.1 The Adiabatic Basis

The adiabatic basis is defined by the eigenvalues of the eigenvalue equation [22, 35]

$$\hat{h}_W\left(R\right)\left|\alpha;R\right\rangle = E_\alpha\left(R\right)\left|\alpha;R\right\rangle, \tag{4.15}$$

where the adiabatic Hamiltonian $\hat{h}_W$, is given by

$$\hat{h}_W\left(R\right) = \frac{\hat{p}^2}{2m} + \hat{V}\left(\hat{q},R\right). \tag{4.16}$$

The first term represents the quantum kinetic operator while the second term represents the potential energy due to the coupling that exists between the quantum subsystem and the bath. Within this basis, the quantum-classical Liouville super-operator has the form [22, 40]

$$\mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'} = \left(\mathrm{i}\omega_{\alpha\alpha'} + \mathrm{i}L_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \mathsf{J}_{\alpha\alpha',\beta\beta'}. \tag{4.17}$$

The full derivation of the result given by Eqn. (4.17) may be found in Appendix B. The first term on the right hand side of the quantum-classical Liouville operator, $\omega_{\alpha\alpha'}$, is known as the Bohr frequency and is defined by the difference in energies of the adiabatic states α and α':

$$\omega_{\alpha\alpha'}\left(R\right) = \frac{E_\alpha\left(R\right) - E_{\alpha'}\left(R\right)}{\hbar}. \tag{4.18}$$

The second term, $\mathrm{i}L_{\alpha\alpha'}$, is the classical-like Liouville operator [22], defined as

$$\mathrm{i}L_{\alpha\alpha'} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F_W^\alpha + F_W^{\alpha'}\right)\frac{\partial}{\partial P}. \tag{4.19}$$

It is responsible for the classical-like evolution of the thermal bath. From its definition, one sees that this evolution is determined by the mean value of the Hellmann-Feynman forces for two adiabatic states α and α' [40]:

$$F_W^{\alpha\alpha'} = -\left\langle \alpha \left| \frac{\partial \hat{V}_W}{\partial R} \right| \alpha' \right\rangle . \tag{4.20}$$

This operator is the only operator which changes when the way one models the bath dynamics changes. The other operators in the Liouville super-operator do not change. The first two terms are responsible for the adiabatic evolution of the system. The final term, $\mathsf{J}_{\alpha\alpha',\beta\beta'}$, represents elements of the J-operator. The J-operator is a completely off diagonal, antisymmetric matrix that is quantum in nature. It describes the quantum jumping between energy states undergone by the system. This jumping between energy states is due to the non-adiabatic transitions which occur within the quantum subsystem. This operator also accounts for the variations of the bath momenta, which accompany these transitions. These variations are a consequence of energy conservation [40]. In this basis, the J-operator has the form

$$\begin{aligned} \mathsf{J}_{\alpha\alpha',\beta\beta'} = & -\frac{P}{M} \cdot d_{\alpha\beta} \left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} \\ & - \frac{P}{M} \cdot d^*_{\alpha'\beta'} \left(1 + \frac{1}{2} S^*_{\alpha'\beta'} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta}, \end{aligned} \tag{4.21}$$

where $S_{\alpha\beta} = \Delta E_{\alpha\beta} \hat{d}_{\alpha\beta} \left(\frac{P}{M} \cdot \hat{d}_{\alpha\beta} \right)^{-1}$, and $\Delta E_{\alpha\beta} = E_\alpha(R) - E_\beta(R)$. In this case, $\Delta E_{\alpha\beta}$ represents the energy difference between adiabatic states α and β. The non-adiabatic coupling matrix element, $d_{\alpha\beta}$, is defined as $d_{\alpha\beta} = \langle \alpha(R) \,|\, \nabla_R \,|\, \beta(R) \rangle$. It gives a measure of the strength of the coupling between the bath and the quantum subsystem when it is dotted with the momentum [40].

4.2 Numerical Implementation of the Evolution Equation

There are a number of possible methods one may use to numerically simulate the dynamics described by Eqn. (4.14), amongst these are the path integral formulation [86], the mean field approximation [87], and surface hopping schemes [40]. For the work presented here surface hopping schemes are utilized. These schemes allow one to simulate the quantum-classical dynamics in terms of swarms of trajectories. For these trajectories, the system undergoes classical-like evolution on single adiabatic potential energy surfaces or means of surfaces, which are interspersed by non-adiabatic trajectories. As such, Eqn. (4.14) needs to be recast into a form that is more suitable for use with surface hopping algorithms [22, 40, 85]. This is achieved through the use of the Dyson operator identity

$$\mathrm{e}^{(\hat{A}+\hat{B})t} = \mathrm{e}^{\hat{A}t} + \int_0^t \mathrm{d}t' \mathrm{e}^{\hat{A}(t-t')}\hat{B}\mathrm{e}^{(\hat{A}+\hat{B})t'} . \tag{4.22}$$

Applying this identity to the exponential term found in the solution yields

$$(\mathrm{e}^{-\mathrm{i}\mathcal{L}t})_{\alpha\alpha',\beta\beta'} = \mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha\alpha'}t}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \sum_{\nu\nu'}\int_0^t \mathrm{d}t' \mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha\alpha'}(t-t')}\mathrm{J}_{\alpha\alpha',\nu\nu'}\left(\mathrm{e}^{-\mathrm{i}\mathcal{L}t'}\right)_{\nu\nu',\beta\beta'} , \tag{4.23}$$

Substituting this result into Eqn. (4.13) then allows one to express the evolution equation as

$$\rho_W^{\alpha\alpha'}(R,P,t) = \mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha\alpha'}t}\rho_W^{\alpha\alpha'}(R,P,0) + \sum_{\nu\nu'}\int_0^t \mathrm{d}t' \mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha\alpha'}(t-t')}\mathrm{J}_{\alpha\alpha',\beta\beta'}\rho_W^{\beta\beta'}(R,P,t') . \tag{4.24}$$

This allows one to express the evolution equation in an iterative manner, which is far easier to implement on a computer for the purposes of simulation. The full solution at some time, t, may then be expressed as [40]

$$\begin{aligned}\rho_W^{\alpha_0\alpha'_0}(R,P,t) &= \mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha_0\alpha'_0}t}\rho_W^{\alpha_0\alpha'_0}(R,P) + \sum_{n=1}^{\infty}\sum_{(\alpha_1\alpha'_1)\ldots(\alpha_n\alpha'_n)}\int_0^{t_0}\mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\ldots\int_0^{t_{n-1}}\mathrm{d}t_n \\ &\times\prod_{k=1}^{n}\left[\mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha_{k-1}\alpha'_{k-1}}(t_{k-1}-t_k)}\mathrm{J}_{\alpha_{k-1}\alpha'_{k-1},\alpha_k\alpha'_k}\right]\mathrm{e}^{-\mathrm{i}\mathcal{L}^0_{\alpha_n\alpha'_n}t_n}\rho_W^{\alpha_n\alpha'_n}(R,P) ,\end{aligned} \tag{4.25}$$

where $\rho_W^{\alpha\alpha'}(R,P)$ is the initial value of the density matrix element. For an arbitrary observable, $\hat{\chi}$, the solution is given by

$$\begin{aligned}\chi_W^{\alpha_0\alpha'_0}(R,P,t) &= \mathrm{e}^{\mathrm{i}\mathcal{L}^0_{\alpha_0\alpha'_0}t}\chi_W^{\alpha_0\alpha'_0}(R,P) + \sum_{n=1}^{\infty}(-1)^n\sum_{(\alpha_1\alpha'_1)\ldots(\alpha_n\alpha'_n)}\int_0^{t_0}\mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\ldots\int_0^{t_{n-1}}\mathrm{d}t_n \\ &\times\prod_{k=1}^{n}\left[\mathrm{e}^{\mathrm{i}\mathcal{L}^0_{\alpha_{k-1}\alpha'_{k-1}}(t_{k-1}-t_k)}\mathrm{J}_{\alpha_{k-1}\alpha'_{k-1},\alpha_k\alpha'_k}\right]\mathrm{e}^{\mathrm{i}\mathcal{L}^0_{\alpha_n\alpha'_n}t_n}\chi_W^{\alpha_n\alpha'_n}(R,P) .\end{aligned} \tag{4.26}$$

By using either Eqn. (4.25) or Eqn. (4.26), along with a hybrid Monte-Carlo molecular-dynamics surface hopping algorithm, one is then able to represent the dynamics in a pertubative way [40]. The first terms on the right hand side of Eqns. (4.25) and (4.26) describe trajectories which do not undergo any non-adiabatic transitions, while the integral terms describe trajectories which have undergone an increasing number of non-adiabatic transitions in a pertubative manner. It should be noted that if the J operator is set to zero, then the integral terms fall away, and the dynamics is purely adiabatic.

4.3 Extended Systems to Model Constant Temperature Baths

If one wants to simulate a thermal bath, using the extended systems discussed earlier, one needs to only modify the antisymmetric matrix $\mathcal{B}^c$, which appears in the Heisenberg equation of motion [1, 35]. This modification amounts to replacing this matrix with the one belonging to the extended system one would like to use. The Hamiltonian operator has the form

$$\hat{H} = H' + \hat{h}_{\mathrm{S}}, \tag{4.27}$$

where $\hat{h}_{\mathrm{S}}$ is the subsystem Hamiltonian defined as

$$\hat{h}_{\mathrm{S}} = \hat{K} + \hat{V}\left(\hat{q}, R\right). \tag{4.28}$$

$\hat{K}$ represents the quantum kinetic operator while $\hat{V}\left(\hat{q}, R\right)$ represents the potential operator coupling the quantum subsystem to the classical bath. In Eqn. (4.27) H' represents the kinetic energy of the bath, as well as the total energy of the fictitious thermostat variables which depends on the thermostat scheme being used. Using the modified matrices $\mathcal{B}$, along with a Hamiltonian operator $\hat{H}$, allows one to derive quantum-classical laws of motion where the quantum subsystem is in contact with a thermal bath. To this end, a sketch of how to apply the NHC constant temperature dynamics within the quantum-classical equation of motion is presented. This is followed by a sketch of how the NHP constant temperature dynamics may then extended to the quantum-classical case.

4.3.1 Quantum-Classical Nosé-Hoover Chains

The NHC Hamiltonian operator is defined as

$$\hat{H}^{NHC} = \frac{\hat{p}^2}{2m} + \frac{P^2}{2M} + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P^2{}_{\eta_2}}{2M_{\eta_2}} + \hat{V}(\hat{q}, R) + gk_{\mathrm{B}}T(\eta_1 + \eta_2)\,.$$

The classical phase-space point for this system is $X = (R, \eta_1, \eta_2, P, P_{\eta_1}, P_{\eta_2})$. For the case shown here we limit ourselves to the study of a chain comprised only of two thermostat coordinates. This is done for simplicity, as well as to keep the algebra manageable. An extension to n-dimensional thermostat coordinates is easily achieved. As stated earlier, the antisymmetric matrix associated with this scheme is

$$\mathcal{B}^{\mathrm{NHC}} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -P & 0 \\ 0 & -1 & 0 & P & 0 & -P_{\eta_1} \\ 0 & 0 & -1 & 0 & P_{\eta_1} & 0 \end{bmatrix}.$$

This matrix may be used to generalize the Liouville super-operator which appears in the equations of motion. To this end, we substitute $\mathcal{B}^{\mathrm{NHC}}$ in place of $\mathcal{B}^{\mathrm{c}}$ in Eqn. (4.9), this produces the NHC matrix super-operator to linear order:

$$\mathcal{D}_{\mathrm{lin}}^{\mathrm{NHC}} = \begin{bmatrix} 0 & 1 + \frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}_{ij}^{\mathrm{NHC}} \overrightarrow{\partial}_j \\ -\left(1 + \frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}_{ij}^{\mathrm{NHC}} \overrightarrow{\partial}_j\right) & 0 \end{bmatrix}. \tag{4.29}$$

The quantum-classical equation of motion is then given by

$$\frac{\partial \hat{\chi}}{\partial t} = \frac{\mathrm{i}}{\hbar} \begin{bmatrix} \hat{H}_W^{\mathrm{NHC}} & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D}_{\mathrm{lin}}^{\mathrm{NHC}} \cdot \begin{bmatrix} \hat{H}_W^{\mathrm{NHC}} \\ \hat{\chi}_W \end{bmatrix}, \tag{4.30}$$

As shown previously, this equation may also be expressed through the use of the Liouville super-operator in the adiabatic basis as

$$\frac{\partial \chi^{\alpha\alpha'}}{\partial t} = \sum_{\beta\beta'} \mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'}^{\mathrm{NHC}} \chi^{\beta\beta'}\,. \tag{4.31}$$

In this basis the NHC Liouville super-operator is given by

$$\mathrm{i}\mathcal{L}^{\mathrm{NHC}}_{\alpha\alpha',\beta\beta'} = \left(\mathrm{i}\omega_{\alpha\alpha'} + \mathrm{i}L^{\mathrm{NHC}}_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} - \mathsf{J}_{\alpha\alpha',\beta\beta'}, \tag{4.32}$$

while the classical-like NHC Liouville operator is

$$\begin{aligned}\mathrm{i}L^{\mathrm{NHC}}_{\alpha\alpha'} = {} & \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F^{\alpha} + F^{\alpha'}\right)\frac{\partial}{\partial P} + \sum_{k=1}^{2}\left(\frac{P_{\eta_k}}{M_{\eta_k}}\frac{\partial}{\partial \eta_k} + F_{P_{\eta_k}}\frac{\partial}{\partial P_{\eta_k}}\right) \\ & - \frac{P_{\eta_2}}{M_{\eta_2}}P_{\eta_1}\frac{\partial}{\partial P_{\eta_1}}. \end{aligned}\tag{4.33}$$

In defining this classical-like operator the system forces

$$F_{P_{\eta_k}} = \frac{P^2_{\eta_k}}{M_{\eta_k}} - gK_bT,$$

have been used.

4.3.2 Quantum-Classical Nosé-Hoover Power Thermostat

Following the same procedure as that of the NHC case, we begin by defining the NHP Hamiltonian operator as

$$\hat{H}^{\mathrm{NHP}} = \frac{\hat{p}^2}{2m} + \frac{P^2}{2M} + \frac{P^2_{\eta}}{2M_{\eta}} + \hat{V}\left(\hat{q}, R\right) + gk_{\mathrm{B}}T\eta, \tag{4.34}$$

where all the symbols have their regular meaning. The classical phase-space point for this scheme is $X = (R, \eta, P, P_\eta)$, while the antisymmetric matrix associated with this scheme is defined in Eqn. (2.29) as

$$\mathcal{B}^{\mathrm{NHP}} = \begin{bmatrix} 0 & 0 & 1 & \tau P/m \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ -\tau P/m & -1 & P & 0 \end{bmatrix}.$$

Substituting $\mathcal{B}^{\mathrm{NHP}}$ in place of $\mathcal{B}^{c}$ produces the NHP matrix super-operator to linear order as

$$\mathcal{D}^{\mathrm{NHP}}_{\mathrm{lin}} = \begin{bmatrix} 0 & 1 + \frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i\mathcal{B}^{\mathrm{NHP}}_{ij}\overrightarrow{\partial}_j \\ -\left(1 + \frac{\mathrm{i}\hbar}{2}\overleftarrow{\partial}_i\mathcal{B}^{\mathrm{NHP}}_{ij}\overrightarrow{\partial}_j\right) & 0 \end{bmatrix}, \tag{4.35}$$

The quantum-classical equation of motion for the NHP thermostat is then given by

$$\frac{\partial\hat{\chi}}{\partial t} = \frac{\mathrm{i}}{\hbar}\begin{bmatrix} \hat{H}_W^{\mathrm{NHP}} & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D}_{\mathrm{lin}}^{\mathrm{NHP}} \cdot \begin{bmatrix} \hat{H}_W^{\mathrm{NHP}} \\ \\ \hat{\chi}_W \end{bmatrix}, \tag{4.36}$$

This may be expressed in terms of the Liouville super-operator in the adiabatic basis as

$$\frac{\partial\chi^{\alpha\alpha'}}{\partial t} = \sum_{\beta\beta'} \mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'}^{\mathrm{NHP}}\chi^{\beta\beta'}. \tag{4.37}$$

In this basis, the NHP Liouville super-operator is given by

$$\mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'}^{\mathrm{NHP}} = \left(\mathrm{i}\omega_{\alpha\alpha'} + \mathrm{i}L_{\alpha\alpha'}^{\mathrm{NHP}}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \mathsf{J}_{\alpha\alpha',\beta\beta'}, \tag{4.38}$$

where the classical-like NHP Liouville operator is

$$\mathrm{i}L_{\alpha\alpha'}^{\mathrm{NHP}} = \left(L_1^{\mathrm{NHP}} + L_2^{\mathrm{NHP}} + L_3^{\mathrm{NHP}}\right) + \frac{F^{\alpha} + F^{\alpha'}}{2}\left[\frac{P}{\partial P} + \tau\frac{P}{M}\frac{\partial}{\partial P_\eta}\right]. \tag{4.39}$$

The Liouville operators appearing in Eqn. (4.39) are given by

$$\begin{aligned} L_1^{\mathrm{NHP}} &= \frac{P}{M}\frac{\partial}{\partial R} + \frac{P^2}{M}\frac{\partial}{\partial P_\eta}, \\ L_2^{\mathrm{NHP}} &= -\frac{\partial V(R)}{\partial R}\left[\frac{\partial}{\partial P} + \tau\frac{P}{M}\frac{\partial}{\partial P_\eta}\right], \\ L_3^{\mathrm{NHP}} &= \frac{P_\eta}{M_\eta}\left[\tau\frac{P}{M}\frac{\partial}{\partial R} + \frac{\partial}{\partial\eta} - P\frac{\partial}{\partial P}\right], \end{aligned}$$

where all the symbols have their regular meanings. Since the extension of NHP thermostat to the quantum-classical case was only recently published [52], the full mathematical details of its super-operator derivation may be found in Appendix C.

4.3.3 Application of NHP to the Spin-Boson Model

To test the NHP algorithm simulations were run using the using the spin-boson model. The main reason that this model was chosen is that it is a very well studied model and, as such, it gives one an easy way to check the efficiency and accuracy of any new algorithms. The spin-boson model is made up of a simple two-level quantum subsystem coupled to a boson bath. The quantum subsystem is made up of a single spin with states $|\uparrow\rangle$ and

$|\downarrow\rangle$, while quantum harmonic oscillators are used to represent the bosonic bath. The Hamiltonian operator for this model is

$$\hat{H}^{\mathrm{sb}} = -\hbar\Omega\hat{\sigma}_x + \sum_{j=1}^{N_{\mathrm{B}}}\left(\frac{\hat{P}_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2\hat{R}_j^2 - c_j\hat{R}_j\hat{\sigma}_z\right), \tag{4.40}$$

where $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are the usual Pauli matrices. The energy gap of the isolated two-level system is given by $2\hbar\Omega$, where Ω is a constant. The summation which appears is over all the bath oscillators. The mass, frequency and coupling strength between the system and the j-th oscillator are denoted by M_j, ω_j and c_j, respectively. These parameters are fixed, by requiring that the harmonic bath be described by an Ohmic spectral density [37]. To ensure this, the coupling strength and frequencies were chosen to be the same as those introduced in [88, 89] namely

$$c_j = \omega_j\sqrt{\xi\hbar\omega_0 M_j}, \tag{4.41}$$

and

$$\omega_j = -\omega_c \ln\left(1 - j\frac{\omega_0}{\omega_c}\right), \tag{4.42}$$

where

$$\omega_0 = \frac{\omega_c}{N_b}\left(1 - e^{-\omega_{\mathrm{max}}/\omega_c}\right). \tag{4.43}$$

In these equations the Kondo parameter, ξ, which gives a measure of the coupling strength between the quantum subsystem and bath has been introduced, along with the cutoff frequency ω_c. Defining c_j and ω_j in this way gives one an efficient way to represent an infinite bath whose spectral density is Ohmic via the use of a finite number of degrees of freedom [84].

Applying the partial Wigner transform to the spin-boson Hamiltonian yields the quantum-classical Hamiltonian operator

$$\hat{H}_{\mathrm{W}}^{\mathrm{sb}} = -\hbar\Omega\hat{\sigma}_x + \sum_{j=1}^{N_{\mathrm{B}}}\left(\frac{P_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2 R_j^2 - c_j R_j\hat{\sigma}_z\right), \tag{4.44}$$

where the subscript W is used to denote the partial Wigner transform. This Hamiltonian operator now depends on both the spin degrees of freedom used to represent the subsystem, and the classical phase-space coordinates used to represent the bath.

This Hamiltonian operator may be decomposed into a sum of three terms as

$$\hat{H}_{\rm W}^{\rm sb} = \hat{h}_{\rm S} + H_{\rm B} + \hat{V}_{\rm C}(R), \tag{4.45}$$

where $\hat{h}_{\rm S}$ represents the quantum subsystem Hamiltonian

$$\hat{h}_{\rm S} = -\hbar\Omega\hat{\sigma}_x, \tag{4.46}$$

the bath Hamiltonian, $H_{\rm B}$, is given by

$$H_{\rm B} = \sum_{j=1}^{N_{\rm B}} \left(\frac{P_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2 R_j^2 \right), \tag{4.47}$$

and the coupling potential energy, $\hat{V}_{\rm C}(R)$, is defined as

$$\hat{V}_{\rm C}(R) = -\sum_{j=1}^{N_{\rm B}} c_j R_j \hat{\sigma}_z. \tag{4.48}$$

It should be noted that, for convenience, all oscillator masses were taken to be the same, although they may in general be different.

The simulation of this model within the microcanonical ensemble (NVE) requires one to represent the bath using $N_{\rm B} = 200$ oscillators. The reason this many oscillators are used is that this is the minimum number required to ensure that the obtained results are in agreement with those predicted by linear response theory [90]. The results of these NVE dynamics are compared with those obtained from the simulations of the spin-boson model where the quantum-classical NHC and NHP dynamics have been used to simulate the bath. For this model both these schemes are comprised of a bath made up by just one harmonic oscillator $N_{\rm B} = 1$.

For the spin-boson model, the quantum-classical NHC Hamiltonian operator is given by

$$\hat{H}_{\rm W}^{\rm NHC} = \hat{H}_{\rm W}^{\rm sb} + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P_{\eta_2}^2}{2M_{\eta_2}} + N_{\rm B}k_{\rm B}T\eta_1 + k_{\rm B}T\eta_2, \tag{4.49}$$

while the NHP Hamiltonian operator for the same model is

$$\hat{H}_{\rm W}^{\rm NHP} = \hat{H}_{\rm W}^{\rm sb} + \frac{P_\eta^2}{2M_\eta} + N_{\rm B}k_{\rm B}T\eta. \tag{4.50}$$

Scaled Units

In the performed simulations, scaled, dimensionless units were used. This was done to ensure that when the simulations were performed, there was no loss of accuracy in the obtained results as a result of the round off error associated with multiplying very large numbers by very small ones. Errors of this nature occur when using SI units. Dimensionless units are obtained through scaling the phase-space variables (R, P) as [84]

$$R'_j = \left(\frac{M_j\omega_c}{\hbar}\right)^{\frac{1}{2}} \quad \text{and} \quad P'_j = \left(\hbar M_j\omega_c\right)^{-\frac{1}{2}} P_j. \tag{4.51}$$

This, in turn, leads to the spin-boson Hamiltonian being redefined in scaled units as

$$\hat{H}_{\mathrm{W}}^{\mathrm{sb}'} = -\Omega'\hat{\sigma}_x + \sum_{j=1}^{N_b}\left(\frac{P_j'^2}{2} + \frac{1}{2}{\omega_j'}^2{R_j'}^2 - {c_j'}^2\hat{\sigma}_z R_j'\right), \tag{4.52}$$

where

$$\Omega' = \frac{\Omega}{\omega_c}, \quad \omega_j = \frac{\omega_j}{\omega_c}, \quad c_j = \omega_j\sqrt{\xi\frac{\omega_0}{\omega_c}}. \tag{4.53}$$

While the dimensionless inverse temperature and time may be expressed as [84]

$$\beta' = \frac{\hbar\omega_c}{k_{\mathrm{B}}T} \quad \text{and} \quad t' = t\omega_c, \tag{4.54}$$

respectively. From now on, only the scaled units will be considered. As such, the primes from the notation will be disregarded, and it will be understood that dimensionless variables have been used.

4.3.4 Simulation Procedures

An Eulerian description of the dynamics is used, with swarms of trajectories propagated forward in time, where each individual trajectory represents the evolution of a phase-space point. The observable is calculated after each time step at the new phase-space coordinate. A schematic representation of the simulation procedure is shown in Fig. 4.1. Each trajectory starts with the bath and system decoupled at time $t = 0$. The initial phase-space point of the trajectory is obtained by sampling from the bath distribution function. The subsystem is initially in a pure eigenstate corresponding to the excited

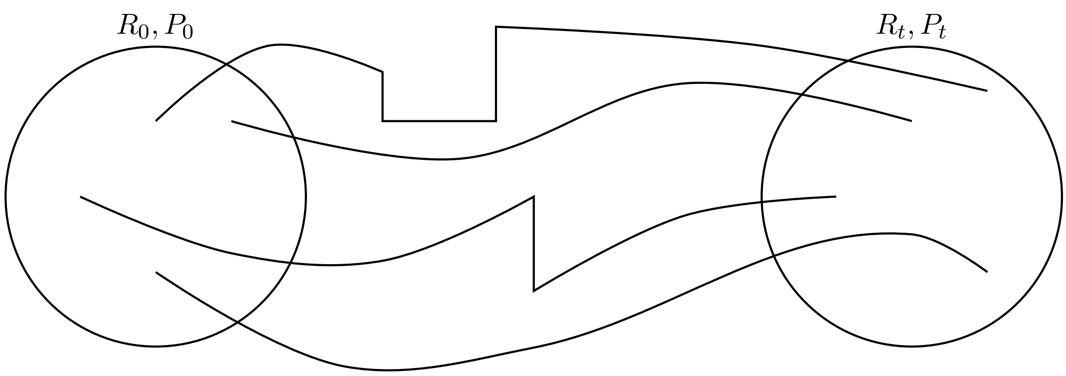

Figure 4.1: Schematic representation of how the simulation is run. Swarms of trajectories are propagated from sampled initial phase space points at time $t = 0$. In addition to their adiabatic evolution, these trajectories may undergo non-adiabatic transitions represented by the vertical lines. The value of the observable is then obtained by averaging over all the trajectories.

state, while the bath is in thermal equilibrium. The initial density matrix is simply a product of the subsystem density matrix and the bath distribution function:

$$\hat{\rho}\left(0\right) = \hat{\rho}_{\mathrm{S}}\left(0\right) \otimes \hat{\rho}_{\mathrm{B}} \ , \tag{4.55}$$

where

$$\hat{\rho}_{\mathrm{S}} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \ . \tag{4.56}$$

The bath distribution function is given by

$$\rho_{\mathrm{B}}\left(R, P\right) = \frac{\mathrm{e}^{-\beta \hat{H}_{\mathrm{B}}}}{Z_{\mathrm{B}}} \tag{4.57}$$

where H_{B} denotes the bath Hamiltonian, and Z_{B} is its partition function. The partial Wigner transform of the initial density operator is

$$\hat{\rho}_{\mathrm{W}}\left(0\right) = \hat{\rho}_{\mathrm{S}}\left(0\right) \rho_{\mathrm{BW}}\left(R, P\right) \ , \tag{4.58}$$

where the Wigner transformed bath distribution function in dimensionless variables is given by [63, 84]

$$\rho_{\mathrm{W\ B}}(R,P)=\prod_{j=1}^{N_{\mathrm{B}}}\frac{\tanh\left(\beta\omega_j/2\right)}{\pi}\times\left[-\frac{2\tanh\left(\beta\omega_j/2\right)}{\omega_j}H_{\mathrm{B}}\right]\ . \tag{4.59}$$

This function is obtained by taking a Wigner transform of the Bloch equation for an ensemble of quantum harmonic oscillators. Its full mathematical derivation may be found in Appendix D.

Calculation of the Observable

The expectation value of an arbitrary observable, $\hat{\chi}$, under the action of a partial Wigner transformation is

$$\langle\chi\rangle=\mathrm{Tr}\int\int \mathrm{d}R\,\mathrm{d}P\ \hat{\chi}_{\mathrm{W}}\hat{\rho}_{\mathrm{W}}\ . \tag{4.60}$$

For the work done here, the expectation value associated with the operator $\hat{\sigma}_z$ was calculated. This operator is simply one of the Pauli spin matrices defined as

$$\hat{\sigma}_z=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\ . \tag{4.61}$$

This particular observable was chosen, as it makes it possible to compare the results we obtained with those found in the literature. The expectation value of this operator

$$\langle\hat{\sigma}_z\left(R,P,t\right)\rangle=\sum_{\alpha\alpha'}\int \mathrm{d}R\,\mathrm{d}P\ \rho_{\mathrm{W}}^{\alpha'\alpha}\sigma_z^{\alpha\alpha'}\left(R,P,t\right)\ , \tag{4.62}$$

represents the population difference of the two energy levels of the quantum subsystem. It was found that the NHP dynamics reproduce the damping of the spin population that would be achieved by a harmonic bath comprised of 200 harmonic oscillators with Ohmic spectral density and no temperature control. This was verified for a range of inverse temperatures, $\beta\in(0.1,3.0)$, and coupling constants, $\xi\in(0.002,0.1)$. Initially the action of the jump operator has been disregarded, which amounts to performing an adiabatic approximation on the dynamics, once the adiabatic simulation calculations were complete, the action of the jump operator was introduced and the non-adiabatic evolution calculated.

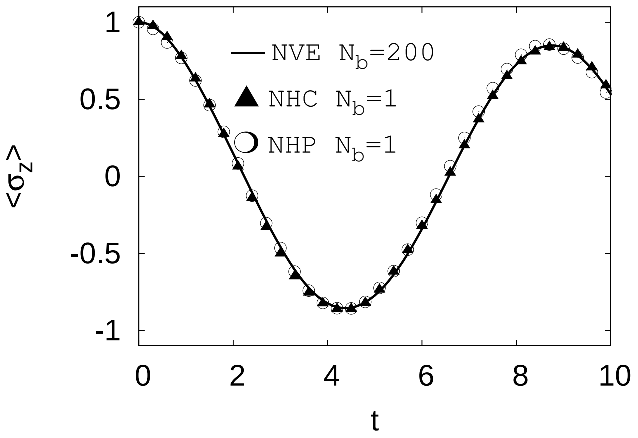

Figure 4.2: The adiabatic dynamics of the spin-boson model with the parameters: $\beta = 0.1$, $\Omega = 1/3$, $\omega_{\max} = 3$, $\xi = 0.002$. The circles represent the NHP results with $N_b = 1$; The triangles represent the NHC results with $N_b = 1$; while the line represents the NVE results with $N_b = 200$.

Figure 4.2 displays the adiabatic dynamics of the spin-boson model with parameters $\beta = 0.1$, $\Omega = 1/3$, $\omega_{\max} = 3$ and $\xi = 0.002$. These are the same parameters found in [37], they were chosen to test if the NHP thermostat could reproduce the results available in the literature. As can clearly be seen from the plots, there is an excellent agreement with the results obtained using the computationally more expensive Hamiltonian (NVE) dynamics. The comparison between the long-time NHP and NHC dynamics given in Fig. 4.3 shows that the NHP thermostat may be used in place of the NHC thermostat for calculations of this type.

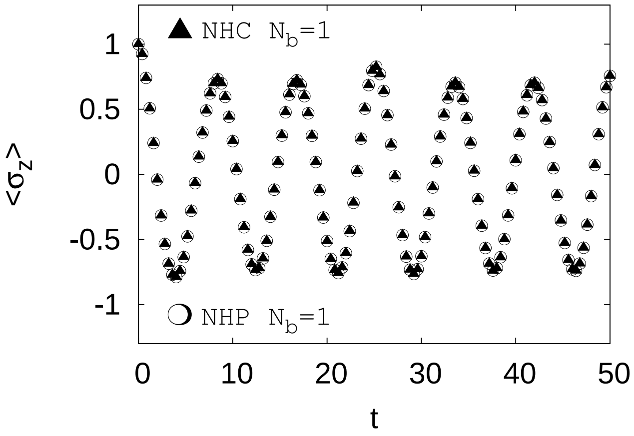

Figure 4.3: Long time adiabatic dynamics of the spin boson model. The simulation parameters were: $\beta = 3.0$, $\Omega = 1/3$, $\omega_{\text{max}} = 3$, $\xi = 0.1$. The circles represent the NHP dynamics with $N_b = 1$ The triangles represent the NHC dynamics with $N_b = 1$.

As stated earlier, this high degree of agreement was found for all adiabatic simulations performed using various parameters within the given range. Calculations were also performed for the case of non-adiabatic dynamics. The results of these calculations are shown in Figs. 4.4 and 4.5. As can clearly be seen a good agreement was found between the NHP and NHC dynamics, which both outperformed the Hamiltonian dynamics calculation.

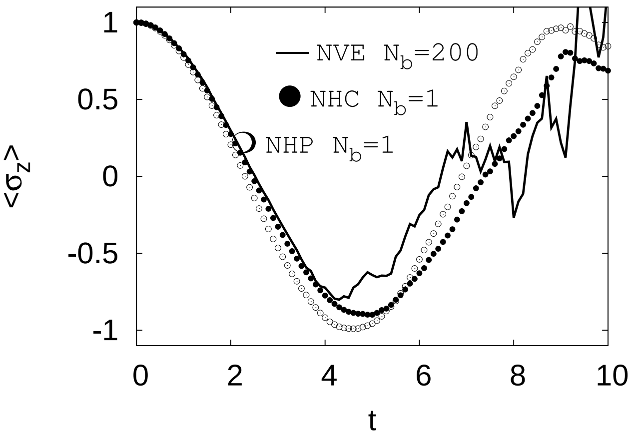

Figure 4.4: Non-adiabatic dynamics of the spin-boson model including up to six quantum transitions. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{\max} = 3$, $\beta = 3.0$. The white circles represent the results obtained with use of the NHP dynamics with $N_b = 1$. The black circles represent the NHC dynamics with $N_b = 1$. The continuous black line represents the NVE dynamics with $N_b = 200$.

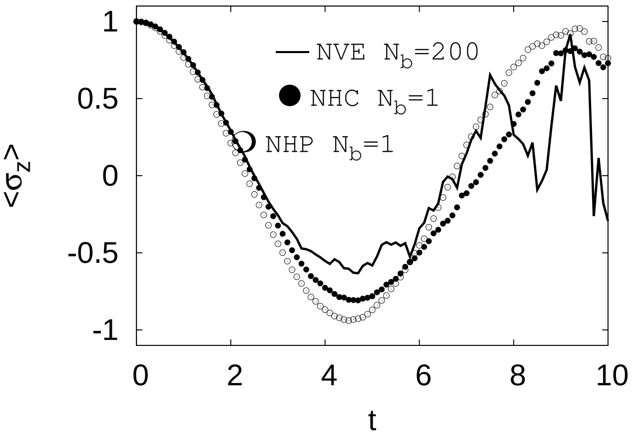

Figure 4.5: Non-adiabatic dynamics of the spin-boson model including up to six quantum transitions. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{\max} = 3$, $\beta = 2.0$,. The white circles represent the results obtained with use of the NHP dynamics with $N_b = 1$. The black circles represent the NHC dynamics with $N_b = 1$. The continuous black line represents the NVE dynamics with $N_b = 200$.

Chapter 5

Numerical Study of a Two-spin Chain

This chapter contains the numerical study of a two-spin chain, where each spin is coupled to its own independent thermal bath. In particular the reduced density matrix and entanglement dynamics are studied with the later done via the concurrence.

The study of systems comprised of coupled qubits, where each qubit is coupled to its own environment is not only of theoretical interest, but occurs frequently in the field of nano-physics. Examples of such occurrences include the transfer of quantum information between the nuclear and electronic spins in semi conductor quantum dots [91–93]. Here the nuclear spin is generally weakly coupled to its environment while the electronic spin experiences strong coupling to various degrees of freedom within the solid [33]. Due to this difference in the coupling strengths the effective environments are different for the two kinds of spins. Another way one might set up two different environments, for such a system, is through the use of nuclear magnetic resonance techniques which may be used to lower the temperature of the nuclear spins in a controlled manor. This lowering of the temperature, for the nuclear degrees of freedom, does not have any significant effect on the temperature of the electronic spins [94, 95]. Doing this creates a situation where the two spin degrees of freedom are in contact with two thermal baths having different effective temperatures. A final example, which may be readily designed, is that of inductively coupled superconductor flux qubits which are in contact with two different environments. Details regarding the workings and design of this system may be found in Ref. [96]. For the work presented here we have chosen to focus our study on a quantum system for which the amount of entanglement may be evaluated exactly [83]. To this end the model used is that of two spins (qubits) coupled to two different thermal baths, at different temperatures. Systems of this nature are generally known as spin-chain systems and may in general consist of more than two spins [97]. The quantum dynamics of these spin-chains, coupled to bosonic thermal baths is a topic of great interest within the field of quantum information [32–34]. While the simulation of such systems is usually tackled via the use of master equations [34], it is possible to use the mixed Wigner-Heisenberg representation of quantum mechanics, which was introduced in Sec. 3.3.1, to numerically simulate the dynamics of these systems. Having this in mind, a study was performed on the evolution in time of the reduced density matrix, along with the entanglement dynamics, via the concurrence, of a minimal chain consisting of two spins, where each spin is coupled to its own bath of harmonic oscillators. The system is constructed in such a way that the temperature of each bath may be defined independently. Doing this allows us to study non-equilibrium situations. It should be noted at this stage that the total system dynamics are unitary and numerically exact for the class of Hamiltonian under study. As such, for the work presented here, there is no need for one to make use of the Markovian or rotating wave approximation.

5.1 System Model

The total system Hamiltonian in the partial Wigner representation is given by

$$\hat{H}_W(R,P) = \hat{H}_S + H_{W,B}(R,P) + \hat{H}_{W,SB}(R) \ . \tag{5.1}$$

The subsystem Hamiltonian which represents the chain of two quantum spins that are coupled to each other is given by,

$$\hat{H}_S = -j_x \hat{\sigma}_x^{(1)} \hat{\sigma}_x^{(2)} - j_y \hat{\sigma}_y^{(1)} \hat{\sigma}_y^{(2)} - j_z \hat{\sigma}_z^{(1)} \hat{\sigma}_z^{(2)} \ . \tag{5.2}$$

The constants j_i, where $i = x, y, z$, dictate the strength of the coupling between the spins which make up the chain. The operators $\hat{\sigma}_i^{k_s}$ represent the Pauli matrix operators for spin k_s where $k_s = 1, 2$. The bath Hamiltonian is given by

$$H_{W,B} = \sum_{k_s=1}^{2} \sum_{I=1}^{N} \frac{P_{I,k_s}^2}{2} + \frac{1}{2} \omega_I^2 R_{I,k_s}^2 + H_{I,k_s}^{\mathrm{NHC}} \ . \tag{5.3}$$

It represents two independent harmonic oscillator baths having coordinates, R_{I,k_s}, and momenta, P_{I,k_s}. The subscript I, where $I = 1, N$, has been used to label the oscillators while k_s has again been used to identify the different spins. For the work presented here N was assigned a value of 200. The harmonic oscillator frequencies, ω_I, have been taken to be bath independent, due the desire that both baths should have an identical Ohmic spectral density. The final term in Eqn. (5.3) represents the fictitious NHC thermostat variables which are attached to the individual bath degrees of freedom

$$H^{\mathrm{NHC}} = \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P_{\eta_2}^2}{2M_{\eta_2}} + g k_{\mathrm{B}} T \left(\eta_1 + \eta_2 \right) \ . \tag{5.4}$$

Attaching these to the individual bath degrees of freedom allows one to control the individual thermal fluctuations of these degrees. The last term of the total system Hamiltonian represents the coupling between the subsystem and bath

$$\hat{H}_{\mathrm{W,SB}} = \sum_{k_s=1}^{2} \sum_{I=1}^{N} C_I R_{I,k_s} \hat{\sigma}_z^{(k_s)} \ , \tag{5.5}$$

where the coupling constants, C_I, have been defined following the method found in [88, 89] such that the spectral density of the bath is Ohmic. The distribution function for this system is given by

$$\rho_{W,B}\left(X, t_0\right) = \prod_{k_s=1}^{2} \prod_{I=1}^{N} \frac{\tanh\left(\beta_{k_s} \omega_I / 2\right)}{\pi} \exp\left[\frac{-2 \tanh\left(\beta_{k_s} \omega_I / 2\right)}{\omega_I} H_{W,B} \right] \ . \tag{5.6}$$

The inverse temperature of each oscillator bath is given by β_{k_s}, while $H_{W,B}$ is the partially Wigner transformed bath Hamiltonian defined in Eqn. (5.3). To control the thermal fluctuations of each individual bath oscillator it becomes necessary to define an effective inverse temperature for each oscillator. To this end we define

$$\tilde{\beta}_{k_s,I} = \frac{2\tanh\left(\beta_{k_s}\omega_I/2\right)}{\omega_I} \tag{5.7}$$

to be the effective inverse temperature of the I-th mode, having an effective Hamiltonian given by

$$H_0^I = \frac{P_{I,k_s}^2}{2m_{I,k_s}} + \frac{1}{2}\omega_I^2 R_{I.k_s}^2 + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P_{\eta_2}^2}{2M_{\eta_2}} + gk_{\mathrm{B}}T\left(\eta_1 + \eta_2\right) \ . \tag{5.8}$$

Substituting Eqns. (5.7) and (5.8) into Eqn. (5.6) allows one to write the Wigner function of the bath as

$$\rho_{W,B}\left(X, t_0\right) = \prod_{k_s=1}^{2}\prod_{I=1}^{N} \frac{\tanh\left(\beta_{k_s}\omega_I/2\right)}{\pi} \ \exp\left[-\tilde{\beta}_{I,k_s} H_0^I\right] \ . \tag{5.9}$$

Since $\tilde{\beta}_{k_s,I}$ is different for each harmonic mode, the equipartition theorem no longer holds for the distribution function given by Eqn. (5.9). However, it can be shown that in the limit of high temperature, $\tilde{\beta}_{k_s,I} \to \beta_{k_s}$, as such the quantum distribution function given by Eqn. (5.9), reduces to

$$\rho_{W,B}\left(X, t_0\right) = \prod_{k_s=1}^{2}\prod_{I=1}^{N} \frac{\tanh\left(\beta_{k_s}\omega_I/2\right)}{\pi} \ \exp\left[-\beta_{k_s} H_0^I\right] \ , \tag{5.10}$$

in the classical limit where $\beta_{k_s} = \left(k_{\mathrm{B}}\, T_{k_s}\right)^{-1}$.

For the work presented here an initially uncorrelated density matrix was assumed. The partial Wigner transform of this density matrix is given by the product of the reduced density matrix of the subsystem and the bath distribution function

$$\hat{\rho}_W\left(t_0\right) = \hat{\rho}_S\left(t_0\right)\rho_{W,B}\left(X, t_0\right) \ . \tag{5.11}$$

This initial system configuration represents a thermal state of the system, as a result, $\rho_{W,B}$ is positive definite everywhere. Since the dynamics of the bath are harmonic with a bilinear coupling between the subsystem and bath, $\rho_{\mathrm{W,B}}$ will not change sign. This is of importance, as it means that the bath will evolve in a classical-like fashion which is exactly equivalent to the dynamics being fully quantum. Using this thermal sampling, along with a thermostatting scheme of our choosing, it becomes possible to study the relaxation of this nano-system. A series of simulations was performed where the temperature of one bath was held constant through out, while that of the second bath was increased from one simulation to the next until the classical limit had been reached.

The dynamics of the reduced density matrix are governed by the von-Neumann equation [Eqn. (4.10)] whose solution is given by Eqn. (4.14):

$$\hat{\rho}_W(R,P,t) = \mathrm{e}^{-\mathrm{i}\mathcal{L}t}\hat{\rho}_W(R,P,0) \ .$$

The dynamics are again formulated in the adiabatic basis to take advantage of the splitting which occurs between the adiabatic and non-adiabatic evolution terms. Within this basis, the solution may be written in its propagator form as

$$\rho_W^{\alpha\alpha'}(R,P,t) = \sum_{\beta\beta'}\left(\mathrm{e}^{-\mathrm{i}\mathcal{L}t}\right)_{\alpha\alpha',\beta\beta'}\rho_W^{\beta\beta'}(R,P,0) \ . \tag{5.12}$$

where the quantum-classical Liouville super-operator has the form

$$\mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'} = \mathcal{L}^0_{\alpha\alpha'\beta\beta'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \mathsf{J}_{\alpha\alpha',\beta\beta'} \ . \tag{5.13}$$

The adiabatic evolution of the dynamics is governed by:

$$\mathcal{L}^0_{\alpha\alpha'\beta\beta'} = \mathrm{i}\omega_{\alpha\alpha'} + \mathrm{i}L_{\alpha\alpha'} \ , \tag{5.14}$$

where

$$\omega_{\alpha\alpha'}(R) = \frac{E_\alpha(R) - E_{\alpha'}(R)}{\hbar} \ .$$

and

$$\mathrm{i}L_{\alpha\alpha'} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F_W^\alpha + F_W^{\alpha'}\right)\frac{\partial}{\partial P} \ ,$$

where all the symbols have the same meaning as those of Section 4.1.1. The operator responsible for the classical-like evolution of the thermal bath, $\mathrm{i}L_{\alpha\alpha'}$is the only operator which changes when the way in which the bath dynamics are modelled changes. The other operators in the Liouville super-operator do not change. For the NHC thermostatted bath the classical like Liouville operator is defined as [35],

$$\begin{aligned}\mathrm{i}L^{\mathrm{NHC}}_{\alpha\alpha'} = {} & \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F_W^\alpha + F_W^{\alpha'}\right)\frac{\partial}{\partial P} + \frac{P_{\eta_1}}{M_{\eta_1}}\frac{\partial}{\partial \eta_1} + F_{P_{\eta_1}}\frac{\partial}{\partial P_{\eta_1}} \\ & + \frac{P_{\eta_2}}{M_{\eta_2}}\frac{\partial}{\partial \eta_2} + F_{P_{\eta_2}}\frac{\partial}{\partial P_{\eta_2}} - \frac{P_{\eta_2}}{M_{\eta_2}}P_{\eta_1}\frac{\partial}{\partial P_{\eta_1}} \ .\end{aligned} \tag{5.15}$$

The final term, $\mathsf{J}_{\alpha\alpha',\beta\beta'}$, represents elements of the jump operator, which is responsible for the non-adiabatic transitions which may occur in the system. This operator also accounts for the variations of the bath momenta which accompany these transitions. These variations are a consequence of energy conservation [40]. For the work presented here a weak coupling between the quantum subsystem and thermal bath has been assumed. This assumption allows us to disregard the action of the jump operator, and amounts to performing an adiabatic approximation of the systems dynamics. Within this approximation the evolution of the density matrix is then simply given by [98]:

$$\begin{aligned} \rho_W^{\alpha\alpha'}(R,P,t) &= \left(e^{-\mathrm{i}t\mathcal{L}^0}\right)_{\alpha\alpha'} \rho_W^{\alpha\alpha'}(R,P,0) \\ &= e^{-\mathrm{i}\int_0^t d\tau\omega_{\alpha\alpha'}} e^{-\mathrm{i}tL_{\alpha\alpha'}} \rho_W^{\alpha\alpha'}(R,P,0) \ . \end{aligned} \tag{5.16}$$

A look at Eqn. (5.16) shows how the dynamics now evolves on only one potential energy surface with the adiabatic approximation in effect. The dynamics of the density matrix are then calculated in time through the same propagation of swarms of classical-like trajectories as discussed in Sec. 4.3.4. The initial phase-space points of the bath are sampled from the distribution function given by Eqn. (5.9).

5.2 Simulation Details and Results

Various simulations were performed for this system, using the mixed Wigner-Heisenberg representation of quantum mechanics and the adiabatic approximation. For each simulation, 50000 initial phase-space points were sampled using Eqn. (5.9), and the reduced density matrix's evolution calculated while the initial bath temperatures were varied. Simulations were run for the cases where the baths start both in, and out of, thermal equilibrium. For all the results presented here, the coupling constants which appear in the subsystem Hamiltonian given by Eqn. (5.2) have been taken to be $j_x = j_y = 1$ and $j_z = 1/2$. The two baths, each comprising $N = 200$ harmonic oscillators, have been assigned an Ohmic spectral density in accordance to the procedure outlined in Sec. 4.3.3, and the dimensionless units introduced there have also been utilized. An adiabatic propagation of the system within the Wigner-Heisenberg representation, with a particular focus upon the evolution in time of the reduced density matrix of the two coupled spins, has been performed. The first calculations performed were a test of the numerical algorithms stability. To this end, the trace of the reduced density matrix, $\hat{\rho}_s$, was calculated as a function of time. This was done for cases where the baths started in thermal equilibrium as well as for those cases where their initial configuration was out of equilibrium. For all simulations we found that the numerical algorithm was stable. This stability is shown in Figs. 5.1 and 5.2. In Fig. 5.1 the two baths are in thermal equilibrium with inverse temperature ($\beta_1 = 0.05$, $\beta_2 = 0.05$). The initial density matrix is given by $\hat{\rho}_s(0) = |1,0\rangle\langle 1,0|$. In Fig. 5.2 the two baths are out of equilibrium with inverse temperatures ($\beta_1 = 0.3$, $\beta_2 = 1.0$). The initial density matrix in this case is given by $\hat{\rho}_s(0) = |\psi_0\rangle\langle\psi_0|$, where $|\psi_0\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle - |1,0\rangle)$.

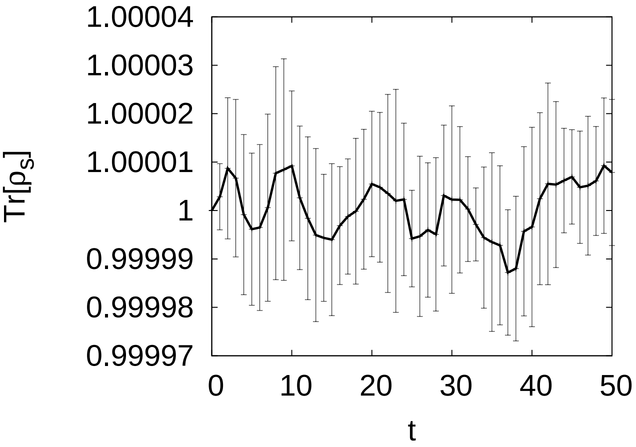

Figure 5.1: The time evolution of the trace of the reduced density matrix vs time. The two thermal baths are in equilibrium, and have inverse temperature $\beta_1 = 0.05$ and $\beta_2 = 0.05$. The initial density matrix $\hat{\rho}_s(0) = |1,0\rangle\langle 1,0|$. The error bars are used to indicate the numerical error

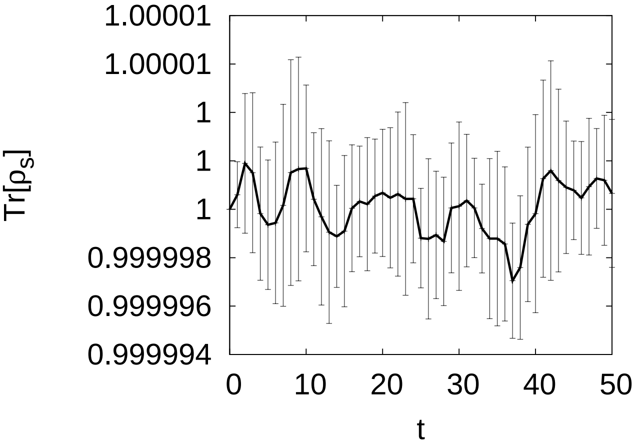

Figure 5.2: The time evolution of the trace of the reduced density matrix vs time. The two thermal baths are not in equilibrium, and have inverse temperature $\beta_1 = 0.3$ and $\beta_2 = 1.0$. The initial density matrix $\hat{\rho}_s(0) = |\psi_0\rangle\langle\psi_0|$, with $|\psi_0\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle - |1,0\rangle)$. The error bars are used to indicate the numerical error

Having been satisfied with the numerical stability of the algorithm, the effect of the number of oscillators used to represent the bath was investigated. This was achieved by varying the number of oscillators in the bath and looking at what effect they had on the evolution of the reduced system's density matrix elements. It was found that for a sufficiently high number of oscillators, one obtains results which are in accordance with those of linear response theory. The filled circles in Fig. 5.3 show the long time behaviour for the evolution of the density matrix element ρ_s^{22} with the baths in thermal equilibrium, $N = 100$, and an initial system configuration of $\hat{\rho}_s(0) = |1,0\rangle\langle 1,0|$. It can clearly be seen that these are indistinguishable from the results obtained using $N = 300$ oscillators (dashed lines). Although simulations were also run for the case of $N = 200$, these results have not been plotted as they were found to be identical to those obtained with $N = 100$ and $N = 300$ bath oscillators. However when using small N, a difference was found with regards to the long time behaviour of the system. This difference is illustrated by the solid line which represents the case of $N = 10$. This behaviour pattern was found for all system configurations which were studied. Having studied the effect of N oscillators on the

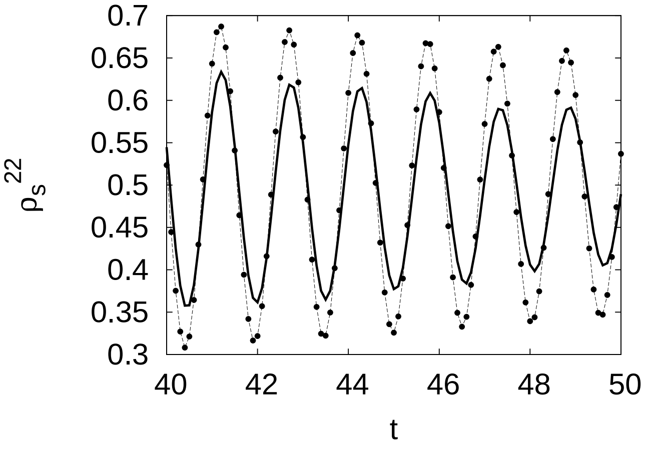

Figure 5.3: The time evolution of the trace of the reduced density matrix element ρ_s^{22} vs time. The two thermal baths are in equilibrium such that $\beta_1 = \beta_2 = 0.05$. The initial density matrix $\hat{\rho}_s(0) = |1, 0\rangle \langle 1, 0|$. The solid line shows the results obtained with $N = 10$ oscillators per bath. The filled in circles show the results obtained with $N = 100$ oscillators per bath while the dashed line shows the results obtained with $N = 300$ oscillators.

simulation, we proceeded to study the entanglement dynamics present within the system. To achieve this, the study performed focused on the concurrence dynamics between the two spins. Simulations were run for various thermal configurations of the two baths. Initially, the two baths started out in thermal equilibrium with an inverse temperature of $\beta = 5$. The initial density matrix used was $\hat{\rho}_s(0) = |\psi_0\rangle \langle \psi_0|$, with $|\psi_0\rangle = \frac{1}{\sqrt{2}} (|1, 1\rangle - |1, 0\rangle)$. After the first simulation was run, the temperature of the second bath was incrementally raised for all subsequent simulations, while that of the first bath was held constant at $\beta_1 = 5$. Selected results of the simulations are shown in Fig. 5.4. As shown in Fig. 5.4, the effect of raising the temperature of one bath is to make the system decohere faster. This is demonstrated by the concurrence going to zero as the system evolves in time, which corresponds to the disappearance of the entanglement as the temperature is raised. To see this, one need only compare sub-plots (a) and (d) of Fig. 5.4. For the Hamiltonian under study, the spin-chain Hamiltonian given by Eqn. (5.2) can entangle the spins for specific times which gives rise to the concurrence oscillations seen in Fig. 5.4. The period

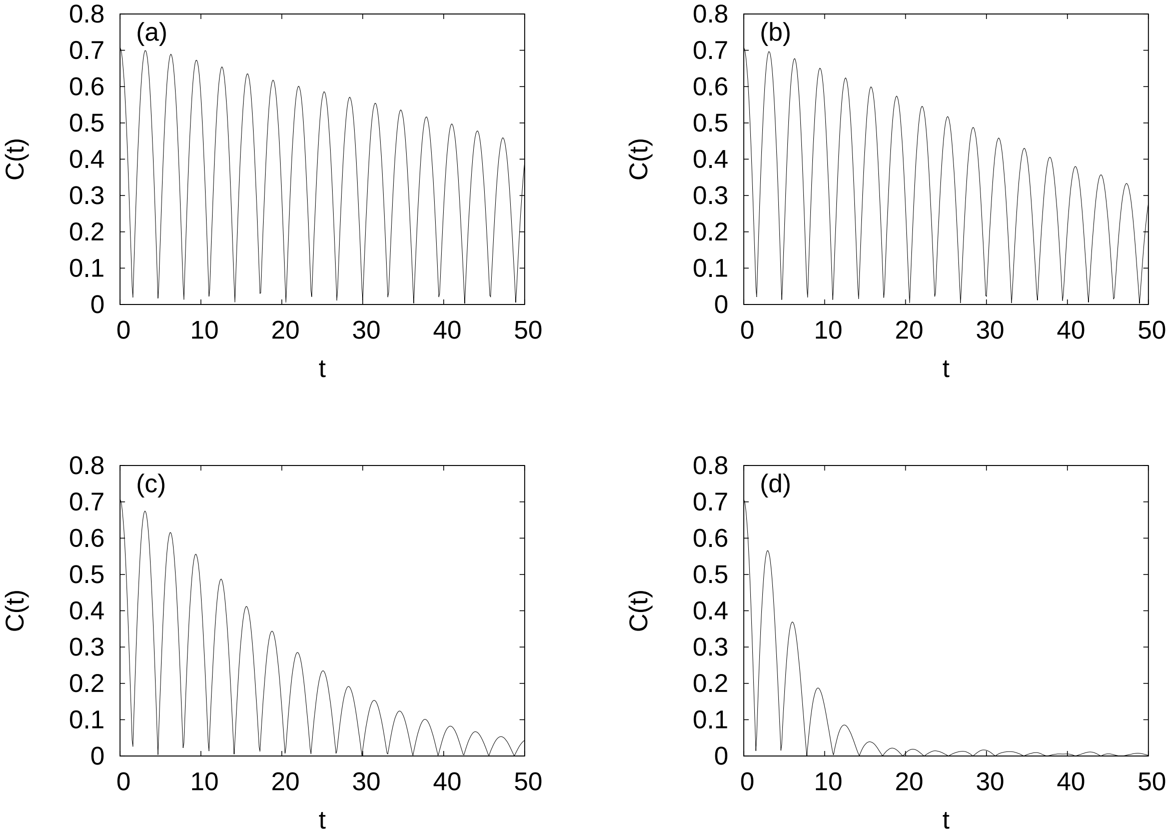

Figure 5.4: The entanglement dynamics of the two-spin chain. The initial density matrix used was $\hat{\rho}_s(0) = |\psi_0\rangle\langle\psi_0|$, with $|\psi_0\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle - |1,0\rangle)$. All the graphs show the concurrence between the two spins. The initial bath temperatures are: (a)$\beta_1 = \beta_2 = 5$, (b) $\beta_1 = 5$, $\beta_2 = 2$, (c)$\beta_1 = 5$, $\beta_2 = 0.5$, (d)$\beta_1 = 5$, $\beta_2 = 0.1$.

of these oscillations may be adjusted by simply changing the constants which appear in the subsystem Hamiltonian and control the strength of the coupling between the two spins.

Chapter 6

Conclusions and Perspectives

Unlike classical physics, where molecular dynamics simulation is used to study the dynamics of molecules and atoms from a classical perspective, there is no overall method for the numerical simulation of quantum systems. Indeed numerical methods for solving quantum dynamics are decided on a system by system basis. When one is interested in simulating the dynamics of open quantum systems, that is systems which interact with their environment, then one usually formulates the dynamics of these systems by means of influence functionals or master equations. Alternatively, a Hamiltonian approach may be used. Such an approach requires one to embed the system of interest in a bath comprising a large number of degrees of freedom, in order to calculate the evolution of the total system. To obtain an open quantum system description one need only integrate the coordinates of the bath out. However, the numerical implementation of this technique is generally too computationally expensive. By using the Hamiltonian approach, one can obtain a phase-space representation of the quantum bath by performing a partial Wigner transform only over the coordinates coupled to the subsystem. Upon taking a suitable approximation, a quantum-classical law of motion for the quantum subsystem coupled to bath coordinates is obtained. This representation is still computationally demanding to implement. However, once the classical bath coordinates are represented in phase space through the partial Wigner transform, well established non-Hamiltonian molecular dynamics equations of motion become available to represent the bath by means of a minimal number of degrees of freedom. With this in mind this thesis began by illustrating the differences between Hamiltonian and non-Hamiltonian theories. This was followed by an introduction of the generic underlying algebraic bracket structure of non-Hamiltonian dynamics. Following this was a chapter on quantum dynamics, where both the Wigner and Partial Wigner transforms were introduced as tools to formulate quantum mechanics in phase space. Next it was shown how one might model and numerically simulate the quantum dynamics of quantum systems in contact with classical-like thermal baths through the use of the mixed Wigner-Heisenberg formulation of quantum mechanics, as well as the quantum-classical approximation. Having done this, the dynamics of a quantum system in contact with a classical thermal bath were then formulated though the use of non-Hamiltonian thermostatting schemes. This formulation was achieved for quantum-classical systems through use of the generalized brackets. Both the NHC and NHP thermostats were extended to the quantum-classical case. The NHP scheme had an advantage over the NHC scheme as it allows one to use the smallest possible number of fictitious degrees of freedom, while still obtaining a correct sampling of the canonical distribution and representing the thermal bath efficiently. The decay of an excited spin in a dissipative environment was then studied using the thermostated dynamics. An excellent agreement was found between the NHC and NHP results, while for certain cases it was shown how the NHP thermostat outperforms the NVE dynamics (see Figs. 4.4 and 4.5). The results obtained seem to suggest that the NHP thermostats may be better suited, than the NHC thermostat, for the simulation of low dimensional open quantum systems. However the calculation of the non-adiabatic terms remains numerically expensive. As such an interesting extension of this work may be obtained, in the future, through incorporating the polaron transformation into the system Hamiltonian [99, 100]. Doing this would allow for the solving of the dynamics in a dressed basis, where the adiabatic basis may prove more adequate than in the bare basis.

Following this study, the mixed Wigner-Heisenberg representation was then used to numerically simulate the quantum dynamics of two coupled spins interacting with their own independent thermal baths. The quantum dynamics were calculated using ensembles of trajectories. To test the numerical stability of the algorithm the trace of the reduced density matrix was calculated as a function of time. It was found that the numerical algorithm was indeed stable. The simulations were run for cases where the two baths are in thermal equilibrium (Fig. 5.1) and the case where they are out of thermal equilibrium (Fig. 5.2). This was followed by a study of the entanglement dynamics between the two spins, which was measured by calculating the concurrence. It was found that raising the temperature of one bath, while holding the other one fixed, results in a loss of entanglement between the two spins(Fig. 5.4). The numerical algorithm, used to study the spin chain dynamics can readily be generalized to study additional coupled spins, where each spin is in contact with its own bosonic bath. It has the nice feature of already being able to handle calculations for both the equilibrium and non-equilibrium cases.

In future the study performed, on the spin-chain dynamics, will be extended to use the NHP thermostat to simulate the dynamics of general spin systems, with applications in nano-systems and spintronics. For the purpose of simulating such systems having thermal baths with the smallest possible number of degrees of freedom is extremely important, as they are usually performed using algorithms based on the discretization of phase-space on grids. Since the NHP thermostat only has a four dimensional extended system phase-space point it is hoped that it will be well suited for use in calculations of this nature. With regards to the numerical algorithm used to simulate the dynamics of the spin chain, we hope to include non-adiabatic corrections to the evolution of the total systems density matrix. In particular, we hope to utilize the recently published combined filtering technique to simulate these dynamics [101]. Following this, the algorithm will be used to simulate the action of external controlling fields on the spin system. For such cases the spin-chain Hamiltonian has an explicit time dependence. We also wish to simulate the effects of a dynamic thermal driving on the system, and calculate the effects of the subsequent dynamic thermal gradient on the entanglement between the two spins and the environment.

Appendix A

Miscellaneous Proofs

A.1 Time-Translation Invariance of Hamiltonian Brackets

If the Liouville operator is defined as

$$L \cdots = (\cdots , H) \ , \tag{A.1}$$

where $\cdots$ represents the object L acts upon, while $(\cdots , \cdots)$ represents some generic braket which may be either quantum or classical in nature, then the equations of motion expressed in Eqn. (2.7) may be written as

$$\dot{u} = Lu \qquad \dot{v} = Lv \ , \tag{A.2}$$

where the dot notation is used to denote the time derivative. These equations have the following solutions,

$$u\left(t\right) = e^{tL} u\left(0\right) , \qquad v\left(t\right) = e^{tL} v\left(0\right) \ . \tag{A.3}$$

Defining the infinitesimal time as ϵ, allows one to Taylor expand Eqns. (A.3) to first order,

$$\begin{aligned} u\left(\epsilon\right) &= e^{\epsilon L} u\left(0\right) \\ &= \left[1 + \epsilon L\right] u\left(0\right) \\ &= u\left(0\right) + \epsilon\left(u, H\right) \ , \end{aligned} \tag{A.4}$$

similarly

$$v\left(\epsilon\right) = v\left(0\right) + \epsilon\left(v, H\right) \ . \tag{A.5}$$

If one considers,

$$\begin{aligned} e^{\epsilon L}(u,v) &= [1+\epsilon L](u,v) \\ &= (u,v) + \epsilon L(u,v) \\ &= (u,v) + \epsilon\left((u,v),H\right) \ , \end{aligned} \tag{A.6}$$

The final term may be rearranged since the bracket is Hamiltonian. From the Jacobi relation

$$((u,v),H) + ((v,H),u) + ((H,u),v) = 0 \ , \tag{A.7}$$

rearranging this one obtains,

$$((u,v),H) = -((v,H),u) - ((H,u),v) \ .$$

The antisymmetric property defined in Eqn. (2.2), gives

$$\begin{aligned} ((u,v),H) &= (u,(v,H)) + ((u,H),v) \\ &= (u,\dot{v}) + (\dot{u},v) \ . \end{aligned}$$

As such when the Jacobi relation is valid one has that

$$e^{\epsilon L}(u,v) = (u,v) + \epsilon(\dot{u},v) + \epsilon(u,\dot{v}) \ . \tag{A.8}$$

Now consider,

$$\begin{aligned} (u(\epsilon),v(\epsilon)) &= (u+\epsilon\dot{u}, v+\epsilon\dot{v}) \\ &= (u, v+\epsilon\dot{v}) + (\epsilon\dot{u}, v+\epsilon\dot{v}) \\ &= (u, v+\epsilon\dot{v}) + \epsilon(\dot{u}, v+\epsilon\dot{v}) \\ &= (u,v) + \epsilon(u,\dot{v}) + \epsilon(\dot{u},v) + \epsilon^2(\dot{u},\dot{v}) \ , \end{aligned}$$

since ϵ is infinitesimal, one may disregard all higher order terms. The above equation then reduces to,

$$(u(\epsilon),v(\epsilon)) = (u,v) + \epsilon(u,\dot{v}) + \epsilon(\dot{u},v) \ ,$$

hence,

$$(u(\epsilon),v(\epsilon)) = e^{\epsilon L}(u,v) \ . \tag{A.9}$$

The time translation invariance of the Hamiltonian bracket algebra is expressed by Eqn. (A.9). This property of time variance is only valid when the Jacobi relation is valid. In other words, when one is dealing with a Hamiltonian (or Lie) algebra.

A.2 Equivalence of Equations of Motion

To show the equivalence of Eqns. (4.7) and (4.8) one begins by recalling that Eqn. (4.8) is

$$\frac{\partial \hat{\chi}_W}{\partial t} = \frac{\mathrm{i}}{\hbar} \begin{bmatrix} \hat{H}_W & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D} \cdot \begin{bmatrix} \hat{H}_W \\ \hat{\chi}_W \end{bmatrix} \tag{A.10}$$

Substituting in the matrix, $\mathcal{D}$, given by Eqn. (4.9) this evolution equation becomes

$$\frac{\partial \hat{\chi}_W}{\partial t} = \frac{\mathrm{i}}{\hbar} \begin{bmatrix} \hat{H}_W & \hat{\chi}_W \end{bmatrix} \cdot \begin{bmatrix} 0 & \left(1 + \frac{\mathrm{i}\hbar}{2} \overleftarrow{\partial}_i \cdot \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) \\ -\left(1 + \frac{\mathrm{i}\hbar}{2} \overleftarrow{\partial}_i \cdot \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) & 0 \end{bmatrix} \cdot \begin{bmatrix} \hat{H}_W \\ \hat{\chi}_W \end{bmatrix}$$

Evaluating this equation produces

$$\begin{aligned}
\frac{\partial \hat{\chi}_W}{\partial t} &= \frac{\mathrm{i}}{\hbar} \begin{bmatrix} \hat{H}_W & \hat{\chi}_W \end{bmatrix} \cdot \begin{bmatrix} \left(1 + \frac{\mathrm{i}\hbar}{2} \overleftarrow{\partial}_i \cdot \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) \hat{\chi}_W \\ -\left(1 + \frac{\mathrm{i}\hbar}{2} \overleftarrow{\partial}_i \cdot \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) \hat{H}_W \end{bmatrix} \\
&= \frac{\mathrm{i}}{\hbar} \left(\hat{H}_W \left(1 + \frac{\mathrm{i}\hbar}{2} \overleftarrow{\partial}_i \cdot \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) \hat{\chi}_W - \hat{\chi}_W \left(1 + \frac{\mathrm{i}\hbar}{2} \overleftarrow{\partial}_i \cdot \mathcal{B}^c_{ij} \overrightarrow{\partial}_j\right) \hat{H}_W \right) \\
&= \frac{\mathrm{i}}{\hbar} \left[\hat{H}_W, \hat{\chi}_W\right] - \frac{1}{2} \left\{\hat{H}_W, \hat{\chi}_W\right\} + -\frac{1}{2} \left\{\hat{H}_W, \hat{\chi}_W\right\} \\
&= \left(\hat{H}_W, \hat{\chi}_W\right)_{\mathrm{QC}} \\
&= \mathrm{i}\mathcal{L}\hat{\chi}_W
\end{aligned} \tag{A.11}$$

The last line of the above equation is identical to Eqn. (4.7) in the main text. As such, this appendix demonstrates that the matrix form of the equation of motion is equivalent to its quantum-classical bracket formulation.

Appendix B

Quantum-Classical Liouville Super-Operator in the Adiabatic Basis

The first step is to take the matrix elements of the quantum-classical Liouville equation for an arbitrary operator:

$$\left\langle \alpha \left| \frac{\partial \hat{\chi}_W}{\partial t} \right| \alpha' \right\rangle = \frac{\mathrm{i}}{\hbar} \left\langle \alpha \left| \left[\hat{H}_W, \hat{\chi}_W \right] \right| \alpha' \right\rangle - \frac{1}{2} \left\langle \alpha \left| \left\{ \hat{H}_W, \hat{\chi}_W \right\} \right| \alpha' \right\rangle . \tag{B.1}$$

Expand the first term on the right hand side

$$\frac{\mathrm{i}}{\hbar} \left\langle \alpha \left| \left[\hat{H}_W, \hat{\chi}_W \right] \right| \alpha' \right\rangle = \frac{\mathrm{i}}{\hbar} \left(\left\langle \alpha \left| \hat{H}_W \hat{\chi}_W \right| \alpha' \right\rangle - \left\langle \alpha \left| \hat{\chi}_W \hat{H}_W \right| \alpha' \right\rangle \right) . \tag{B.2}$$

Using the fact that $\hat{H}_W = P^2/2M + \hat{h}_W$ and $\hat{h}_W \left|\alpha\right\rangle = E_\alpha \left|\alpha\right\rangle$, this becomes

$$\begin{aligned} \frac{\mathrm{i}}{\hbar} \left(\left\langle \alpha \left| \hat{H}_W \hat{\chi}_W \right| \alpha' \right\rangle - \left\langle \alpha \left| \hat{\chi}_W \hat{H}_W \right| \alpha' \right\rangle \right) &= \frac{\mathrm{i}}{\hbar} \left(E_\alpha \left\langle \alpha \,\middle|\, \hat{\chi}_W \,\middle|\, \alpha' \right\rangle - E_{\alpha'} \left\langle \alpha \,\middle|\, \hat{\chi}_W \,\middle|\, \alpha' \right\rangle \right) \\ &= \mathrm{i}\omega_{\alpha\alpha'} \chi_W^{\alpha\alpha'} , \end{aligned} \tag{B.3}$$

where $\chi_W^{\alpha\alpha'} = \left\langle \alpha \,\middle|\, \hat{\chi}_W \,\middle|\, \alpha' \right\rangle$, and $\omega_{\alpha\alpha'} = \frac{E_\alpha - E_{\alpha'}}{\hbar}$. The second term of Eqn (B.1) will now be expanded to give:

$$\left\langle \alpha \left| \left\{ \hat{H}_W, \hat{\chi}_W \right\} \right| \alpha' \right\rangle = \left\langle \alpha \left| \frac{\partial \hat{H}_W}{\partial R} \frac{\partial \hat{\chi}_W}{\partial P} \right| \alpha' \right\rangle - \left\langle \alpha \left| \frac{\partial \hat{H}_W}{\partial P} \frac{\partial \hat{\chi}_W}{\partial R} \right| \alpha' \right\rangle . \tag{B.4}$$

Using the completness relation, this becomes

$$\left\langle \alpha \,\middle|\, \left\{ \hat{H}_W, \hat{\chi}_W \right\} \,\middle|\, \alpha' \right\rangle = \left\langle \alpha \,\middle|\, \frac{\partial \hat{H}_W}{\partial R} \sum_\beta |\beta\rangle \langle\beta| \frac{\partial \hat{\chi}_W}{\partial P} \,\middle|\, \alpha' \right\rangle - \left\langle \alpha \,\middle|\, \frac{\partial \hat{H}_W}{\partial P} \sum_\beta |\beta\rangle \langle\beta| \frac{\partial \hat{\chi}_W}{\partial R} \,\middle|\, \alpha' \right\rangle$$
$$= -\sum_\beta F_W^{\alpha\beta} \frac{\partial \chi_W^{\beta\alpha'}}{\partial P} - \sum_\beta \frac{P}{M} \delta_{\alpha\beta} \left\langle \beta \,\middle|\, \frac{\partial \hat{\chi}_W}{\partial R} \,\middle|\, \alpha' \right\rangle \,, \tag{B.5}$$

where the fact that $\langle \alpha \,|\, \beta \rangle = \delta_{\alpha\beta}$ has been used, along with $\frac{\partial \hat{V}_W}{\partial R} = \frac{\partial \hat{H}_W}{\partial R}$ and $\frac{\partial \hat{H}_W}{\partial P} = \frac{P}{M}$. The Hellmann-Feynman matrix elements in the partial Wigner representation are given by [22] $F_W^{\alpha\beta} = -\left\langle \alpha \,\middle|\, \frac{\partial \hat{V}_W}{\partial R} \,\middle|\, \beta \right\rangle$. The third term in Eqn. (B.1) can be similarly expanded to get

$$\left\langle \alpha \,\middle|\, \left\{ \hat{\chi}_W, \hat{H}_W \right\} \,\middle|\, \alpha' \right\rangle = \sum_{\beta'} \left\langle \alpha \,\middle|\, \frac{\partial \hat{\chi}_W}{\partial R} \,\middle|\, \beta' \right\rangle \frac{P}{M} \delta_{\beta'\alpha'} + \sum_{\beta'} \frac{\partial \chi_W^{\alpha\beta'}}{\partial P} F_W^{\beta'\alpha'} \,. \tag{B.6}$$

Adding equations (B.3), (B.5) and (B.6) gives

$$\frac{\partial \chi_W^{\alpha\alpha'}}{\partial t} = \mathrm{i}\omega_{\alpha\alpha'} \chi_W^{\alpha\alpha'} + \frac{1}{2} \left(\sum_\beta F_W^{\alpha\beta} \frac{\partial \chi_W^{\beta\alpha'}}{\partial P} + \sum_{\beta'} \frac{\partial \chi_W^{\alpha\beta\prime}}{\partial P} F_W^{\beta\prime\alpha'} \right)$$
$$+ \frac{1}{2} \left(\sum_\beta \frac{P}{M} \delta_{\alpha\beta} \left\langle \beta \,\middle|\, \frac{\partial \hat{\chi}_W}{\partial R} \,\middle|\, \alpha' \right\rangle + \sum_{\beta'} \left\langle \alpha \,\middle|\, \frac{\partial \hat{\chi}_W}{\partial R} \,\middle|\, \beta' \right\rangle \frac{P}{M} \delta_{\beta'\alpha'} \right) \,. \tag{B.7}$$

The quantum-classical Liouville equation may thus be written as

$$\frac{\partial \chi_W^{\alpha\alpha'}}{\partial t} = \mathrm{i}\omega_{\alpha\alpha'} \chi_W^{\alpha\alpha'} + \frac{1}{2} \left(\sum_\beta F_W^{\alpha\beta} \frac{\partial \chi_W^{\beta\alpha'}}{\partial P} + \sum_{\beta'} \frac{\partial \chi_W^{\alpha\beta\prime}}{\partial P} F_W^{\beta\prime\alpha'} \right)$$
$$+ \frac{P}{M} \left\langle \alpha \,\middle|\, \frac{\partial \chi_W}{\partial R} \,\middle|\, \alpha' \right\rangle \,. \tag{B.8}$$

Since the states $|\alpha\rangle$ depend on the position coordinate the partial derivative with respect to this coordinate, which applies in the last term of the above equation, needs to be treated differently as it affects both the arbitrary operator $\hat{\chi}_W$ and state vector $|\alpha\rangle$. To find a way to express the last term in a more suitable form one starts by considering $\frac{\partial}{\partial R}\chi_W^{\alpha\alpha'}$

$$\frac{\partial}{\partial R}\chi_W^{\alpha\alpha'} = \frac{\partial}{\partial R} \langle \alpha \,|\, \chi_W \,|\, \alpha' \rangle$$
$$= \left\langle \frac{\partial \alpha}{\partial R} \,\middle|\, \chi_W \,\middle|\, \alpha' \right\rangle + \left\langle \alpha \,\middle|\, \frac{\partial \chi_W}{\partial R} \,\middle|\, \alpha' \right\rangle + \left\langle \alpha \,\middle|\, \chi_W \,\middle|\, \frac{\partial \alpha'}{\partial R} \right\rangle$$
$$= \left\langle \alpha \,\middle|\, \frac{\partial \hat{\chi}_W}{\partial R} \,\middle|\, \alpha' \right\rangle + \left(\sum_\beta \left\langle \frac{\partial \alpha}{\partial R} \,\middle|\, \beta \right\rangle \chi_W^{\beta\alpha'} + \sum_{\beta'} \chi_W^{\alpha\beta'} \left\langle \beta' \,\middle|\, \frac{\partial \alpha'}{\partial R} \right\rangle \right) \,, \tag{B.9}$$

where the completness relation has once again been used. By definition [22], $d_{\beta'\alpha'} = \left\langle \beta' \,\middle|\, \frac{\partial}{\partial R} \,\middle|\, \alpha' \right\rangle$. It is possible to simplify $\left\langle \frac{\partial \alpha}{\partial R} \,\middle|\, \beta \right\rangle$ by considering the following

$$\frac{\partial}{\partial R} \langle \alpha \,|\, \beta \rangle = \left\langle \frac{\partial \alpha}{\partial R} \middle| \beta \right\rangle + \left\langle \alpha \middle| \frac{\partial \beta}{\partial R} \right\rangle , \tag{B.10}$$

now from the orthonormality condition $\frac{\partial}{\partial R} \langle \alpha \,|\, \beta \rangle = 0$, since $\langle \alpha \,|\, \beta \rangle = \delta_{\alpha\beta}$. As such one arrives at the identity

$$\left\langle \frac{\partial \alpha}{\partial R} \middle| \beta \right\rangle = -\left\langle \alpha \middle| \frac{\partial \beta}{\partial R} \right\rangle \tag{B.11}$$

$$= -d_{\alpha\beta} \ . \tag{B.12}$$

Using this identity in (B.9) and making $\left\langle \alpha \middle| \frac{\partial \hat{\chi}_W}{\partial R} \middle| \alpha' \right\rangle$ the subject of the formula gives

$$\left\langle \alpha \middle| \frac{\partial \hat{\chi}_W}{\partial R} \middle| \alpha' \right\rangle = \frac{\partial \chi_W^{\alpha\alpha'}}{\partial R} - \left(\sum_{\beta'} \chi_W^{\alpha\beta'} d_{\beta'\alpha'} - \sum_{\beta} d_{\alpha\beta} \chi_W^{\beta\alpha'} \right) . \tag{B.13}$$

Substituting this expression for $\left\langle \alpha \middle| \frac{\partial \hat{\chi}_W}{\partial R} \middle| \alpha' \right\rangle$ back into Eqn.(B.8) one obtains an expression for the quantum-classical Liouville equation in the partial Wigner transform:

$$\begin{aligned}
\frac{\partial \chi_W^{\alpha\alpha'}}{\partial t} &= \mathrm{i}\omega_{\alpha\alpha'} \chi_W^{\alpha\alpha'} + \frac{1}{2} \sum_{\beta} F_W^{\alpha\beta} \frac{\partial \chi_W^{\beta\alpha'}}{\partial P} + \frac{1}{2} \sum_{\beta'} \frac{\partial \chi_W^{\alpha\beta'}}{\partial P} F_W^{\beta'\alpha'} \\
&\quad + \frac{P}{M} \frac{\partial \chi_W^{\alpha\alpha'}}{\partial R} - \frac{P}{M} \sum_{\beta'} \chi_W^{\alpha\beta'} d_{\beta'\alpha'} + \frac{P}{M} \sum_{\beta} d_{\alpha\beta} \chi_W^{\beta\alpha'} \\
&= \sum_{\beta\beta'} \Bigg[\mathrm{i}\omega_{\alpha\alpha'} \delta_{\alpha\beta} \delta_{\alpha'\beta'} + \frac{1}{2} \left(F_W^{\alpha\beta} \delta_{\alpha'\beta'} \frac{\partial}{\partial P} + F_W^{\beta'\alpha'} \delta_{\alpha\beta} \frac{\partial}{\partial P} \right) \\
&\quad + \frac{P}{M} \delta_{\alpha\beta} \delta_{\alpha'\beta'} \frac{\partial}{\partial R} - \frac{P}{M} \left(d_{\beta'\alpha'} \delta_{\alpha\beta} - d_{\alpha\beta} \delta_{\alpha'\beta'} \right) \Bigg] \chi_W^{\beta\beta'} \\
\frac{\partial \chi_W^{\alpha\alpha'}}{\partial t} &= \sum_{\beta\beta'} \mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'} \chi_W^{\beta\beta'} \ .
\end{aligned} \tag{B.14}$$

In writing Eqn. (B.14), the quantum-classical Liouville super-operator has been introduced. This operator is given by the terms contained within the square brackets. It will now be shown how one may rewrite this operator such that it has the same form as that given in Eqn. (4.17). To accomplish this one adds and subtracts the term [35],

$$\delta_{\alpha\beta} \delta_{\alpha'\beta'} \frac{1}{2} \left(F_W^{\alpha} + F_W^{\alpha'} \right) \frac{\partial}{\partial P} ,$$

to the Liouville super-operator. This term involves the average of the Hellman-Feynman forces for two states α and α' [22]. Performing this addition and subtraction gives us

$$\begin{aligned} \mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'} = & \left(\mathrm{i}\omega_{\alpha\alpha'} + \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F_W^{\alpha} + F_W^{\alpha'}\right)\frac{\partial}{\partial P}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} \\ & - \left[\frac{P}{M}\left(d_{\beta'\alpha'}\delta_{\alpha\beta} - d_{\alpha\beta}\delta_{\alpha'\beta'}\right) - \frac{1}{2}\left(F_W^{\alpha\beta}\delta_{\alpha'\beta'}\right.\right. \\ & \left.\left. + F_W^{\beta'\alpha'}\delta_{\alpha\beta} - \left(F_W^{\alpha} + F_W^{\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'}\right)\frac{\partial}{\partial P}\right] . \end{aligned} \tag{B.15}$$

The classical Liouville operator is defined as [40]

$$\mathrm{i}L_{\alpha\alpha'} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F_W^{\alpha} + F_W^{\alpha'}\right)\frac{\partial}{\partial P} , \tag{B.16}$$

this operator describes the classical evolution of the bath coordinates and is given in terms of the Hellmann-Feynman forces for the adiabatic states, α and α'. The quantum-classical Liouville super-operator may now be expressed as

$$\begin{aligned} \mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'} = & \left(\mathrm{i}\omega_{\alpha\alpha'} + \mathrm{i}L_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} \\ & - \left[\frac{P}{M}\left(d_{\beta'\alpha'}\delta_{\alpha\beta} - d_{\alpha\beta}\delta_{\alpha'\beta'}\right) - \frac{1}{2}\left(F_W^{\alpha\beta}\delta_{\alpha'\beta'}\right.\right. \\ & \left.\left. + F_W^{\beta'\alpha'}\delta_{\alpha\beta} - \left(F_W^{\alpha} + F_W^{\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'}\right)\frac{\partial}{\partial P}\right] . \end{aligned} \tag{B.17}$$

The term in the square brackets represents the J-operator. It will now be shown how this term may be expressed in the same form as Eqn. (4.21)

$$\begin{aligned} \mathsf{J}_{\alpha\alpha',\beta\beta'} = & \left[\frac{P}{M}\left(d_{\beta'\alpha'}\delta_{\alpha\beta} - d_{\alpha\beta}\delta_{\alpha'\beta'}\right) - \frac{1}{2}\left(F_W^{\alpha\beta}\delta_{\alpha'\beta'}\right.\right. \\ & \left.\left. + F_W^{\beta'\alpha'}\delta_{\alpha\beta} - \left(F_W^{\alpha} + F_W^{\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'}\right)\frac{\partial}{\partial P}\right] . \end{aligned} \tag{B.18}$$

To this end one begins by grouping all the terms which contain $\delta_{\alpha'\beta'}$ together and all the terms which contain $\delta_{\alpha\beta}$ together. This gives

$$\begin{aligned} \mathsf{J}_{\alpha\alpha',\beta\beta'} = & \left[\frac{P}{M}d_{\beta'\alpha'} - \frac{1}{2}\left(F_W^{\beta'\alpha'} - F_W^{\alpha'}\delta_{\alpha'\beta'}\right)\frac{\partial}{\partial P}\right]\delta_{\alpha\beta} \\ & - \left[\frac{P}{M}d_{\alpha\beta} + \frac{1}{2}\left(F_W^{\alpha\beta} - F_W^{\alpha}\delta_{\alpha\beta}\right)\frac{\partial}{\partial P}\right]\delta_{\alpha'\beta'} \\ = & -\frac{P}{M}d_{\alpha\beta}\left[1 + \frac{1}{2}\left(F_W^{\alpha\beta} - F_W^{\alpha}\delta_{\alpha\beta}\right)\left(\frac{P}{M}d_{\alpha\beta}\right)^{-1}\frac{\partial}{\partial P}\right]\delta_{\alpha'\beta'} \\ & + \frac{P}{M}d_{\beta'\alpha'}\left[1 - \frac{1}{2}\left(F_W^{\beta'\alpha'} - F_W^{\alpha'}\delta_{\alpha'\beta'}\right)\left(\frac{P}{M}d_{\beta'\alpha'}\right)^{-1}\frac{\partial}{\partial P}\right]\delta_{\alpha\beta}. \end{aligned}$$

Now since the non-adiabatic coupling matrix is anti-Hermitian in nature, $d_{\beta'\alpha'} = -d^*_{\alpha'\beta'}$, this equation becomes

$$\begin{aligned} \mathsf{J}_{\alpha\alpha',\beta\beta'} = &-\frac{P}{M}d_{\alpha\beta}\left[1+\frac{1}{2}\left(F_W^{\alpha\beta}-F_W^{\alpha}\delta_{\alpha\beta}\right)\left(\frac{P}{M}d_{\alpha\beta}\right)^{-1}\frac{\partial}{\partial P}\right]\delta_{\alpha'\beta'} \\ &-\frac{P}{M}d^*_{\alpha'\beta'}\left[1+\frac{1}{2}\left(F_W^{\beta'\alpha'}-F_W^{\alpha'}\delta_{\alpha'\beta'}\right)\left(\frac{P}{M}d^*_{\alpha'\beta'}\right)^{-1}\frac{\partial}{\partial P}\right]\delta_{\alpha\beta}\ . \end{aligned} \tag{B.19}$$

By defining

$$S_{\alpha\beta} = \left(F_W^{\alpha\beta}-F_W^{\alpha}\delta_{\alpha\beta}\right)\left(\frac{P}{M}d_{\alpha\beta}\right)^{-1}, \tag{B.20}$$

and making use of the relation [22, 35]

$$F^{\alpha\beta} = F^{\alpha} + \left(E_\alpha - E_\beta\right) d_{\alpha\beta}, \tag{B.21}$$

one obtains that

$$S_{\alpha\beta} = \left(E_\alpha - E_\beta\right) d_{\alpha\beta}\left(\frac{P}{M}d_{\alpha\beta}\right)^{-1}. \tag{B.22}$$

Similarly one may also define

$$S^*_{\alpha'\beta'} = \left(E_{\alpha'} - E_{\beta'}\right) d^*_{\alpha'\beta'}\left(\frac{P}{M}d_{\alpha'\beta'}\right)^{-1}. \tag{B.23}$$

Substituting this into the equation for the jump operator, one obtains

$$\begin{aligned} \mathsf{J}_{\alpha\alpha',\beta\beta'} = &-\frac{P}{M}d_{\alpha\beta}\left(1+\frac{1}{2}S_{\alpha\beta}\frac{\partial}{\partial P}\right)\delta_{\alpha'\beta'} \\ &-\frac{P}{M}d^*_{\alpha'\beta'}\left(1+\frac{1}{2}S^*_{\alpha'\beta'}\frac{\partial}{\partial P}\right)\delta_{\alpha\beta}, \end{aligned} \tag{B.24}$$

which is the form of the jump operator given in Eqn. (4.21) .

Appendix C

NHP Quantum-Classical Liouville Super-Operator Representation

Like the general case one starts by taking the matrix elements of the quantum-classical NHP Liouville equation of motion for an operator

$$\begin{aligned}\left\langle \alpha \left| \frac{\partial \hat{\chi}_W}{\partial t} \right| \alpha' \right\rangle = \frac{\mathrm{i}}{\hbar} \left\langle \alpha \left| \left[\hat{H}_W, \hat{\chi}_W \right] \right| \alpha' \right\rangle + \Bigg\langle \alpha \Bigg| &- \frac{1}{2} \left(\frac{\partial \hat{V}_W}{\partial R} \frac{\partial \hat{\chi}_W}{\partial P} + \frac{\partial \hat{\chi}_W}{\partial P} \frac{\partial \hat{V}_W}{\partial R} \right) \\ &+ \left(\frac{P}{M} + \frac{P_\eta}{M_\eta} \frac{\tau P}{M} \right) \frac{\partial \hat{\chi}_W}{\partial R} + \frac{P_\eta}{M_\eta} \frac{\partial \hat{\chi}_W}{\partial \eta} - \frac{P_\eta}{M_\eta} P \frac{\partial \hat{\chi}_W}{\partial P} \\ &+ F_p \frac{\partial \hat{\chi}_W}{\partial P_\eta} - \frac{1}{2} \frac{\partial \hat{V}_W}{\partial R} \frac{\tau P}{M} \frac{\partial \hat{\chi}_W}{\partial P_\eta} \\ &- \frac{1}{2} \frac{\partial \hat{\chi}_W}{\partial P_\eta} \frac{\tau P}{M} \frac{\partial \hat{V}_W}{\partial R} \Bigg| \alpha' \Bigg\rangle . \end{aligned} \tag{C.1}$$

Expand the first term on the right hand side

$$\frac{\mathrm{i}}{\hbar} \left\langle \alpha \left| \left[\hat{H}_W, \hat{\chi}_W \right] \right| \alpha' \right\rangle = \frac{\mathrm{i}}{\hbar} \left(\langle \alpha | \hat{H}_W \hat{\chi}_W | \alpha' \rangle - \langle \alpha | \hat{\chi}_W \hat{H}_W | \alpha' \rangle \right) \tag{C.2}$$

Using the fact that $\hat{H}_W = H^{NHP} + \hat{h}_W$ and $\hat{h}_W \left| \alpha \right\rangle = E_\alpha \left| \alpha \right\rangle$, this becomes

$$\begin{aligned}\frac{\mathrm{i}}{\hbar} \left(\langle \alpha | \hat{H}_W \hat{\chi}_W | \alpha' \rangle - \langle \alpha | \hat{\chi}_W \hat{H}_W | \alpha' \rangle \right) &= \frac{\mathrm{i}}{\hbar} \left(E_\alpha \left\langle \alpha | \hat{\chi}_W | \alpha' \right\rangle - E_{\alpha'} \left\langle \alpha | \hat{\chi}_W | \alpha' \right\rangle \right) \\ &= \mathrm{i} \omega_{\alpha\alpha'} \chi_W^{\alpha\alpha'} , \end{aligned} \tag{C.3}$$

where $\omega_{\alpha\alpha'} = \frac{E_\alpha - E_{\alpha'}}{\hbar}$, and $\chi_W^{\alpha\alpha'} = \langle\alpha\,|\,\chi_W\,|\,\alpha'\rangle$. The second term $-\frac{1}{2}\left\langle\alpha\left|\,\frac{\partial\hat{V}_W}{\partial R}\frac{\partial\hat{\chi}_W}{\partial P}\,\right|\alpha'\right\rangle$, may be expanded to give:

$$\begin{aligned}
-\frac{1}{2}\left\langle\alpha\left|\,\frac{\partial\hat{V}_W}{\partial R}\frac{\partial\hat{\chi}_W}{\partial P}\,\right|\alpha'\right\rangle &= -\frac{1}{2}\sum_\beta\left\langle\alpha\left|\,\frac{\partial\hat{V}_W}{\partial R}\,\right|\beta\right\rangle\langle\beta|\frac{\partial\hat{\chi}_W}{\partial P}|\alpha'\rangle \\
&= \frac{1}{2}\sum_\beta F^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P}\ ,
\end{aligned} \tag{C.4}$$

Where the completeness relation along with $\langle\alpha\,|\,\beta\rangle = \delta_{\alpha\beta}$, and the introduction of the Hellmann-Feynman force matrix elements $F^{\alpha\beta} = \left\langle\alpha\left|\,\frac{\partial\hat{V}_W}{\partial R}\,\right|\alpha'\right\rangle$. Following a similar procedure to this, produces

$$-\frac{1}{2}\left\langle\alpha\left|\,\frac{\partial\hat{\chi}_W}{\partial P}\frac{\partial\hat{V}_W}{\partial R}\,\right|\alpha'\right\rangle = \frac{1}{2}\sum_\beta\frac{\partial\chi_W^{\alpha\beta}}{\partial P}F^{\beta\alpha'}\ . \tag{C.5}$$

The next term may be expanded to obtain

$$\begin{aligned}
\left\langle\alpha\left|\,F_p\frac{\partial\hat{\chi}_W}{\partial P_\eta}\,\right|\alpha'\right\rangle &= F_p\frac{\partial}{\partial P_\eta}\langle\alpha|\hat{\chi}_W|\alpha'\rangle \\
&= F_p\frac{\partial\chi_W^{\alpha\alpha'}}{\partial P_\eta}\ ,
\end{aligned} \tag{C.6}$$

while

$$\begin{aligned}
-\frac{1}{2}\left\langle\alpha\left|\,\frac{\partial\hat{V}_W}{\partial R}\frac{\tau P}{M}\frac{\partial\hat{\chi}_W}{\partial P_\eta}\,\right|\alpha'\right\rangle &= -\frac{1}{2}\frac{\tau P}{M}\left\langle\alpha\left|\,\frac{\partial\hat{V}_W}{\partial R}\frac{\partial\hat{\chi}_W}{\partial P_\eta}\,\right|\alpha'\right\rangle \\
&= \frac{\tau P}{2M}\sum_\beta F^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P_\eta}\ .
\end{aligned} \tag{C.7}$$

Similarity

$$\begin{aligned}
-\frac{1}{2}\left\langle\alpha\left|\,\frac{\partial\hat{\chi}_W}{\partial P_\eta}\frac{\tau P}{M}\frac{\partial\hat{V}_W}{\partial R}\,\right|\alpha'\right\rangle &= -\frac{1}{2}\frac{\tau P}{M}\left\langle\alpha\left|\,\frac{\partial\hat{\chi}_W}{\partial P_\eta}\frac{\partial\hat{V}_W}{\partial R}\,\right|\alpha'\right\rangle \\
&= \frac{\tau P}{2M}\sum_\beta\frac{\partial\chi_W^{\alpha\beta}}{\partial P_\eta}F^{\beta\alpha'}\ .
\end{aligned} \tag{C.8}$$

The next term to be considered is

$$\left\langle\alpha\left|\left(\frac{P}{M}+\frac{P_\eta}{M_\eta}\frac{\tau P}{M}\right)\frac{\partial\hat{\chi}_W}{\partial R}\,\right|\alpha'\right\rangle = \left(\frac{P}{M}+\frac{P_\eta}{M_\eta}\frac{\tau P}{M}\right)\left\langle\alpha\left|\,\frac{\partial\hat{\chi}_W}{\partial R}\,\right|\alpha'\right\rangle$$

Since the states depend on the position coordinates the partial derivative with respect to this coordinate which occurs in the above equation requires a different treatment as it affects both the arbitrary operator $\hat{\chi}_W$ and the state vector $|\alpha'\rangle$. To express this term in a more suitable form one first considers

$$\begin{aligned}\frac{\partial}{\partial R}\langle\alpha\,|\,\hat{\chi}_W\,|\,\alpha'\rangle &= \left\langle\frac{\partial\alpha}{\partial R}\middle|\,\hat{\chi}_W\,\middle|\alpha'\right\rangle + \left\langle\alpha\middle|\frac{\partial\hat{\chi}_W}{\partial R}\middle|\alpha'\right\rangle + \left\langle\alpha\middle|\,\hat{\chi}_W\,\middle|\frac{\partial\alpha'}{\partial R}\right\rangle,\\ &= \left\langle\alpha\middle|\frac{\partial\hat{\chi}_W}{\partial R}\middle|\alpha'\right\rangle + \sum_\beta\left(\left\langle\frac{\partial\alpha}{\partial R}\middle|\beta\right\rangle\chi_W^{\beta\alpha'} + \chi_W^{\alpha\beta}\left\langle\beta\middle|\frac{\partial\alpha'}{\partial R}\right\rangle\right)\ ,\end{aligned} \tag{C.9}$$

where the completeness relation has again been used. By definition the non-adiabatic coupling matrix element may be expressed as $d_{\beta\alpha'} = \langle\beta\,|\,\frac{\partial}{\partial R}\,|\,\alpha'\rangle = \left\langle\beta\,\middle|\,\frac{\partial\alpha'}{\partial R}\right\rangle$ [22, 35]. In order to find simplify $\left\langle\frac{\partial\alpha}{\partial R}\,\middle|\,\beta\right\rangle$ one considers the following

$$\frac{\partial}{\partial R}\langle\alpha|\beta\rangle = \left\langle\frac{\partial\alpha}{\partial R}\middle|\beta\right\rangle + \left\langle\alpha\middle|\frac{\partial\beta}{\partial R}\right\rangle$$

using the orthonormal condition produces the identity

$$\begin{aligned}\left\langle\frac{\partial\alpha}{\partial R}\middle|\beta\right\rangle &= -\left\langle\alpha\middle|\frac{\partial\beta}{\partial R}\right\rangle\\ &= -d_{\alpha\beta}\ .\end{aligned}$$

As such

$$\frac{\partial}{\partial R}\langle\alpha\,|\,\hat{\chi}_W\,|\,\alpha'\rangle = \left\langle\alpha\middle|\frac{\partial\hat{\chi}_W}{\partial R}\middle|\alpha'\right\rangle + \sum_\beta\left(-d_{\alpha\beta}\chi_W^{\beta\alpha'} + \chi_W^{\alpha\beta}d_{\beta\alpha'}\right). \tag{C.10}$$

Using this identity and making $\left\langle\alpha\,\middle|\,\frac{\partial\hat{\chi}_W}{\partial R}\,\middle|\,\alpha'\right\rangle$ the subject of the formula yields

$$\left\langle\alpha\middle|\frac{\partial\hat{\chi}_W}{\partial R}\middle|\alpha'\right\rangle = \frac{\partial\chi_W^{\alpha\alpha'}}{\partial R} - \sum_\beta\left(-d_{\alpha\beta}\chi_W^{\beta\alpha'} + \chi_W^{\alpha\beta}d_{\beta\alpha'}\right)\ . \tag{C.11}$$

Substituting this expression for $\left\langle\alpha\,\middle|\,\frac{\partial\hat{\chi}_W}{\partial R}\,\middle|\,\alpha'\right\rangle$ back into the term we are trying to evaluate gives

$$\left(\frac{P}{M} + \frac{P_\eta}{M_\eta}\frac{\tau P}{M}\right)\left\langle\alpha\middle|\frac{\partial\hat{\chi}_W}{\partial R}\middle|\alpha'\right\rangle = \left(\frac{P}{M} + \frac{P_\eta}{M_\eta}\frac{\tau P}{M}\right)\left(\frac{\partial\chi_W^{\alpha\alpha'}}{\partial R} - \sum_\beta\left(-d_{\alpha\beta}\chi_W^{\beta\alpha'} + \chi_W^{\alpha\beta}d_{\beta\alpha'}\right)\right)\ . \tag{C.12}$$

The second to last term may be expanded to obtain

$$\left\langle\alpha\middle|\frac{P_\eta}{M_\eta}\frac{\partial\hat{\chi}_W}{\partial\eta}\middle|\alpha'\right\rangle = \frac{P_\eta}{M_\eta}\frac{\partial\chi^{\alpha\alpha'}}{\partial\eta}\ , \tag{C.13}$$

while the final term produces

$$-\left\langle \alpha \left| \frac{P_\eta}{M_\eta} P \frac{\partial \hat{\chi}_W}{\partial P} \right| \alpha' \right\rangle = -\frac{P_\eta}{M_\eta} P \frac{\partial \chi_W^{\alpha\alpha'}}{\partial P}. \tag{C.14}$$

As such the equation of motion may thus be expressed as

$$\begin{aligned}\frac{\partial \chi_W^{\alpha\alpha'}}{\partial t} &= \mathrm{i}\omega_{\alpha\alpha'}\chi_W^{\alpha\alpha'} + \left[\left(\frac{P^2}{2M} - gk_BT\right)\frac{\partial}{\partial\eta} + \frac{P_\eta}{M_\eta}\frac{\partial}{\partial\eta}\right. \\ &\left. -\frac{P_\eta}{M_\eta}P\frac{\partial}{\partial P} + \frac{P}{M}\frac{\partial}{\partial R} + \frac{P_\eta}{M_\eta}\frac{\tau P}{M}\frac{\partial}{\partial R}\right]\chi_W^{\alpha\alpha'} \\ &+ \frac{1}{2}\sum_\beta F^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P} + \frac{1}{2}\sum_\beta \frac{\partial\chi_W^{\alpha\beta}}{\partial P}F^{\beta\alpha'} \\ &+ \frac{\tau P}{2M}\sum_\beta F^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P_\eta} + \frac{\tau P}{2M}\sum_\beta \frac{\partial\chi_W^{\alpha\beta}}{\partial P_\eta}F^{\beta\alpha'} \\ &+ \left(\frac{P}{M} + \frac{P_\eta}{M_\eta}\frac{\tau P}{M}\right)\left[-\sum_\beta\left(-d_{\alpha\beta}\chi_W^{\beta\alpha'} + \chi_W^{\alpha\beta}d_{\beta\alpha'}\right)\right]. \end{aligned} \tag{C.15}$$

Making use of explicit Liouville operators the above equation may be written as

$$\begin{aligned}\frac{\partial \chi_W^{\alpha\alpha'}}{\partial t} &= \sum_{\beta\beta'}\left[\mathrm{i}\omega_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \left(L_1^{NHP} + L_3^{NHP} + L_4^{NHP}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'}\right. \\ &+ \frac{1}{2}\left(F^{\alpha\beta}\delta_{\alpha'\beta'}\frac{\partial}{\partial P} + \frac{\partial}{\partial P}\delta_{\alpha\beta}F^{\beta\alpha'}\right) \\ &+ \frac{\tau P}{2M}\left(F^{\alpha\beta}\delta_{\alpha'\beta'}\frac{\partial}{\partial P_\eta} + \frac{\partial}{\partial P_\eta}\delta_{\alpha\beta'}F^{\beta\alpha'}\right) \\ &\left. + \left(\frac{P}{M} + \frac{P_\eta}{M_\eta}\frac{\tau P}{M}\right)\left(d_{\alpha\beta}\delta_{\alpha'\beta'} - \delta_{\beta\alpha'}d_{\beta\alpha'}\right)\right]\chi^{\beta\beta'} \\ &= \sum_{\beta\beta'}\mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'}\chi_W^{\beta\beta'}. \end{aligned} \tag{C.16}$$

On the last line of the above equation we have defined the quantum-classical Liouville super-operator, we will now express it into its more traditional form. This may be accomplished by defining the classical Liouville operator as

$$\mathrm{i}L_{\alpha\alpha'} = (L_1 + L_2 + L_3)\,\delta_{\alpha\alpha'} + \frac{(F^\alpha - F^{\alpha'})}{2}\left[\frac{\partial}{\partial P} + \tau\frac{P}{M}\right]\frac{\partial}{\partial P_\eta}. \tag{C.17}$$

The classical-like Liouville operator is the only operator which changes when the implementation of the bath dynamics changes. As such it is possible to follow the procedure outlined in Appendix B to obtain the J-operator into its traditional form. Doing this allows one to express the Liouville super-operator as

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'} = i\left(\omega_{\alpha\alpha'} + L_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'}\ . \tag{C.18}$$

The simulation of the non-adiabatic dynamics described by the above equation may achieved through the use of a stochastic algorithm. An example of such an algorithm may be found in [40].

Appendix D

Derivation of the Phase-Space Distribution-Function

Within the canonical ensemble, the normalised density matrix may be written as

$$\hat{\rho} = \frac{1}{Z(\beta)} \mathrm{e}^{-\beta \hat{H}} \equiv \frac{1}{Z(\beta)} \hat{\Omega} \ , \tag{D.1}$$

where $\beta = 1/k_{\mathrm{B}}T$ represents the inverse temperature. The Boltzmann constant is denoted by k_{B}, while T represents the absolute temperature of the ensemble, and $Z(\beta)$ is the canonical partition function defined as

$$Z(\beta) = \mathrm{Tr}\left(\mathrm{e}^{-\beta \hat{H}}\right) .$$

The unnormalised density matrix is represented by $\hat{\Omega}$ and satisfies the Bloch equation

$$\frac{\partial \hat{\Omega}}{\partial \beta} = -\hat{H}\hat{\Omega} = -\hat{\Omega}\hat{H} \ , \tag{D.2}$$

subject to the initial condition $\hat{\Omega}\,(\beta = 0) = \hat{\mathcal{I}}$, where $\hat{\mathcal{I}}$ is the identity operator. The Wigner transform of Eqn. (D.2), is then

$$\begin{aligned} \frac{\partial \Omega_{\mathrm{W}}(q,p)}{\partial \beta} &= -H_{\mathrm{W}}(q,p)\mathrm{e}^{\frac{\hbar\Lambda}{2\mathrm{i}}}\Omega_{\mathrm{W}}(q,p) \\ &= -\Omega_{\mathrm{W}}(q,p)\mathrm{e}^{\frac{\hbar\Lambda}{2\mathrm{i}}}H_{\mathrm{W}}(q,p) \ , \end{aligned} \tag{D.3}$$

where the identity for the Wigner transform of two operators [Eqn. (3.39)], has been used. In Eqn. (D.3) Λ has been used to denote the anti-Poisson bracket and is defined as

$$a\Lambda b = -\{a,b\} = -\frac{\partial a}{\partial X_i}\mathcal{B}^c_{ij}\frac{\partial b}{\partial X_j}\ , \tag{D.4}$$

for two arbitrary phase-space functions, a and b [39], while (q,p) represent phase-space coordinates. Using Eqn. (D.3), as well as Eqn. (3.39), produces

$$H_{\mathrm{W}}(q,p)\mathrm{e}^{\frac{\hbar\Lambda}{2\mathrm{i}}}\Omega_{\mathrm{W}}(q,p) = H_{\mathrm{W}}(q,p)\mathrm{e}^{-\frac{\hbar\Lambda}{2\mathrm{i}}}\Omega_{\mathrm{W}}(q,p)\ . \tag{D.5}$$

As such the transformed Bloch equation may be written as

$$\frac{\partial\Omega_{\mathrm{W}}(q,p)}{\partial\beta} = \frac{1}{2}\left[-H_{\mathrm{W}}(q,p)\mathrm{e}^{\frac{\hbar\Lambda}{2\mathrm{i}}}\Omega_{\mathrm{W}}(q,p) - H_{\mathrm{W}}(q,p)\mathrm{e}^{-\frac{\hbar\Lambda}{2\mathrm{i}}}\Omega_{\mathrm{W}}(q,p)\right]\ . \tag{D.6}$$

The complex exponentials which appear in the above equation may be expanded using the Euler formula. Doing so gives

$$\begin{aligned}\frac{\partial\Omega_{\mathrm{W}}(q,p)}{\partial\beta} &= \frac{1}{2}\left[-H_{\mathrm{W}}\left(\cos\left(\frac{\hbar\Lambda}{2}\right) - \mathrm{i}\sin\left(\frac{\hbar\Lambda}{2}\right)\right)\Omega_{\mathrm{W}}\right.\\ &\quad\left. - H_{\mathrm{W}}\left(\cos\left(\frac{\hbar\Lambda}{2}\right) + \mathrm{i}\sin\left(\frac{\hbar\Lambda}{2}\right)\right)\Omega_{\mathrm{W}}\right]\\ &= -H_{\mathrm{W}}(q,p)\cos\left(\frac{\hbar\Lambda}{2}\right)\Omega_{\mathrm{W}}(q,p)\ .\end{aligned} \tag{D.7}$$

For an ensemble of harmonic oscillators, H_{W} is given by

$$H_{\mathrm{W}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2q^2\ . \tag{D.8}$$

where a multidimensional notation $(q,p) = (q_1, q_2, ..., p_1, p_2, ...)$ has been used. Substituting this Hamiltonian into Eqn. (D.7) gives

$$\frac{\partial\Omega_{\mathrm{W}}}{\partial\beta} = -\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2q^2\right)\cos\left(\frac{\hbar}{2}\left[\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right]\right)\Omega_{\mathrm{W}}\ . \tag{D.9}$$

Next one needs to consider the cosine term which appears in Eqn. (D.9). This term may be approximated by performing a series expansion to second order in $\hbar$

$$\cos\left[\frac{\hbar}{2}\left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right)\right] \approx 1 - \frac{1}{2}\left(\frac{\hbar}{2}\right)^2\left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right)^2\ . \tag{D.10}$$

Expanding the square of the derivative terms in the round brackets yields

$$\begin{aligned}
\left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p}-\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right)^2 =& \frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p}\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p}-\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p}\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}-\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p}+\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\\
=&\frac{\overleftarrow{\partial}^2}{\partial q^2}\frac{\overrightarrow{\partial}^2}{\partial p^2}-\frac{\overleftarrow{\partial}^2}{\partial q\partial p}\frac{\overrightarrow{\partial}^2}{\partial q\partial p}-\frac{\overleftarrow{\partial}^2}{\partial p\partial q}\frac{\overrightarrow{\partial}^2}{\partial q\partial p}+\frac{\overleftarrow{\partial}^2}{\partial p^2}\frac{\overrightarrow{\partial}^2}{\partial q^2}\\
=&\frac{\overleftarrow{\partial}^2}{\partial q^2}\frac{\overrightarrow{\partial}^2}{\partial p^2}-2\,\frac{\overleftarrow{\partial}^2}{\partial q\partial p}\frac{\overrightarrow{\partial}^2}{\partial q\partial p}+\frac{\overleftarrow{\partial}^2}{\partial p^2}\frac{\overrightarrow{\partial}^2}{\partial q^2}\ .
\end{aligned}\tag{D.11}$$

Substituting Eqn. (D.11) back into Eqn. (D.9) one gets that

$$\begin{aligned}
\frac{\partial\Omega_{\rm W}}{\partial\beta}=&-\frac{p^2}{2m}\left[1-\frac{\hbar^2}{8}\left(\frac{\overleftarrow{\partial}^2}{\partial q^2}\frac{\overrightarrow{\partial}^2}{\partial p^2}-2\,\frac{\overleftarrow{\partial}^2}{\partial q\partial p}\frac{\overrightarrow{\partial}^2}{\partial q\partial p}+\frac{\overleftarrow{\partial}^2}{\partial p^2}\frac{\overrightarrow{\partial}^2}{\partial q^2}\right)\right]\Omega_{\rm W}\\
&-\frac{m\omega^2q^2}{2}\left[1-\frac{\hbar^2}{8}\left(\frac{\overleftarrow{\partial}^2}{\partial q^2}\frac{\overrightarrow{\partial}^2}{\partial p^2}-2\,\frac{\overleftarrow{\partial}^2}{\partial q\partial p}\frac{\overrightarrow{\partial}^2}{\partial q\partial p}+\frac{\overleftarrow{\partial}^2}{\partial p^2}\frac{\overrightarrow{\partial}^2}{\partial q^2}\right)\right]\Omega_{\rm W}\\
=&-\left(\frac{p^2}{2m}-\frac{1}{2}m\omega^2q^2\right)\Omega_{\rm W}+\frac{\hbar^2}{8m}\frac{\partial^2\Omega_{\rm W}}{\partial q^2}+\frac{\hbar^2}{8}m\omega^2\frac{\partial^2\Omega_{\rm W}}{\partial p^2}\ .
\end{aligned}\tag{D.12}$$

Equation (D.12) is the Wigner transformed Bloch equation for the harmonic oscillator. Since the harmonic Hamiltonian is only made up of terms that are at most quadratic in q and p, Eqn. (D.12) is exact. This is due to the fact that the higher order terms in the cosine expansion only contain derivatives of order higher than two. When these derivatives are acted upon the Hamiltonian they produce a result of zero. However, it should be noted that, Eqn. (D.12) is still difficult to solve in its current form. To overcome this, an ansatz may be made regarding the form of $\Omega_{\rm W}$:

$$\Omega_{\rm W}(q,p)=e^{-A(\beta)H_{\rm W}(q,p)+B(\beta)}\ ,\tag{D.13}$$

where the functions A and B are subject to initial conditions $A(0)=B(0)=0$. To obtain the unnormalised density matrix, one needs to determine the functions $A(\beta)$ and $B(\beta)$. With this in mind, the derivatives of $\Omega_{\rm W}$ with respect to the spatial coordinate are calculated

$$\frac{\partial\Omega_{\rm W}}{\partial q}=\Omega_{\rm W}\left(-A\frac{\partial H_{\rm W}}{\partial q}\right)\ ,\tag{D.14}$$

and

$$\begin{aligned}\frac{\partial^2 \Omega_{\mathrm{W}}}{\partial q^2} &= \frac{\partial \Omega_{\mathrm{W}}}{\partial q}\left(-A\frac{\partial H_{\mathrm{W}}}{\partial q}\right) - A\Omega_{\mathrm{W}}\frac{\partial^2 H_{\mathrm{W}}}{\partial q^2} \\ &= \left(-A\frac{\partial H_{\mathrm{W}}}{\partial q}\right)^2 \Omega_{\mathrm{W}} - A\Omega_{\mathrm{W}}\frac{\partial^2 H_{\mathrm{W}}}{\partial q^2} \\ &= \left(A^2 m^2 \omega^4 q^2 - Am\omega^2\right)\Omega_{\mathrm{W}}\ . \end{aligned} \tag{D.15}$$

The derivatives with respect to the momentum coordinate are also calculated,

$$\frac{\partial \Omega_{\mathrm{W}}}{\partial p} = -A\frac{\partial H_{\mathrm{W}}}{\partial p}\Omega_{\mathrm{W}}\ , \tag{D.16}$$

and

$$\begin{aligned}\frac{\partial^2 \Omega_{\mathrm{W}}}{\partial p^2} &= -A\frac{\partial^2 H_{\mathrm{W}}}{\partial p^2}\Omega_{\mathrm{W}} - A\frac{\partial H_{\mathrm{W}}}{\partial p}\frac{\partial \Omega_{\mathrm{W}}}{\partial p} \\ &= -A\frac{\partial^2 H_{\mathrm{W}}}{\partial p^2}\Omega_{\mathrm{W}} + \left(A\frac{\partial H_{\mathrm{W}}}{\partial p}\right)^2 \\ &= -\frac{A}{m}\Omega_{\mathrm{W}} + \left(A\frac{p}{m}\right)^2\Omega_{\mathrm{W}} \\ &= -\frac{A}{m}\Omega + A^2\frac{p^2}{m^2}\Omega_{\mathrm{W}}\ . \end{aligned} \tag{D.17}$$

Finally the derivative with respect to β is calculated

$$\frac{\partial \Omega_{\mathrm{W}}}{\partial \beta} = \left(-\frac{\partial A}{\partial \beta}H_{\mathrm{W}} + \frac{\partial B}{\partial \beta}\right)\Omega_{\mathrm{W}}\ . \tag{D.18}$$

Substituting Eqns. (D.15), (D.17) and (D.18) back into Eqn. (D.12), and dividing through by Ω_W produces,

$$\begin{aligned}-\frac{\partial A}{\partial \beta}H_{\mathrm{W}} + \frac{\partial B}{\partial \beta} &= -\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\right) + \frac{\hbar^2}{8}A^2 m\omega^4 q^2 - \frac{\hbar}{8}A\omega^2 - \frac{\hbar^2}{8}\omega^2 A + \frac{\hbar^2}{8}\omega^2 A^2\frac{p^2}{m} \\ &= -H_{\mathrm{W}} + \frac{\hbar^2}{8}\left[A^2 m\omega^4 q^2 - A\omega^2 - \omega^2 A + \omega^2 A^2\frac{p^2}{m}\right] \\ &= -H_{\mathrm{W}} + \frac{\hbar^2}{4}\left[-A\omega^2 + \omega^2 A^2\left(\frac{1}{2}m\omega^2 q^2 + \frac{p^2}{2m}\right)\right] \\ &= -H_{\mathrm{W}} + \left(\frac{\hbar\omega}{2}\right)^2\left[-A + A^2 H_W\right]\ . \end{aligned} \tag{D.19}$$

One may rearrange this expression to obtain

$$-\frac{\partial A}{\partial \beta}H_{\mathrm{W}} + H_{\mathrm{W}} = -\frac{\partial B}{\partial \beta} + \left(\frac{\hbar\omega}{2}\right)^2\left[-A + A^2 H_{\mathrm{W}}\right]\ ,$$

from which one gets that

$$\left[-\frac{\partial A}{\partial \beta}+1-\left(\frac{\hbar\omega A}{2}\right)^2\right]H_{\mathrm{W}}+\left[\frac{\partial B}{\partial \beta}+\left(\frac{\hbar\omega}{2}\right)^2 A\right]=0\ . \tag{D.20}$$

This equation must be true for all values of (q,p), as the terms within the square brackets are not dependant on the phase-space coordinates. Therefore each set of square brackets must vanish independently. As such one has that

$$\frac{\mathrm{d}A}{\mathrm{d}\beta}-1+\frac{(\hbar\omega)^2}{4}A^2=0\ , \tag{D.21}$$

and

$$\frac{\mathrm{d}B}{\mathrm{d}\beta}+\frac{(\hbar\omega)^2}{4}A=0\ . \tag{D.22}$$

One now needs to consider Eqn. (D.21), since this equation only contains the function $A(\beta)$, it may be rewritten as

$$\frac{\mathrm{d}A}{1-\frac{(\hbar\omega)^2}{4}A^2}=\mathrm{d}\beta\ . \tag{D.23}$$

This may then be solved by performing a change of variables. To this end one lets $x=\frac{\hbar\omega}{2}A$, then $\mathrm{d}A=\frac{2}{\hbar\omega}\mathrm{d}x$, Eqn. (D.21) becomes

$$\frac{2}{\hbar\omega}\int\frac{\mathrm{d}x}{1-x^2}=\int\mathrm{d}\beta\ . \tag{D.24}$$

Using the identity

$$\frac{1}{1-x^2}=\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}x}\ln\left(\frac{1+x}{1-x}\right)\ , \tag{D.25}$$

produces the result

$$\begin{aligned}\beta&=\frac{1}{\hbar\omega}\int\mathrm{d}x\,\frac{\mathrm{d}}{\mathrm{d}x}\,\ln\left(\frac{1+x}{1-x}\right)\\&=\frac{1}{\hbar\omega}\ln\left(\frac{1+x}{1-x}\right)\\&=\frac{1}{\hbar\omega}\ln\left(\frac{1+\frac{\hbar\omega}{2}A}{1-\frac{\hbar\omega}{2}A}\right)\ ,\end{aligned} \tag{D.26}$$

which may be written in exponential form as

$$\mathrm{e}^{\hbar\omega\beta}=\frac{1+\frac{\hbar\omega}{2}A}{1-\frac{\hbar\omega}{2}A}\ .$$

Rearranging this result to obtain an expression for $A(\beta)$, one gets:

$$\begin{aligned} A(\beta) &= \frac{2}{\hbar\omega}\frac{\mathrm{e}^{\hbar\omega\beta}-1}{\mathrm{e}^{\hbar\omega\beta}+1} \\ &= \frac{2}{\hbar\omega}\frac{\mathrm{e}^{\frac{\hbar\omega}{2}\beta}-\mathrm{e}^{-\frac{\hbar\omega}{2}\beta}}{\mathrm{e}^{\frac{\hbar\omega}{2}\beta}+\mathrm{e}^{-\frac{\hbar\omega}{2}\beta}} \\ &= \frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega}{2}\beta\right) \ . \end{aligned} \tag{D.27}$$

To obtain the function $B(\beta)$, one is now required to substitute Eqn. (D.27) into Eqn. (D.22):

$$\frac{\partial B}{\partial \beta} + \left(\frac{\hbar\omega}{2}\right)\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega}{2}\beta\right) = 0 \ . \tag{D.28}$$

Making B the subject of the formula gives

$$B = -\frac{\hbar\omega}{2}\int \mathrm{d}\beta \tanh\left(\frac{\hbar\omega\beta}{2}\right) \ . \tag{D.29}$$

To find a solution to this integral one need only consider

$$\begin{aligned} \tanh x &= \frac{\sinh x}{\cosh x} \\ &= \frac{\mathrm{d}}{\mathrm{d}x}\ln(\cosh x) \ . \end{aligned} \tag{D.30}$$

Letting $x = \frac{\hbar\omega\beta}{2} \rightarrow \mathrm{d}\beta = \frac{2}{\hbar\omega}\mathrm{d}x$, produces

$$\begin{aligned} B &= -\frac{\hbar\omega}{2}\frac{2}{\hbar\omega}\int \mathrm{d}x \tanh x \\ &= -\int \mathrm{d}x \ \frac{\mathrm{d}}{\mathrm{d}x}\ln\left(\cosh x\right) \\ &= -\ln\left(\cosh x\right) \\ &= -\ln\left[\cosh\left(\frac{\hbar\omega\beta}{2}\right)\right] \ . \end{aligned} \tag{D.31}$$

Having derived expressions for $A(\beta)$ and $B(\beta)$ one can now substitute them back into the our original ansatz for the Ω_W

$$\begin{aligned} \Omega_\mathrm{W} &= \mathrm{e}^{-A(\beta)H_\mathrm{W}(q,p)+B(\beta)} \\ &= \mathrm{e}^{-\ln\cosh\left(\frac{\hbar\omega\beta}{2}\right)}\mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)H_\mathrm{W}(q,p)} \\ &= \frac{1}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)}\mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)H_\mathrm{W}(q,p)} \ . \end{aligned} \tag{D.32}$$

All that remains now is determining the partition function $Z(\beta)$, which is given by

$$\begin{aligned} Z(\beta) &= \int\int \mathrm{d}q\ \mathrm{d}p\, \Omega_{\mathrm{W}}(q,p,\beta) \\ &= \frac{1}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)} \int\int \mathrm{d}q\ \mathrm{d}p\, \mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)\left(\frac{p^2}{2m}+\frac{1}{2}m\omega^2q^2\right)} , \end{aligned} \tag{D.33}$$

where the integrals are performed over all of phase space. The integrals in Eqn. (D.33) can be factorised into q-dependent and p-dependent terms, this produces

$$Z(\beta) = \frac{1}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)} \int \mathrm{d}p\, \mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)\frac{p^2}{2m}} \int \mathrm{d}q\, \mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)\frac{m\omega^2}{2}q^2} . \tag{D.34}$$

Both the integrals in this expression are simple Gaussian functions, as such

$$\begin{aligned} Z(\beta) &= \frac{1}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)} \left(\frac{\pi}{\left(\frac{1}{\hbar\omega m}\right)\tanh\left(\hbar\omega\beta\right)}\right)^{\frac{1}{2}} \left(\frac{\pi}{\left(\frac{m\omega}{\hbar}\right)\tanh\left(\hbar\omega\beta\right)}\right)^{\frac{1}{2}} \\ &= \frac{1}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)} \frac{\pi}{\tanh\left(\frac{\hbar\omega\beta}{2}\right)} \frac{1}{\sqrt{\frac{1}{\hbar\omega m}\frac{m\omega}{\hbar}}} \\ &= \frac{\pi\hbar}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)} \frac{\cosh\left(\frac{\hbar\omega\beta}{2}\right)}{\sinh\left(\frac{\hbar\omega\beta}{2}\right)} \\ &= \frac{\pi\hbar}{\sinh\left(\frac{\hbar\omega\beta}{2}\right)} . \end{aligned} \tag{D.35}$$

Recalling that the Wigner transformed, normalised, distribution function is given by

$$\rho_{\mathrm{W}}(q,p,\beta) = \frac{1}{Z(\beta)}\Omega_{\mathrm{W}}(q,p,\beta) .$$

One then need only substitute the expressions for Ω_{W} and $Z(\beta)$, given by Eqns. (D.32) and (D.35), respectively, to obtain the final result:

$$\begin{aligned} \rho_{\mathrm{W}}(q,p,\beta) &= \frac{\sinh\left(\frac{\hbar\omega\beta}{2}\right)}{\pi\hbar} \frac{\mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)H}}{\cosh\left(\frac{\hbar\omega\beta}{2}\right)} \\ &= \frac{1}{\pi\hbar}\tanh\left(\frac{\hbar\omega\beta}{2}\right) \mathrm{e}^{-\frac{2}{\hbar\omega}\tanh\left(\frac{\hbar\omega\beta}{2}\right)H} . \end{aligned} \tag{D.36}$$

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