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Quantum Dynamics in Classical Constant-Temperature Baths

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by

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

Signed:......................... Name: Dr. A. Sergi Date:.........................

Abstract

In this dissertation the formulation of various integration algorithms is studied, with a view to simulate quantum-classical systems in contact with a thermal bath. In particular focus is given to the constant temperature dynamics of the Nosé-Hoover, Nosé-Hoover Chain and Nosé-Hoover Power thermostat schemes. Through the use of the time symmetric Trotter factorisation of the Liouville operator, algorithms are derived that are both time-reversible and measure-preserving. The efficiency of these algorithms is tested via the constant temperature simulation of a low-dimensional harmonic system. In addition The Nosé-Hoover Power thermostat was then extended to the quantum-classical case. The damping of a tunnelling spin coupled to a thermalised harmonic mode was simulated and the results are presented.

Preface

The computational work described in this dissertation was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Pietermaritzburg, from January 2011 to November 2012, under the supervision of Doctor Alessandro Sergi.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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Chapter 1

Introduction

All theoretical physics is based upon mathematical models which are used to explain and predict natural phenomena, while experimental physics uses experimental tools to probe the latter. Computer simulations lie in between these two approaches, and give us 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 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 [1].

However, unlike classical physics, there is no general method for simulating the quantum dynamics of many body systems [1, 2]. This is a consequence of the theory itself involving non-commuting operators, and the dimensionality of Hilbert space, which requires computational resources far larger than those realistically available. As stated in [3], it is not even possible to either store or calculate the many body wave-function with the numerical precision required, due to the limitations on the available resources. For quantum systems, certain approximations have to be made if one wishes to obtain some sort of solution. The development of efficient algorithms for the simulation of quantum dynamics currently forms a large area of research within the field of computational physics.

When formulating the open dynamics of a quantum system one usually makes use either of the master equation or of the Hamiltonian approach [2]. The Hamiltonian approach requires one to place the system of interest within a bath containing a large number of degrees of freedom. The evolution of the entire system (consisting of the quantum system of interest and the bath) is then calculated before the coordinates of the bath are traced out. Due to the large number of degrees of freedom associated with this evolution, such a

method is very computationally demanding. In certain cases, the bath is not quantum in its nature and may in fact be classical. One may then make use of either the classical bath, or the phase space representation of a quantum bath. In order to obtain this representation one takes a partial Wigner transformation over all the coordinates coupled to the subsystem of interest (in other words one has to perform a partial Wigner transformation over the entire bath). It has been shown in [4] that, if one makes suitable approximations, a combined quantum-classical law of motion may be obtained for a quantum subsystem coupled to such a phase space bath. However in order to simulate this system one is still required to calculate the dynamics of the whole system, as such it is still a very computationally demanding technique. Such phase space baths may, however, be represented in terms of a few degrees of freedom, whose evolution is defined by non-Hamiltonian dynamics. Such non-Hamiltonian molecular dynamics equations of motion are described in [3, 5, 6]. These equations of motion give a dissipative character to the dynamics of the system, via the use of a minimal number of degrees of freedom. One then uses the resulting non-Hamiltonian bath to simulate a high-dimensional bath. This approach has been suggested in [7, 8], and is computationally less demanding than the approaches mentioned before.

The purpose of this dissertation was to further develop and make improvements to this approach. There are two key improvements made to the work already found in the literature. The first of these is the derivation of a time-reversible measure-preserving integration scheme for the Nosé-Hoover Power (NHP) dynamics. This is achieved by following the procedure for deriving algorithms which preserve the invariant measure of phase space outlined in [9]. The NHP thermostat was originally proposed in [5], where a time-reversible integration scheme was developed for it. The second improvement is the use of an even lower dimensional non-Hamiltonian bath than that used in [7, 8] for the simulation of a quantum-classical system. This second improvement is achieved by generalising the NHP measure-preserving integration scheme from the classical to the quantum-classical case.

This dissertation is structured as follows: In Chapter 2 the differences between Hamiltonian and non-Hamiltonian theories are given, followed by a discussion about the general algebraic bracket structure underlying non-Hamiltonian systems. Before the three extended system thermostat schemes of interest are introduced. In Chapter 3 focus is given to how integration schemes for non-Hamiltonian dynamics may be obtained in general. Al-

gorithms are given for both the purely time-reversible schemes as well as for those which preserve the invariant measure of phase space. Algorithms based on these prescriptions are developed for the thermostat schemes of interest. The stability of these schemes is tested via the simulation of a one dimensional harmonic oscillator. In Chapter 4 a detailed discussion of the theory of quantum-classical dynamics is given. This includes a brief recap of Heisenberg's formulation of quantum mechanics, which leads into a discussion about quantum statistical mechanics, and here the concept of the density matrix operator is introduced. The phase space representation of quantum mechanics is then discussed with focus given to the Wigner representation. The modelling of quantum dynamics within classical baths is presented next, this includes a derivation of the quantum-classical Liouville equation expressed in the adiabatic basis. Before an extension of the NHC and NHP thermostat schemes to the quantum-classical case is presented. In Chapter 5 the details of the numerical simulations are given. In particular the model chosen is discussed in detail. This discussion is accompanied by a description of the scaled units used in the simulations. The simulation procedures are also discussed here. Finally in this chapter the obtained results are given and discussed. In Chapter 6 a summary of the work done in this dissertation is given along with some conclusions. In the Appendices several aspects of the theory are derived.

Chapter 2

Classical Non-Hamiltonian Theory

In this chapter the theory associated with non-Hamiltonian dynamics is discussed. It starts with a brief summary of both Hamiltonian and non-Hamiltonian theories. This is followed by a discussion about the general algebraic bracket structure underlying non-Hamiltonian dynamics. Finally three extended system thermostat schemes are introduced and discussed.

2.1 Hamiltonian Theory

In order to define what it means for a theory to be Hamiltonian, the concept of a Lie algebra must first be introduced. To this end one may consider some mathematical space which contains a set of mathematical objects (u, v, w). According to [10], a Lie algebra for such a mathematical space is one which has the following properties

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

$$\{au, v\} = a\{u, v\} \ , \tag{2.2}$$

where a is a complex number which does not belong to the mathematical space.

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

in order for an algebra to be considered a Lie algebra there is one more less obvious property which it needs to satisfy. This property is known as the Jacobi relation and is

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given by

$$\mathcal{J} = \{u, \{v, w\}\} + \{v, \{w, u\}\} + \{w, \{u, v\}\} = 0 \ . \tag{2.4}$$

In Eqs. (2.1) to (2.4) $\{\cdots, \cdots\}$ has been used to denote a generic bracket. This bracket may be classical or quantum in its nature. This is due to the fact that there is a similarity which exists within the mathematical structure of the bracket formulation of both classical and quantum mechanics [7]. The classical theory may be defined by the Poisson bracket, while the quantum theory may be defined by the commutator. In order for any bracket algebra to considered Hamiltonian, it must satisfy all four of these properties, in other words it must be a Lie algebra. The antisymmetric nature of such a bracket is shown by Eqn. (2.1) and plays a role in defining its time evolution, while Eqns. (2.2) and (2.3) show that such a bracket is a linear operator with respect to complex numbers, a, along with other elements of its own mathematical space respectively.

If the elements of the mathematical space are time independent, then a bracket made up of these conserved quantities is also conserved. Consider an element of the space, H, this H is usually taken to be the Hamiltonian. The equations of motion may be defined as [3]

$$\frac{du}{dt} = \{u, H\} \ . \tag{2.5}$$

Due to the antisymmetric nature of the bracket, it can easily be shown that Eqn. (2.5) has the implication that H is a constant of motion [10]. 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,

$$\frac{du}{dt} = \{u, H\} = 0 \qquad \frac{dv}{dt} = \{v, H\} = 0 \ . \tag{2.6}$$

A bracket of these two elements, $\{u, v\}$ is also a constant of motion [10]

$$\{\{u, v\}, H\} = 0 \ . \tag{2.7}$$

This shows that the Hamiltonian algebra is invariant under time translation. A full derivation of the time invariance property 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. (2.1) to (2.3). However this theory fails to satisfy the Jacobi relation, namely,

$$\mathcal{J} = \{u, \{v, w\}\} + \{v, \{w, u\}\} + \{w, \{u, v\}\} \neq 0 \, . \tag{2.8}$$

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. The advantages of using a non-Hamiltonian approach only start becoming apparent when one starts looking at systems which contain many degrees of freedom.

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 systems temperature. In order to successfully perform such a task using Hamiltonian theories one requires an infinite number of degrees of freedom. However, if one makes use of non-Hamiltonian theories, it becomes possible to achieve the desired result through the use of only a few additional degrees of freedom [7].

Another example of where non-Hamiltonian theory plays a crucial role is in the simulation of quantum systems. Since 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 [3]. However through the use of a non-Hamiltonian approach it is possible to perform such simulations, in the limit of certain approximations [8, 11, 12, 13].

2.3 General Bracket Formulation of Dynamics

In the previous sections both Hamiltonian and non-Hamiltonian dynamics have been introduced. 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. In order to introduce this bracket formulation, one begins

by introducing an antisymmetric matrix

$$\mathcal{B}_{ij} = -\mathcal{B}_{ji} \qquad i, j = 1, 2N \; ,$$

where, $2N$ represents the dimension of the phase space. The generalised non-Hamiltonian bracket may then be defined as [6],

$$\{a, b\}_{\mathcal{B}} = \sum_{j=1}^{2N} \frac{\partial a}{\partial X_j} \mathcal{B}_{ij} \frac{\partial b}{\partial X_j} \; ,$$

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

$$\dot{X} = \{X, H\}_{\mathcal{B}} = \sum_{jk} \frac{\partial X}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \; , \tag{2.9}$$

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

$$\dot{X}_j = \sum_k \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \; , \tag{2.10}$$

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

$$\mathcal{B}^c = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \; , \tag{2.11}$$

then Eqn. (2.9) simply produces the canonical equations of motion for a Hamiltonian system, which correspond to a canonical transformation of X [10]. However if a non canonical transformation is applied to X, then the form of the equations of motion is conserved, while the elements of the matrix $\mathcal{B}$ may then be defined in terms of complex phase space functions. In this case the matrix $\mathcal{B}$ loses its canonical form but remains antisymmetric [5]. A consequence of the antisymmetry of $\mathcal{B}$, it that any phase space flow which is defined by Eqn. (2.9) for a time independent Hamiltonian will be a constant of

motion [6]. This can easily be verified by taking the total time derivative of H,

$$
\begin{aligned}
\frac{dH}{dt} = \dot{H} &= \{H, H\}_{\mathcal{B}} \\
&= \sum_{jk} \frac{\partial H}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \\
&= 0 \ .
\end{aligned}
\tag{2.12}
$$

The reason that this equals zero, is that it is equivalent to taking the trace of the product of the antisymmetric matrix $\mathcal{B}_{jk}$ with the symmetric one $\partial H/\partial X_j \partial H/\partial X_k$, and as such is equal to zero. If $\mathcal{B}$ is antisymmetric then Eqn. (2.12) is always valid. This means that if one wishes to define a non-Hamiltonian flow which possess a conserved energy, then one need only require that some general matrix $\mathcal{B}$ be antisymmetric [5]. This has been used as a way to define conservative non-Hamiltonian phase space flows [5, 6].

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

$$
\sum_{n=1}^{2N} \mathcal{B}_{in} \frac{\partial \mathcal{B}_{jk}}{\partial X_n} + \mathcal{B}_{kn} \frac{\partial \mathcal{B}_{ij}}{\partial X_n} + \mathcal{B}_{jn} \frac{\partial \mathcal{B}_{ki}}{\partial X_n} = 0 \ ,
\tag{2.13}
$$

for any given choice of i, j and k [5, 14]. Moreover if $\mathcal{B}$ is antisymmetric and Eqn. (2.13) holds, then according to [14, 15], Eqn. (2.9) produces non-canonical Hamiltonian flows in phase space. However, if Eqn. (2.13) does not hold, then the phase space flow described by Eqn. (2.9) produces non-Hamiltonian phase space flows [5]. If the flows are non-Hamiltonian, then one may define the phase space compressibility as [16]

$$
\begin{aligned}
\kappa &= \nabla \dot{X} \\
&= \sum_j \frac{\partial}{\partial X_j} \dot{X}_j \\
&= \sum_j \frac{\partial}{\partial X_j} \sum_k \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \\
&= \sum_j \sum_k \frac{\partial}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \ .
\end{aligned}
\tag{2.14}
$$

In general this will be non-zero for non-Hamiltonian dynamics, although there are a few exceptions to this [17]. A consequence of the compressibility not being zero is that the phase space measure, dX, is no longer invariant [18]. 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 [16]

$$J\left(X_t; X_0\right) = \frac{\partial X_t}{\partial X_0} \ . \tag{2.15}$$

It has been shown [18] that $J\left(X_t; X_0\right)$ satisfies the evolution equation

$$\frac{d}{dt} J\left(X_t; X_0\right) = \kappa \ J\left(X_t; X_0\right) \ , \tag{2.16}$$

with the initial condition that $J\left(0\right) = 1$. Considering this equation of motion, it is clear that $J = 1$ for all time, if and only if $\kappa = 0$. However for non-Hamiltonian systems $\kappa \neq 0$. Rearranging Eqn. (2.15) allows one to express the measure transformation as

$$dX_t = J\left(X_t; X_0\right) \ dX_0 \ , \tag{2.17}$$

clearly if $J \neq 1$, then $dX_t \neq dX_0$, meaning that the measure is not preserved. Therefore if the systems compressibility is non-zero, the corresponding Jacobian of transformation will not be unitary.

A consequence of the phase space measure not being conserved is that the dynamics no longer sample phase space uniformly. There are however several ways to overcome this, one way which has been suggested in [5], 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 $\mathcal{B}$. This is equivalent to essentially designing conservative non-Hamiltonian equations of motion. Such equations possess a controlled statistical weighting of the phase space, this assists them in sampling the phase space uniformly [5, 19].

2.4 Constant Temperature Dynamics

Real life experiments are often performed in a controlled environment under isothermal conditions. 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 in not isolated, and is allowed to exchange energy with a heat bath (its environment). However the total energy of the bath and system is fixed, while the absolute temperature T, is defined by the heat bath. There are 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.

This dissertation will be focusing on three such schemes, namely the Nosé-Hoover, Nosé-Hoover Chain and Nosé-Hoover Power thermostat schemes. These schemes are introduced in greater detail in the following sections.

2.4.1 Nosé-Hoover Thermostat

The Nosé-Hoover (NH) thermostat was first introduced in [20]. In this section a brief overview of this thermostat scheme is presented, before integration schemes based upon it are derived. Its extended system Hamiltonian is given by

$$H^{NH} = H_c + \frac{P_\eta^2}{2M_\eta} + gk_bT\eta \ . \tag{2.18}$$

In Eqn. (2.18) H_c represents the Hamiltonian which describes some classical system of interest. H_c is defined as,

$$H_c = \frac{P^2}{2M} + V(R) \ , \tag{2.19}$$

where R and P represent the system coordinates and momenta respectively, while M and $V(R)$ represent the mass and interaction potential of the system respectively.

In Eqn. (2.18), 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 the thermal bath, while 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,

$$\dot{X} = \left\{X, H^{NH}\right\}_{\mathcal{B}^{NH}} = \sum_{j\,k} \frac{\partial X}{\partial X_j} \mathcal{B}_{j\,k}^{NH} \frac{\partial H^{NH}}{\partial X_k} \ . \tag{2.20}$$

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

$$\mathcal{B}^{NH} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ 0 & -1 & P & 0 \end{bmatrix} , \tag{2.21}$$

while the phase space point of the extended system is $X = (R, \eta, P, P_\eta)$. The NH equations of motion represented by Eqn. (2.20) may be explicitly expressed as

$$\dot{R} = \frac{P}{M} , \tag{2.22a}$$

$$\dot{\eta} = \frac{P_\eta}{M_\eta} , \tag{2.22b}$$

$$\dot{P} = -\frac{\partial V(R)}{\partial R} - P\frac{P_\eta}{M_\eta} , \tag{2.22c}$$

$$\dot{P}_\eta = \frac{P^2}{M} - gk_bT . \tag{2.22d}$$

The phase space compressibility, associated with this scheme, is given by

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

2.4.2 Nosé-Hoover Chain Thermostat

The Nosé-Hoover Chain (NHC) thermostat was first introduced in [21]. A review of this thermostat scheme is presented here, before various integration schemes based upon it are derived. The NHC extended system Hamiltonian for a system with only one additional thermostat variable is,

$$H^{NHC} = H_c + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P_{\eta_2}^2}{2M_{\eta_2}} + gk_bT\eta_1 + k_bT\eta_2 . \tag{2.23}$$

Using this simplified version of the NHC thermostat 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 expressed. In Eqn. (2.23) H_c represents the Hamiltonian that describes a classical system of physical interest, and is defined by Eqn. (2.19). 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, while g is a constant that is equal to the number of degrees of freedom associated with the system.

Making use of Eqn. (2.9) the equations of motion for this extended system may be expressed by means of a generalised bracket as

$$\dot{X} = \left\{ X, H^{NHC} \right\}_{\mathcal{B}^{NHC}} = \sum_{jk} \frac{\partial X}{\partial X_j} \mathcal{B}^{NHC}_{jk} \frac{\partial H^{NHC}}{\partial X_k} . \tag{2.24}$$

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

$$\mathcal{B}^{NHC} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -P & 0 \\ 0 & -1 & 0 & P & 0 & -P_{\eta_1} \\ 0 & 0 & -1 & 0 & P_{\eta_1} & 0 \end{bmatrix} , \tag{2.25}$$

while the phase space point of the extended system is $X = (R, \eta_1, \eta_2, P, P_{\eta_1}, P_{\eta_2})$.

The NHC equations of motion, represented by Eqn. (2.24), may be explicitly expressed as,

$$\dot{R} = \frac{P}{M} , \tag{2.26a}$$

$$\dot{\eta}_1 = \frac{P_{\eta_1}}{M_{\eta_1}} , \tag{2.26b}$$

$$\dot{\eta}_2 = \frac{P_{\eta_2}}{M_{\eta_2}} , \tag{2.26c}$$

$$\dot{P} = -\frac{\partial V(R)}{\partial R} - \frac{P_{\eta_1}}{M_{\eta_1}} P , \tag{2.26d}$$

$$\dot{P}_{\eta_1} = \frac{P^2}{2M} - g k_b T - P_{\eta_1} \frac{P_{\eta_2}}{M_{\eta_2}} , \tag{2.26e}$$

$$\dot{P}_{\eta_2} = \frac{P_{\eta_1}}{M_{\eta_1}} - g k_b T . \tag{2.26f}$$

The phase space compressibility, associated with this scheme, is given by

$$\kappa = \sum_j \sum_k \frac{\partial \mathcal{B}_{jk}^{NHC}}{\partial X_j} \frac{\partial H^{NHC}}{\partial X_k}$$

$$= -g\frac{P_{\eta_1}}{M_{\eta_1}} - \frac{P_{\eta_2}}{M_{\eta_2}} \ .$$

2.4.3   Nosé-Hoover Power Thermostat

The Nosé-Hoover Power (NHP) thermostat was first introduced in [5]. In this section a brief overview of this thermostat scheme is presented, before integration schemes based upon it are derived. The NHP extended system Hamiltonian is given by

$$H^{NHP} = H_c + \frac{P_\eta^2}{2M_\eta} + gk_bT\eta \ , \tag{2.27}$$

where H_c again represents the Hamiltonian that describes a classical system of physical interest, and is defined by Eqn. (2.19), where all the symbols have the same meaning. 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_b, T is the absolute temperature of the the thermal bath, while 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,

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

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

$$\mathcal{B}^{NHP} = \begin{bmatrix} 0 & 0 & 1 & \tau P/M \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -P \\ -\tau p/M & -1 & P & 0 \end{bmatrix} \ , \tag{2.29}$$

while the phase space point of the extended system is $X = (R, \eta, P, P_\eta)$. This scheme is very similar to that of the NH dynamics, in fact if one sets $\tau = 0$, then one simply recovers the NH dynamics. The NHP equations of motion represented by Eqn. (2.28) may be

explicitly expressed as

$$\dot{R} = \frac{P}{M} \left(1 + \tau \frac{P_\eta}{M_\eta} \right) , \tag{2.30a}$$

$$\dot{\eta} = \frac{P_\eta}{M_\eta} , \tag{2.30b}$$

$$\dot{P} = -\frac{\partial V(R)}{\partial R} - P \frac{P_\eta}{M_\eta} , \tag{2.30c}$$

$$\dot{P_\eta} = \frac{P^2}{M} - g k_b T - \tau \frac{P}{M} \frac{\partial V(R)}{\partial R} . \tag{2.30d}$$

The phase space compressibility, associated with this scheme, is given by

$$\kappa = \sum_j \sum_k \frac{\partial \mathcal{B}_{jk}^{NHP}}{\partial X_j} \frac{\partial H^{NHP}}{\partial X_k}$$

$$= -g \frac{P_\eta}{M_\eta} .$$

Chapter 3

Time-Reversible and Measure-Preserving Algorithms

In this chapter various integration schemes are discussed. It begins with a general discussion about time-reversible schemes, in particular a time-reversible integration scheme for the NHP thermostat is devised. Following this a prescription for developing integration schemes that preserve the invariant measure of phase space is presented. This is followed by the derivation of an integration scheme for the NHP dynamics that is not only time-reversible but also preserves the invariant measure of phase space. Finally the stability and ergodic properties of the measure-preserving integration schemes are studied.

3.1   Time-Reversible Algorithms

In the previous chapter it was shown how non-Hamiltonian dynamics breaks certain properties, such as the time translation invariance of the bracket algebra. There are however certain fundamental properties possessed by Hamiltonian dynamics which cannot be ignored. One such property is that of time reversibility. It is of vital importance that any numerical integration scheme one devises or chooses to implement does not violate this property.

To this end one may begin by noting that it is possible to write the generalised equations of motion given by Eqn. (2.9), as operator equations. This is achieved by defining an operator which acts on the systems phase space vector, X, as

$$iLX = \{X, H\}_{\mathcal{B}} \ .$$

(3.1)

This operator, iL, is called the Liouville operator. There are several ways to express this operator each having their own advantages. Amongst these are the more general definition,

$$iL = \{ \cdots , H \} \ , \tag{3.2}$$

where the dots within the generalised bracket represent any function iL is acting upon. Another way to express this operator is in its differential form,

$$iL = \sum_{jk} \frac{\partial \cdots}{\partial X_j} \mathcal{B}_{jk} \frac{\partial H}{\partial X_k} \ , \tag{3.3}$$

where the dots have again been used to represent any function that iL is acting upon. Comparing this differential form to the generalised equation of motion given by Eqn. (2.9), makes it possible to write the equations of motion in terms of the Liouville operator as,

$$\dot{X} = iLX \ . \tag{3.4}$$

In this form, the equations of motion have a formal solution [22]

$$X(t) = e^{iLt} X(0) \ , \tag{3.5}$$

where $X(0)$ corresponds to the systems initial conditions. The operator $\exp(iLt)$ which appears on the right hand side of Eqn. (3.5), is called the classical propagator. In this dissertation this operator is denoted by

$$U(t) = \exp(iLt) \ . \tag{3.6}$$

The Liouville operator is Hermitian in nature as such $L^\dagger = L$ [22]. Given this property it is easy to show that the classical propagator is a unitary operator, meaning that

$$U^\dagger(t) U(t) = 1 \ , \tag{3.7}$$

where 1 is the identity matrix. In order to show this one need only consider

$$U(t) = e^{iLt} \ , \tag{3.8}$$

and,

$$U^\dagger(t) = e^{-iL^\dagger t} = e^{-iLt} . \tag{3.9}$$

Taking the product of the two gives,

$$U^\dagger(t) U(t) = e^{-iLt} e^{iLt} = 1 . \tag{3.10}$$

The fact that the propagator is unitary implies that the system's equations of motion possess the property of being time-reversible. This means that if the system propagates forward in time from some initial state, for an arbitrary time t, and then one allows the clock to run backwards for a time $-t$, the system simply returns to its initial state [22]. In order to show that the propagator being unitary implies the time reversibility of the dynamics, one first notes that $U(-t) = \exp(-iLt)$. The solution to the equation of motion may be written as

$$X(t) = U(t) X(0) . \tag{3.11}$$

Applying $U(-t)$ to this one obtains,

$$\begin{aligned} U(-t) X(t) &= U(-t) U(t) X(0) \\ &= e^{-iLt} e^{iLt} X(0) \\ &= X(0) , \end{aligned} \tag{3.12}$$

clearly this is only valid if the propagator is unitary. At this point in time it should be noted that the solution to the equations of motion given by Eqn. (3.5) is in general, not very useful. Since evaluating the right hand side of the equation is equivalent to the exact integration of the classical equations of motion. However in a few cases the formal solution is known explicitly. Suppose that the Liouville operator may be decomposed into several parts such that

$$\begin{aligned} iL &= iL_1 + iL_2 + iL_3 + \cdots \\ &= \sum_{j=1}^{n} iL_j , \end{aligned}$$

where n represents the dimensionality of the systems phase space, and the different iL_j terms do not commute. For simplicity only a two-dimensional phase space, having a phase space vector $X = (x, p)$ will be considered, as such $n = 2$. The Liouville operator may be

split as

$$iL = iL_1 + iL_2 \ . \tag{3.13}$$

Since the terms on the right hand side do not commute with one another, it should be noted that $\exp(iLt) = \exp(iL1 + iL2)$ is not equivalent to $\exp(iL_1)\ \exp(iL_2)$. A consequence of this is that, if one wishes to factorise the classical propagator, one needs to make use of the Trotter theorem. This theorem states that,

$$e^{(A+B)} = \lim_{M \to \infty} \left[e^{A/2M} e^{B/M} e^{B/2M} \right]^{M} \ , \tag{3.14}$$

it's proof may be found in [23]. In the limit $M \to \infty$ this relation is formally correct but of very little practical value. To get it into a more useful form one chooses some large but finite value for M, within this limit Eqn. (3.14) becomes [24]

$$e^{(A+B)} = \left(e^{A/2M} e^{B/M} e^{A/2M} \right)^{M} e^{\mathcal{O}(1/M^2)} \ . \tag{3.15}$$

To apply this theorem to the formal solution of the Liouville equation we let

$$\frac{A}{M} = \frac{iL_2 t}{M} \qquad \text{and} \qquad \frac{B}{M} = \frac{iL_1 t}{M} \ . \tag{3.16}$$

Thereby obtaining that

$$e^{(iL_1 + iL_2) \frac{t}{M}} \approx \left(e^{iL_2/2} e^{iL_1} e^{iL_2/2} \right)^{\frac{t}{M}} \ . \tag{3.17}$$

The right hand side of this equation represents an approximated propagation of the system for a small time interval, t/M. If one takes this time to be a single time step, h, one may then express the single time step approximation of the system propagator as

$$e^{i(L_1 + L_2)h} \approx e^{iL_2 h/2} e^{iL_1 h} e^{iL_2 h/2} \ . \tag{3.18}$$

In Eqn. (3.18) the left hand side represents the exact propagator, $U(h)$, while the right hand side represents the approximated propagator, which shall be denoted as $\tilde{U}(h)$. It can easily be shown that $\tilde{U}(h)$ is a unitary operator [22], since it is comprised of unitary operators, as such it preserves the property of time reversibility. $\tilde{U}(h)$ is accurate up to

second order, h^2, proof of this may be found in Appendix A.2. As such one has that

$$e^{iLh} = e^{iL_2 h/2} e^{iL_1 h} e^{iL_2 h/2} + \mathcal{O}\left(h^3\right) \ . \tag{3.19}$$

By considering propagators which are second order in time, one may drop the tilde on the approximate propagator. The action of $U(h)$ on some arbitrary phase space vector, X, may then be evaluated through the use of a technique known as the direct translation method. If this action is expressed as

$$U(h) X = e^{iL_2 h/2} e^{iL_1 h} e^{iL_2 h/2} X \ , \tag{3.20}$$

then under this method the action of the first operator $\exp(iL_2 h/2)$ on X, may be thought of as producing a new phase space point X'. This new point will be what the second operator $\exp(iL_1 h)$ acts upon to produce a new phase space point X''. This then becomes the input into the last operator $\exp(iL_2 h/2)$ [22]. The main advantage of this technique is that it allows one to use each operator within the factorisation as an update step. This has the effect of allowing one to use the result of its action as the input for the next operator. As such if one knows how the operators which make up the factorisation act, it becomes a simple task to create a set of update steps which may then be easily converted either into pseudo-code or a working algorithm.

In evaluating the action of each operator, the following mathematical identities are very useful to remember:

$$\exp\left[c\frac{\partial}{\partial x}\right] f(x) = f(x + c) \ , \tag{3.21a}$$

$$\exp\left[cx\frac{\partial}{\partial x}\right] f(x) = f(x \ \exp[c]) \ , \tag{3.21b}$$

$$\exp\left[\tau\left(-\frac{P_\eta}{M_\eta}P + F(x)\frac{\partial}{\partial P}\right)\right] P = p \ \exp\left[-\tau\frac{P_\eta}{M_\eta}\right] + \tau F(x) \times$$
$$\exp\left[-\frac{\tau}{2}\frac{P_\eta}{M_\eta}\right] \sinh\left[-\frac{\tau}{2}\frac{P_\eta}{M_\eta}\right] \ . \tag{3.21c}$$

An example of how to apply this theory in order to derive time-reversible algorithms will now be presented. In particular focus will be given to the NHP thermostat dynamics.

3.1.1 Time-Reversible Integration of Nosé-Hoover Power Thermostat Dynamics

A derivation of a time-reversible integration scheme for the NHP dynamics is be presented in this section. In order to achieve such an integration scheme, one begins by defining the Liouville operators as

$$L^{NHP} = \sum_n L_n \ . \tag{3.22}$$

To find the L_n terms, one makes use of the Liouville operator definition given by Eqn. (3.4) along with the NHP equations of motion given by Eqns. (2.30). This Liouville operator definition combined with Eqn. (2.30a) yields

$$\dot{R} = L_1 R$$
$$= \left(\frac{P}{M} + \tau \frac{P}{M} \frac{P_\eta}{M_\eta} \right) \frac{\partial}{\partial R} R \tag{3.23}$$

from which one can clearly see that $L_1 = \left(\frac{P}{M} + \tau \frac{P}{M} \frac{P_\eta}{M_\eta} \right) \frac{\partial}{\partial R}$. Following a similar procedure with regards to the other equations, which make up the set of Eqns. (2.30) one obtains the following set of Liouville operators

$$L_1^{NHP} = \left(\frac{P}{M} + \tau \frac{P}{M} \frac{P_\eta}{M_\eta} \right) \frac{\partial}{\partial R} \ , \tag{3.24a}$$

$$L_2^{NHP} = F_R \frac{\partial}{\partial P} \ , \tag{3.24b}$$

$$L_3^{NHP} = -P \frac{P_\eta}{M_\eta} \frac{\partial}{\partial P} \ , \tag{3.24c}$$

$$L_4^{NHP} = \frac{P_\eta}{M_\eta} \frac{\partial}{\partial \eta} \ , \tag{3.24d}$$

$$L_5^{NHP} = \left(\tau \frac{P}{M} F_R + F_P \right) \frac{\partial}{\partial P_\eta} \ . \tag{3.24e}$$

$$\tag{3.24f}$$

Where the forces acting on the system have been defined as

$$F_R = -\frac{\partial V(R)}{\partial R} \ , \tag{3.25}$$

and

$$F_p = \frac{P^2}{M} - g k_B T \ . \tag{3.26}$$

By considering a small time step, h, along with a direct symmetric Trotter factorisation of the Liouville operator one gets that

$$e^{hL} \approx e^{L_5^{NHP}h/2} e^{L_4^{NHP}h/2} e^{L_3^{NHP}h/2} e^{L_2^{NHP}h/2} e^{L_1^{NHP}h}$$

$$\times e^{L_2^{NHP}h/2} e^{L_3^{NHP}h/2} e^{L_4^{NHP}h/2} e^{L_5^{NHP}h/2} . \tag{3.27}$$

A possible integration scheme may then be obtained using the direct translation technique applied to the following propagator

$$U^{NHP}(h) = \exp\left(\frac{h}{2}L_5^{NHP}\right) \exp\left(\frac{h}{2}L_4^{NHP}\right) \exp\left(\frac{h}{2}L_3^{NHP}\right)$$

$$\times \exp\left(\frac{h}{2}L_2^{NHP}\right) \exp\left(hL_1^{NHP}\right) \exp\left(\frac{h}{2}L_2^{NHP}\right) \tag{3.28}$$

$$\times \exp\left(\frac{h}{2}L_3^{NHP}\right) \exp\left(\frac{h}{2}L_4^{NHP}\right) \exp\left(\frac{h}{2}L_5^{NHP}\right) ,$$

where $U_\alpha^{NHP}(h) = \exp\left[hL_\alpha^{NHP}\right]$. However it has been shown in [5] that the algorithm one obtains using the above propagator leads to a divergent Hamiltonian. This problem is overcome by making use of a higher order propagator, which is obtained through the use of Yoshida's prescription [5, 25]. Making use of this prescription, the higher order propagator may be expressed as

$$U^{NHP}(h) = \prod_{y=1}^{n_y} \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_5^{NHP}\right) \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_4^{NHP}\right) \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_3^{NHP}\right)$$

$$\times \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_2^{NHP}\right) \exp\left(h\frac{w_y}{n_y}L_1^{NHP}\right) \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_2^{NHP}\right) \tag{3.29}$$

$$\times \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_3^{NHP}\right) \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_4^{NHP}\right) \exp\left(\frac{h}{2}\frac{w_y}{n_y}L_5^{NHP}\right) ,$$

where n_y represents the number of Yoshida weights, while w_y represents the Yoshida weights themselves. In this dissertation the number of weights used was $n_y = 3$, with the corresponding weights given by $w_1 = \frac{1}{2-2^{\frac{1}{3}}}$, $w_2 = 1 - 2w_1$ and $w_3 = w_1$. Making use of the higher order propagator, in conjunction with the identities given by the Eqns. (3.21)

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one arrives at the following pseudo-code form of the algorithm:

$$\text{DO IT} = 1, NTS$$

$$\text{DO } j = 1, n_y$$

$$P_\eta = P_\eta + \frac{w_j}{nj}\frac{h}{2}\left(F_p + \tau\frac{P}{M}F_R\right) \tag{3.30}$$

$$\eta = \eta + \frac{w_j}{nj}\frac{h}{2}\frac{P_\eta}{M_\eta} \tag{3.31}$$

$$P = P\exp\left[-\left((w_j/nj)h/2\right)P_\eta/M_\eta\right] \tag{3.32}$$

$$P = P + \frac{w_j}{nj}\frac{h}{2}F_R \tag{3.33}$$

$$R = R + \frac{w_j}{nj}hP/M\left(1 + \tau\frac{P_\eta}{M_\eta}\right) \tag{3.34}$$

$$\text{CALCULATE } F_R$$

$$P = P + \frac{w_j}{nj}\frac{h}{2}F_R \tag{3.35}$$

$$P = P\exp\left[-\left((w_j/nj)h/2\right)P_\eta/M_\eta\right] \tag{3.36}$$

$$\text{CALCULATE } F_p$$

$$\eta = \eta + \frac{w_j}{nj}\frac{h}{2}\frac{P_\eta}{M_\eta} \tag{3.37}$$

$$P_\eta = P_\eta + \frac{w_j}{nj}\frac{h}{2}\left(F_p + \tau\frac{P}{M}F_R\right) \tag{3.38}$$

$$\text{End DO}$$

$$\text{End DO}$$

The mathematical details regarding how the translation rules for this algorithm were obtained may be found in Appendix B.1. For completeness the derivations of the NH and NHC time-reversible algorithms are presented in Appendices C.1 and C.2 respectively.

3.2 Measure-Preserving Algorithms

Having shown how time-reversible algorithms may be derived, a method which not only produces algorithms that are time-reversible but ones that also preserve the invariant measure of phase space will now be presented. In so doing the prescription detailed in [9] is followed. To this end one begins by splitting the Hamiltonian into a sum of n terms

such that

$$H = \sum_{\alpha=1}^{n} H^{\alpha} \, , \tag{3.39}$$

where the splitting of H is not unique. This splitting of the Hamiltonian gives rise to a corresponding splitting of the phase space vector, $X = \sum_{\alpha=1}^{n} X^{\alpha}$, where the individual vector component equations of motion are given by Eqn. (2.10). A secondary consequence of the Hamiltonian splitting is the resulting split of the Liouville operator such that

$$L = \sum_{\alpha=1}^{n} L^{\alpha} \tag{3.40}$$

where each L^{α} component is given by [9, 26]

$$
\begin{aligned}
L^{\alpha} &= X_i^{\alpha} \frac{\partial}{\partial X_i} \\
&= \sum_i \sum_j \mathcal{B}_{ij} \frac{\partial H^{\alpha}}{\partial X_j} \frac{\partial}{\partial X_i} \, .
\end{aligned} \tag{3.41}
$$

If the components of the Liouville operator are to preserve the invariant measure of phase space, then they must satisfy

$$L^{\alpha} \omega = 0 \, , \tag{3.42}$$

where ω represents the conventional phase space volume element

$$\omega = dx^1 \wedge dx^2 \wedge \cdots dx^{2N} \, . \tag{3.43}$$

It has however been shown [9, 18, 27] that if the phase space flow has non-zero compressibility the statistical mechanics of the system need to be formulated in terms of a new modified phase space measure

$$\bar{\omega} = e^{-\sigma(X)} \omega \, , \tag{3.44}$$

where the statistical weight, $\sigma(X)$, is related to the compressibility by [16, 27]

$$\frac{d\sigma(X)}{dt} = \kappa(X) \, . \tag{3.45}$$

Provided that the condition

$$\frac{\partial}{\partial X_k} \left[e^{-\sigma(X)} \mathcal{B}_{jk} \right] = 0 \qquad j = 1, \cdots, 2N \tag{3.46}$$

holds [9, 27], then

$$L^\alpha \bar{\omega} = 0 \qquad \forall \, \alpha \, . \tag{3.47}$$

This means that the modified volume element, $\bar{\omega}$, is invariant under the action of each L^α. As such one may now use the split Liouville operators in the same way as when one was trying to obtain the time-reversible integration schemes. This means making use of a symmetric Trotter factorisation, before applying the direct translation technique to evaluate the action of the individual propagators. Since the modified volume element is invariant under the action of each L^α, each part of the propagator will preserve the modified volume form, in addition to being time-reversible. An example of how to apply this theory in order to derive time-reversible measure-preserving algorithms will now be presented. In particular focus will be given to the NHP thermostat dynamics.

3.2.1 Measure-Preserving Integration of Nosé-Hoover Power Thermostat Dynamics

In order to derive a measure-preserving integration scheme for the NHP thermostat, one starts by splitting the Liouville operator such that,

$$L^{NHP} = \sum_{\alpha=1}^{4} L_\alpha^{NHP} \, , \tag{3.48}$$

where each L_α^{NHP} is defined as,

$$L_\alpha^{NHP} = \mathcal{B}_{jk}^{NHP} \frac{\partial H_\alpha^{NHP}}{\partial X_k} \frac{\partial}{\partial X_j} \tag{3.49}$$

and preserves the invariant measure of the phase space [9]. Here H_α^{NHP} represents the splitting of the NHP Hamiltonian such that $H^{NHP} = \sum_{\alpha=1}^{4} H_\alpha$, the most natural way to split the NHP Hamiltonian leads to the following components

$$H_1 = \frac{P^2}{2M} \, , \tag{3.50a}$$

$$H_2 = V(R) \, , \tag{3.50b}$$

$$H_3 = \frac{P_\eta^2}{2M_\eta} \, , \tag{3.50c}$$

$$H_4 = g k_b T \eta \, . \tag{3.50d}$$

Making use of Eqn. (3.49), along with Eqns. (3.50a)-(3.50d), one obtains the following explicit form of the Liouville operators:

$$L_1^{NHP} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{P^2}{M}\frac{\partial}{\partial P_\eta} \tag{3.51a}$$

$$L_2^{NHP} = -\frac{\partial V(R)}{\partial R}\left[\frac{\partial}{\partial P} + \tau\frac{P}{M}\frac{\partial}{\partial P_\eta}\right] \tag{3.51b}$$

$$L_3^{NHP} = \frac{P_\eta}{M_\eta}\left[\tau\frac{P}{M}\frac{\partial}{\partial R} + \frac{\partial}{\partial \eta} - P\frac{\partial}{\partial P}\right] \tag{3.51c}$$

$$L_4^{NHP} = -gk_BT\frac{\partial}{\partial P_\eta} \; . \tag{3.51d}$$

In order to obtain a more efficient algorithm one defines

$$L_A^{NHP} = L_1^{NHP} + L_4^{NHP} \; , \tag{3.52a}$$

$$L_B^{NHP} = L_2^{NHP} \; , \tag{3.52b}$$

$$L_C^{NHP} = L_3^{NHP} \; , \tag{3.52c}$$

where commuting Liouville operators have been combined to obtain L_A^{NHP}, along with the renaming of L_2 and L_3 to keep the notation consistent. Next the propagator associated with the nth Liouville operator, L_n^{NHP}, is defined as $U_\alpha^{NHP}(h) = \exp\left[hL_\alpha^{NHP}\right]$, where $\alpha = A, B, C$ and h represents a single numerical time step. A possible measure-preserving integration scheme for the NHP dynamics may then be found through the use of a symmetric Trotter factorisation, and may be approximated by the propagator

$$U^{NHP}(h) = U_B^{NHP}(h/2)\, U_C^{NHP}(h/2)\, U_A^{NHP}(h)$$
$$\times\, U_C^{NHP}(h/2)\, U_B^{NHP}(h/2) \; . \tag{3.53}$$

Using the direct translation method to evaluate the action of this propagator one obtains the following pseudo-code structure:

$$\left.\begin{array}{rcl} P_\eta & \to & P_\eta + \frac{h\tau}{2M}F_R\left(P + \frac{h}{4}F_R\right) \\ P & \to & P + \frac{h}{2}F_R \end{array}\right\} : U_B(h/2)\,, \tag{3.54}$$

$$\left.\begin{array}{rcl} \eta & \to & \eta + \frac{h}{2}\frac{P_\eta}{M_\eta} \\ R & \to & R + \frac{\tau}{M}P\left[1 - \exp\left(-\frac{h}{2}\frac{P_\eta}{M_\eta}\right)\right] \\ P & \to & P\,\exp\left[-\frac{h}{2}\frac{P_\eta}{M_\eta}\right] \end{array}\right\} : U_C(h/2)\,, \tag{3.55}$$

$$\left. \begin{aligned} R & \rightarrow & R + h\frac{P}{M} \\ P_\eta & \rightarrow & P_\eta + hF_P \end{aligned} \right\} : U_A\left(h\right), \tag{3.56}$$

$$\left. \begin{aligned} \eta & \rightarrow & \eta + \frac{h}{2}\frac{P_\eta}{M_\eta} \\ R & \rightarrow & R + \frac{\tau}{M}P\left[1 - \exp\left(-\frac{h}{2}\frac{P_\eta}{M_\eta}\right)\right] \\ P & \rightarrow & P\,\exp\left[-\frac{h}{2}\frac{P_\eta}{M_\eta}\right] \end{aligned} \right\} : U_C\left(h/2\right), \tag{3.57}$$

$$\left. \begin{aligned} P_\eta & \rightarrow & P_\eta + \frac{h\tau}{2M}F_R\left(P + \frac{h}{4}F_R\right) \\ P & \rightarrow & P + \frac{h}{2}F_R \end{aligned} \right\} : U_B\left(h/2\right), \tag{3.58}$$

where the forces F_R, F_P are defined by Eqns. (3.25) and (3.26) respectively. The mathematical details regarding how the translation rules for the above algorithm were obtained may be found in Appendix B.2. As in the previous section, the algorithms for the NH and NHC measure-preserving time-reversible schemes were also derived. These derivations may be found in Appendices D.1 and D.2 respectively.

3.3   Classical Simulations

In this section, the results of the study performed with regards to the stability and ergodic properties of the NHC and NHP dynamics are presented. In order to perform this study the thermostats were coupled to a classical one-dimensional harmonic oscillator, having a quadratic potential,

$$V\left(R\right) = \frac{1}{2}kR^2$$

where, k is the spring constant. The radial phase space probabilities were then calculated, while a check was also performed to ensure that the extended system Hamiltonians were conserved by these integration schemes. However these properties were not calculated for the NH dynamics, since it is well established that these dynamics are not ergodic, as such they do not generate the correct canonical ensemble [21, 28, 29, 30]. For the simulation results shown here, only the time-reversible measure-preserving algorithms were used to investigate the properties of the NHC and NHP thermostat schemes. The reason for this choice was that the ultimate goal of this dissertation was to extend the NHP dynamics to the quantum-classical framework. Within this framework the hybrid Monte Carlo dynamics used for simulations require that, the algorithms used preserve the measure of phase space [31]. The following results were obtained
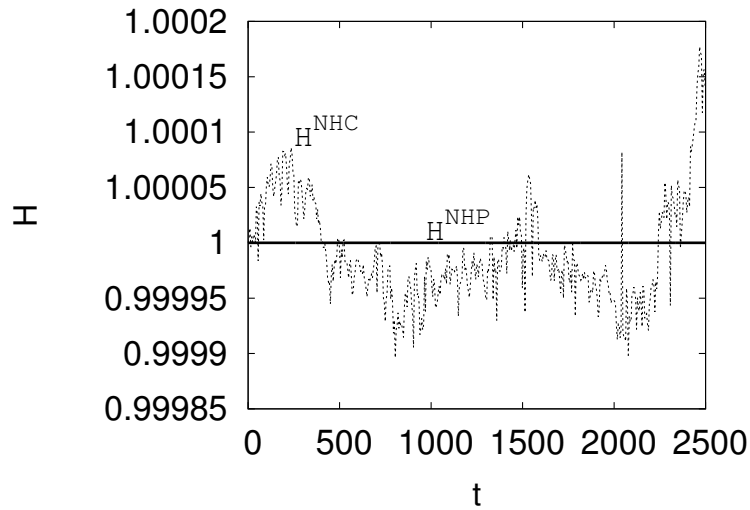
Figure 3.1: Numerical stability of the measure-preserving time-reversible integration scheme. A comparison is shown between the NHC and NHP dynamics for a one dimensional harmonic oscillator. The energy functions shown have been normalised and as such oscillate about $H = 1$. The energy function for the NHP dynamics, H^{NHP}, is represented by the solid line while the energy function for the NHC dynamics, H^{NHC}, is represented by the dashed line. The time step used for this simulation was $h = 0.0025$.
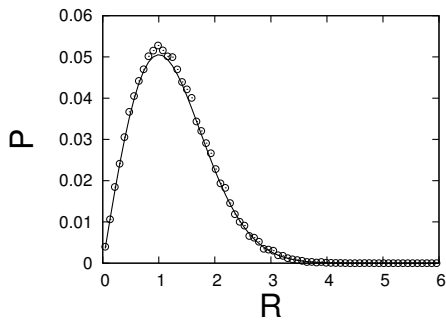
Figure 3.2: Comparison between the analytical and the numerically sampled radial phase space probability of a one dimensional harmonic oscillator evolving under the NHC dynamics. The continuous line shows the theoretical value while the hollow bullets show the numerical results.
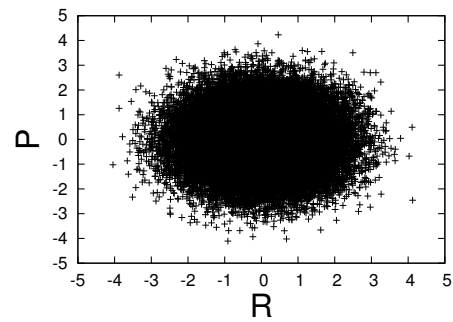
Figure 3.3: This figure displays a plot of the NHC phase space distribution obtained from the NHC dynamics of a one dimensional harmonic oscillator.
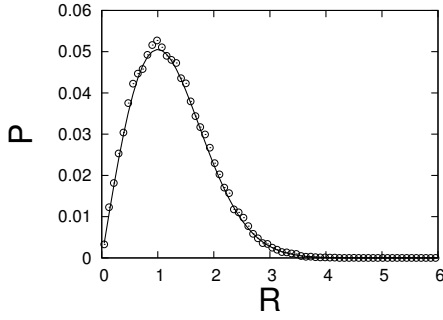
Figure 3.4: Comparison between the analytical and the numerically sampled radial phase space probability of a one dimensional harmonic oscillator evolving under the NHP dynamics. The continuous line shows the theoretical value while the hollow bullets show the numerical results.
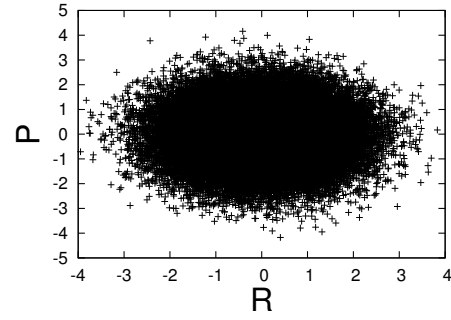
Figure 3.5: This figure displays a plot of the NHP phase space distribution obtained from the NHP dynamics of a one dimensional harmonic oscillator.

The two normalised extended system Hamiltonian functions are shown in Fig. 3.1. As one can see from this plot both integration schemes are numerically stable. The NHC dynamics has fluctuations of the order 10^{-4}. The higher order propagator for the NHP dynamics might not seem to have any fluctuations, however it should be noted that this is due mainly to the fact that in Fig. 3.1 it is being compared against the NHC dynamics. It was found that it had fluctuations of the order 10^{-6}.

To show that the NHC dynamics not only conserve the system Hamiltonian, but also sample phase space uniformly Fig. 3.2 and Fig. 3.3 are displayed. The numerically calculated and theoretically predicted radial phase space distributions for this thermostat are shown in Fig. 3.2, while the phase space distribution of the generated points is shown in Fig. 3.3. From these two figures, one is able to conclude that the NHC thermostat samples phase space uniformly and as such satisfies the ergodic hypothesis.

To show that the NHP dynamics not only conserve the system Hamiltonian, but also sample phase space uniformly Fig. 3.4 and Fig. 3.5 are displayed. The numerically calculated and theoretically predicted radial phase space distributions for this thermostat are shown in Fig. 3.4, while the phase space distribution of the generated points is shown in Fig. 3.5. From these two figures, one is able to conclude that the NHP thermostat samples phase space uniformly, and as such satisfies the ergodic hypothesis.

Having been satisfied with the stability of the integration schemes the next challenge was to extended them to the quantum-classical case. In the following chapter the theory

of quantum-classical systems in thermal baths is presented with a view of representing such thermal baths with both the NHC and NHP thermostat schemes.

Chapter 4

Quantum-Classical Systems in Thermal Baths

In this chapter a detailed discussion of the theory required to understand and simulate quantum-classical dynamics is presented. It starts with a presentation of Heisenberg's formulation of quantum mechanics. This is followed by a brief overview of quantum statistical mechanics, where the density matrix operator is introduced. The phase space representation of quantum mechanics is then presented with a focus on the Wigner representation. The theory of how to model quantum dynamics within a classical bath is discussed, along with the derivation of the quantum-classical Liouville equation of motion; then this equation is expressed in the adiabatic basis. Finally this chapter concludes with the extension of the NHC and NHP thermostats to the quantum-classical case.

4.1   Heisenberg's Formulation of Quantum Mechanics

The Heisenberg formulation of quantum mechanics was developed in 1925 by W. Heisenberg. It is also known as the matrix formulation of quantum mechanics, or simply matrix mechanics. In this formulation, all operators are represented by $N \times N$ matrices where N is the number of basis states needed to form a complete basis set for the system, while the systems quantum states, are represented by vectors with dimensions $N \times 1$ [32]. Naturally this formulation is equivalent to the wave theory of Schrödinger. The main difference between these two formulations lies within the location of the time dependence [32, 33]. Within Schrödinger's formulation, the time dependence lies within the states, $|\psi\rangle = |\psi(t)\rangle$, and not the operators, $\hat{A} \neq \hat{A}(t)$. The opposite is true for Heisenberg's

formulation, within this formulation the states do not change in time, $|\psi\rangle \neq |\psi(t)\rangle$, while all the time dependence is transferred onto the quantum operators such that $\hat{A} = \hat{A}(t)$.

The change in time of the operators is governed by the Heisenberg equation of motion. This equation is given by

$$\frac{\partial \hat{A}(t)}{\partial t} = \frac{i}{\hbar} \left[\hat{H}, \hat{A}(t) \right] + \frac{\partial \hat{A}(t)}{\partial t} \ , \tag{4.1}$$

where $\left[\hat{H}, \hat{A}(t) \right] \equiv \hat{H}\hat{A} - \hat{A}\hat{H}$. If the operators do not contain an explicit time dependence then the above equation may be written as

$$\frac{\partial \hat{A}(t)}{\partial t} = \frac{i}{\hbar} \left[\hat{H}, \hat{A}(t) \right] \ . \tag{4.2}$$

For the remainder of this dissertation, only operators that do not carry an explicit time dependence have been considered, as such Eqn. (4.2) is used as the equation of motion for an arbitrary observable.

4.2   Quantum Statistical Mechanics

Quantum mechanics is an intrinsically statistical theory, where the statistics enter the theory in two ways [34]. Firstly because of 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. If one knows everything there is to know about the state of a system, then the system is said to be in a pure state $|\psi\rangle$. Within Schrödinger's formulation the pure state of a system may be represented by a wave function, $\psi(x, t)$, while the average value of an arbitrary observable, $\hat{A}$ is given by [35]

$$\bar{A} = \langle A \rangle = \int \psi^*(x, t) \, A \psi(x, t) \ \mathrm{d}x \ . \tag{4.3}$$

For a system in a pure state, the state vector $|\psi\rangle$ may be expressed in an orthonormal basis $|\phi_j\rangle$ as

$$|\psi\rangle = \sum_j c_j |\phi_j\rangle \ , \tag{4.4}$$

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

$$\bar{A} = \langle A \rangle = \left\langle \psi \,\middle|\, \hat{A} \,\middle|\, \psi \right\rangle$$

$$= \sum_k c_k^* \left\langle \phi_k \,\middle|\, \hat{A} \sum_j c_j \,\middle|\, \phi_j \right\rangle$$

$$= \sum_j \sum_k c_j c_k^* \left\langle \phi_k \,\middle|\, \hat{A} \,\middle|\, \phi_j \right\rangle$$

$$= \sum_j \sum_k c_j c_k^* A_{kj} \ . \tag{4.5}$$

For a system in a pure state, Eqns. (4.3) and (4.5) are equivalent [33].

The statistical description which has been used thus far, has been for systems in a pure state. However a different approach is required if one either does not have all the information about the state of the system, or if one is dealing with an ensemble of systems [33, 36], such cases correspond to the system being in what are known as mixed states. For such states one can no longer use Eqn. (4.3) to calculate the observable averages. To see this consider some 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. (4.5), since the summation which appears on the right hand side simply produces another pure state as apposed to the mixed state of the system [32]. In order to represent such a mixed state one needs to make use of the density matrix operator which will be introduced in the following section.

4.2.1 Density Matrix

The density matrix description for mixed quantum systems was introduced by J. von Neumann [37]. This matrix is sometimes referred to in the literature as the density matrix operator or von Neumann density matrix. Here it shall be introduced by first considering how the observable average for such mixed sates may be calculated. For 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 [38]. The observable

average given by Eqn. (4.5) is modified by these probabilities to produce a weighted average,

$$\langle A \rangle = \sum_i \gamma_i \bar{A}_i \ , \tag{4.6}$$

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

$$\bar{A}_i = \sum_j \sum_k c_k^{i*} c_j^i A_{kj} \ , \tag{4.7}$$

substituting this into Eqn. (4.6) allows one to write down the average value for an observable of a mixed state as,

$$\langle A \rangle = \sum_i \gamma_i \sum_j \sum_k c_k^{i*} c_j^i A_{kj}$$
$$= \sum_j \sum_k \rho_{jk} A_{kj} \ . \tag{4.8}$$

In Eqn. (4.8), the density matrix elements have been introduced. These elements are defined as

$$\rho_{jk} = \sum_i \gamma_i c_k^{i*} c_j^i \ , \tag{4.9}$$

and when combined form what is known as the density matrix operator $\hat{\rho}$. These elements may also be expressed using Dirac's notation as

$$\rho_{jk} = \langle j \,|\, \hat{\rho} \,|\, k \rangle \ . \tag{4.10}$$

Using this notation along with the completeness relation allows one to rewrite Eqn. (4.8) as

$$\langle A \rangle = \sum_j \sum_k \langle j \,|\, \hat{\rho} \,|\, k \rangle \left\langle k \,\middle|\, \hat{A} \,\middle|\, j \right\rangle$$
$$= \sum_j \left\langle j \,\middle|\, \hat{\rho}\hat{A} \,\middle|\, j \right\rangle \ . \tag{4.11}$$

The summation which appears in Eqn. (4.11) is over all the diagonal elements of the density matrix. It is also known as the trace, and is denoted denote as

$$\langle A \rangle = T_R\left(\hat{\rho}\hat{A}\right) = T_R\left(\hat{A}\hat{\rho}\right) \ , \tag{4.12}$$

since the trace of two operators is invariant under cyclic permutations [36]. The evolution of the density matrix in time is given by the von Neumann equation

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}(t)\right] \ . \tag{4.13}$$

The density matrix has several important properties, which 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

$$
\begin{aligned}
Tr\left(\hat{\rho}\right) &= \sum_j \rho_{jj} \\
&= \sum_i \gamma_i \sum_j \left|c_j^i\right|^2 \\
&= \sum_i \gamma_i \ = 1 \ .
\end{aligned}
\tag{4.14}
$$

Along with being normalised, it is also Hermitian

$$
\begin{aligned}
(\rho_{kj})^* &= \left(\sum_i \gamma_i c_k^i c_j^{i*}\right)^* \\
&= \sum_i \gamma_i c_k^{i*} c_j^i \\
&= \rho_{jk} \ .
\end{aligned}
$$

The density matrix of a pure state only has one non-zero element since all but one of the γ_i terms will be zero. This is not the case for a mixed system. The diagonal elements, ρ_{jj}, give the probability that the system is in state j [39]. While the off diagonal elements, ρ_{jk}, may be both positive or negative [36], Subsequently these elements may not be interpreted as probabilities [39]. 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 [40]. These elements are also related to the phase correlation between the states j and k.

4.3 Phase Space Representation of Quantum Mechanics

In classical mechanics, Hamilton's equations of motion give a correlation between the positions and momenta of a particle [10]. This correlation may be seen in the probability distributions of these two variables.

If one wishes to obtain a fully classical description of quantum mechanics, then one is required to describe the quantum system of interest in phase space [36]. However, from Heisenberg's uncertainty principle, one can not simultaneously have well defined knowledge about the position and momentum for such systems. This makes it 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 obey some, but not all, of the conditions that need to be satisfied by probability distribution functions. They are however still of great use, in the study of quantum systems [41], as they provide insights into the connections which exist between classical and quantum mechanics. They are able to do this as they express a 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 [42]. In the following section, this quasiprobability distribution function is presented.

4.3.1 Wigner Representation of Quantum Mechanics

A discussion of the Weyl transform is first presented, before the Wigner transform is introduced. The Weyl transform, for an arbitrary operator $\hat{A}$ in the position basis, is [43]

$$\tilde{A}(x,p) = \int e^{-ipy/\hbar} \left\langle x + y/2 \left| \hat{A} \right| x - y/2 \right\rangle \, \mathrm{d}y \,, \tag{4.15}$$

where the tilde is used to denote the Weyl transform. Naturally this transform may also be expressed in the momentum basis as

$$\tilde{A}(x,p) = \int e^{ixz/\hbar} \left\langle p + z/2 \left| \hat{A} \right| p - z/2 \right\rangle \, \mathrm{d}z \,. \tag{4.16}$$

From its definition, one sees that the Weyl transform may be used to transform an operator into a phase space function.

An important property of this transform, which plays a crucial role when it comes to

calculating expectation values in the Wigner representation, states that the trace of two arbitrary operators $\hat{A}$ and $\hat{B}$ is equivalent to the integral over phase space of the product of their Weyl transforms [43],

$$Tr\left(\hat{A}\hat{B}\right) = \frac{1}{h}\int\int \tilde{A}\left(x,p\right)\tilde{B}\left(x,p\right)\ \mathrm{d}x\ \mathrm{d}p\ . \tag{4.17}$$

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 [43, 42, 41]

$$W\left(x,p\right) = \frac{\tilde{\rho}}{h}\ .$$

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

$$\begin{aligned}
W\left(x,p\right) &= \frac{1}{h}\int e^{-ipy/\hbar}\left\langle x+y/2\left|\hat{\rho}\right|x-y/2\right\rangle\ \mathrm{d}y \\
&= \frac{1}{h}\int e^{-ipz/\hbar}\left\langle p+z/2\left|\hat{\rho}\right|p-z/2\right\rangle\ \mathrm{d}z\ ,
\end{aligned}$$

respectively. Making use of Eqn.(4.17), the expectation values within this representation may be expressed as

$$\begin{aligned}
\left\langle A\right\rangle &= Tr\left(\hat{\rho}\hat{A}\right) \\
&= \frac{1}{h}\int\int \tilde{\rho}\left(x,p\right)\tilde{A}\left(x,p\right)\ \mathrm{d}x\ \mathrm{d}p \\
&= \int\int W\left(x,p\right)\tilde{A}\left(x,p\right)\ \mathrm{d}x\ \mathrm{d}p\ . \tag{4.18}
\end{aligned}$$

The last line of Eqn. (4.18) shows how the Wigner function may be interpreted as a probability density which characterises some physical quantity, where this quantity is represented by the Weyl transform of the observable [43]. 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.

The identity matrix is used to check the normalisability of the Wigner function in phase space. Performing this check requires one to make use of the Weyl transform of the

identity matrix. This transform is

$$
\begin{aligned}
\tilde{1} &= \int e^{-ipy/\hbar} \left\langle x + y/2 \,\middle|\, \hat{1} \,\middle|\, x - y/2 \right\rangle dy \\
&= \int e^{-ipy/\hbar} \delta \left(x + y/2 - (x - y/2) \right) dy \; = 1 \; .
\end{aligned}
\tag{4.19}
$$

To perform this check one considers the trace of the density matrix and the identity matrix,

$$
\begin{aligned}
Tr\left(\hat{\rho}\hat{1}\right) &= \frac{1}{h} \int \int \tilde{\rho}\left(x,p\right) \tilde{1} \; \mathrm{d}x \; \mathrm{d}p \\
&= \int \int W\left(x,p\right) \; \mathrm{d}x \; \mathrm{d}p \\
&= Tr\left(\hat{\rho}\right) = 1 \; .
\end{aligned}
\tag{4.20}
$$

As Eqn. (4.20) shows, this function is normalised.

To check if it satisfies the non-negativity condition, one considers two orthogonal sates of the system $|\psi\rangle$ and $|\phi\rangle$ each having a corresponding density matrix $\hat{\rho}_\psi$ and $\hat{\rho}_\phi$ respectively, such that

$$
\begin{aligned}
Tr\left(\hat{\rho}_\psi \hat{\rho}_\phi\right) &= \frac{1}{h} \int \int W_\psi\left(x,p\right) W_\phi\left(x,p\right) \; \mathrm{d}x \; \mathrm{d}p \\
&= \left|\langle\psi|\phi\rangle\right|^2 \; .
\end{aligned}
\tag{4.21}
$$

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

$$
\frac{1}{h} \int \int W_\psi\left(x,p\right) W_\phi\left(x,p\right) \; \mathrm{d}x \; \mathrm{d}p = 0 \; .
\tag{4.22}
$$

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. Due to this the Wigner function can not be a probability distribution function, and is classified as a quasiprobability distribution function.

Another important property of the Wigner function which is required for the upcoming sections is that, the Wigner transform for the product of two arbitrary operators, is given by [4, 44],

$$
\left(\hat{A}\hat{B}\right)_W = \hat{A}_W\left(R,P\right) \; e^{\frac{\hbar\Lambda}{2i}} \; \hat{B}_W\left(R,P\right) \; .
\tag{4.23}
$$

Here Λ is the negative of the Poisson bracket. This identity is important as the commutator which appears in the Heisenberg equation of motion contains a product of two observables. One thus requires the Wigner transform of an operator product, if one wants to use this equation within this representation.

4.3.2 Partial Wigner Representation of Quantum Mechanics

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 classical phase space degrees of freedom are used to represent the bath [13].

In order 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.

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

$$\hat{\rho}_W (R, P) = \frac{1}{(2\pi\hbar)^{3N}} \int \, \mathrm{d}z \, e^{iP \cdot z/\hbar} \langle R - z/2 \, | \, \hat{\rho} \, | \, R + z/2 \rangle \,, \qquad (4.24)$$

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 [13]. For an arbitrary operator of the system, $\hat{A}$, the partial Wigner transform is

$$\hat{A}_W (R, P) = \int \, \mathrm{d}z \, e^{iP \cdot z/\hbar} \left\langle R - z/2 \, \middle| \, \hat{A} \, \middle| \, R + z/2 \right\rangle \,. \qquad (4.25)$$

In this transformed representation, $\hat{A}_W$ becomes an operator on both the quantum subsystem's Hilbert space and the bath's phase space.

The remainder of this dissertation deals with quantum-classical systems, formulated

using this transform. The properties of the Wigner function defined in the previous section are sill valid for the partial Wigner transform representation. However the system's dynamics will now evolve according to some quantum-classical equation of motion.

4.4 Quantum Dynamics in a Classical Thermal Bath

4.4.1 The Quantum-Classical Liouville Equation

In order to derive the quantum-classical Liouville equation one may begin by considering the Heisenberg equation of motion for an arbitrary operator $\hat{\chi} = \hat{\chi}(X, t)$, where X again represents the classical phase space variables (R, P). One recalls that the Heisenberg equation of motion is given by

$$\begin{aligned} \frac{\partial \hat{\chi}}{\partial t} &= \frac{i}{\hbar} \left[\hat{H}, \hat{\chi} \right] \\ &= \frac{i}{\hbar} \left(\hat{H}\hat{\chi} - \hat{\chi}\hat{H} \right) . \end{aligned} \tag{4.26}$$

In order to obtain the partial Wigner transform of this equation of motion, Eqn. (4.23) is used. In Eqn. (4.23), the action of Λ on two arbitrary phase space functions, a and b, is given by [12]

$$a\Lambda b = -\{a, b\} = -\frac{\partial a}{\partial X_i} \mathcal{B}_{ij}^c \frac{\partial b}{\partial X_j} , \tag{4.27}$$

here $\{\cdots, \cdots\}$ is used to denote the Poisson bracket, while $\mathcal{B}_{ij}^c$ are elements of the symplectic matrix,

$$\mathcal{B}^c = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} .$$

Applying the partial Wigner transform to the equation of motion allows one to express the time evolution of $\hat{\chi}$ as,

$$\begin{aligned} \frac{\partial \hat{\chi}_W}{\partial t} &= \frac{i}{\hbar} \left(\left(\hat{H}\hat{\chi} \right)_W - \left(\hat{\chi}\hat{H} \right)_W \right) \\ &= \frac{i}{\hbar} \left(\hat{H}_W \, e^{\frac{\hbar\Lambda}{2i}} \, \hat{\chi}_W - \hat{\chi}_W \, e^{\frac{\hbar\Lambda}{2i}} \, \hat{H} \right) . \end{aligned}$$

Substituting in the definition of Λ, yields

$$\frac{\partial \hat{\chi}_W}{\partial t} = \frac{i}{\hbar} \left(\hat{H}_W \, e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j} \hat{\chi}_W - \hat{\chi}_W e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j} \hat{H}_W \right) , \tag{4.28}$$

where $\partial_i = \frac{\partial}{\partial X_i}$, and the overhead arrows represent the directions in which these operators act. In general, Eqn. (4.28) is very difficult to solve. However if the bath is harmonic, then one may expand the exponential terms up to linear order and in so doing obtain an equation that is exact. The reason that this evolution is exact is that for systems comprising of harmonic baths, the higher order terms within the expansion all go to zero when acting on the Hamiltonian [45]. Taylor expanding the evolution equation to first order produces

$$
\begin{aligned}
\frac{\partial \hat{\chi}}{\partial t} &= \frac{i}{\hbar} \left(\hat{H}_W \left(1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right) \hat{\chi}_W - \hat{\chi}_W \left(1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right) \hat{H}_W \right) \\
&= \frac{i}{\hbar} \left(\hat{H}_W \hat{\chi}_W - \hat{\chi}_W \hat{H}_W \right) - \frac{1}{2} \left(\hat{H}_W \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \hat{\chi}_W - \hat{\chi}_W \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \hat{H}_W \right) \\
&= \frac{i}{\hbar} \left[\hat{H}_W, \hat{\chi}_W \right] - \frac{1}{2} \left\{ \hat{H}_W, \hat{\chi}_W \right\} + \frac{1}{2} \left\{ \hat{\chi}_W, \hat{H}_W \right\} \\
&= \left(\hat{H}_W, \hat{\chi}_W \right) \\
&= i\mathcal{L} \hat{\chi}_W \; .
\end{aligned}
\tag{4.29}
$$

In the above the quantum-classical bracket $\left(\hat{H}_W, \hat{\chi}_W \right)$ 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, $i\mathcal{L}$, 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 becomes [3, 7, 8, 11]

$$
\frac{\partial \hat{\chi}}{\partial t} = \frac{i}{\hbar} \left[\begin{array}{cc} \hat{H}_W & \hat{\chi}_W \end{array} \right] \cdot \mathcal{D} \cdot \left[\begin{array}{c} \hat{H}_W \\ \hat{\chi}_W \end{array} \right] ,
\tag{4.30}
$$

where the antisymmetric matrix super-operator is given by

$$
\mathcal{D} = \left[\begin{array}{cc} 0 & 1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \\ -\left(1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^c \overrightarrow{\partial}_j \right) & 0 \end{array} \right] .
\tag{4.31}
$$

Since $\mathcal{D}$ is antisymmetric the Hamiltonian operator $\hat{H}$ is still a constant of motion [7]. The equivalence of the two forms of the evolution equation given by Eqns. (4.29) and (4.30) is explicitly shown in Appendix A.3.

For a time independent Hamiltonian the evolution equation has a formal solution [13]

$$\hat{\chi}_W(R, P, t) = e^{i\mathcal{L}t}\hat{\chi}_W(R, P, 0) \ . \tag{4.32}$$

This formal solution is an abstract quantity with regards to the quantum subsystem's degrees of freedom. In order 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 solution may be expressed within that particular basis as [3, 13]

$$\chi_W^{\alpha\alpha'}(R, P, t) = \sum_{\beta\beta'} \left(e^{i\mathcal{L}t}\right)_{\alpha\alpha',\beta\beta'} \chi_W^{\beta\beta'}(R, P, 0) \ . \tag{4.33}$$

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. Having said this, it should be noted that the most convenient basis for solving a problem is usually determined by the type of problem one is trying to solve. 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 [4, 13, 46].

4.4.2 The Adiabatic Basis

The adiabatic basis is defined by the eigenvalues of the eigenvalue equation [4, 7]

$$\hat{h}_W(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle \ , \tag{4.34}$$

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

$$\hat{h}_W(R) = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{q}, R) \ . \tag{4.35}$$

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 [4, 13]

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'} = \left(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'} \ . \tag{4.36}$$

The full derivation of the result given by Eqn. (4.36) may be found in Appendix E. The first term on the right hand side of the quantum-classical Liouville operator, $\omega_{\alpha\alpha'}$, is known as the Bhor frequency and is defined by the difference in energies of the adiabatic states as

$$\omega_{\alpha\alpha'}(R) = \frac{E_\alpha(R) - E_{\alpha'}(R)}{\hbar} \ . \tag{4.37}$$

The second term, $iL_{\alpha\alpha'}$, is the classical like Liouville operator [4], defined as

$$iL_{\alpha\alpha'} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}\left(F_W^\alpha + F_W^{\alpha'}\right)\frac{\partial}{\partial P} \ . \tag{4.38}$$

It is responsible for the classical 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 [13]. This operator is the only operator which changes, if the way we model 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, $J_{\alpha\alpha',\beta\beta'}$, 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 [13]. In this basis, the J-operator has the form

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} = &-\frac{P}{M}\cdot d_{\alpha\beta}\left(1 + \frac{1}{2}S_{\alpha\beta}\cdot\frac{\partial}{\partial P}\right)\delta_{\alpha'\beta'} \\ &-\frac{P}{M}\cdot d_{\alpha'\beta'}^*\left(1 + \frac{1}{2}S_{\alpha'\beta'}^*\cdot\frac{\partial}{\partial P}\right)\delta_{\alpha\beta} \end{aligned} \tag{4.39}$$

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 [13]. Finally $\hat{d}_{\alpha\beta}$ denotes the normalised coupling matrix element.

4.5 Using 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 [5, 7]. 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

$$\hat{H} = H + \hat{h}_s \ , \tag{4.40}$$

where $\hat{h}_s$ is the subsystem Hamiltonian defined as

$$\hat{h}_s = \hat{K} + \hat{V}\left(\hat{q}, R\right) \ . \tag{4.41}$$

$\hat{K}$ 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. 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. Having completed this the Nosé-Hoover Power constant temperature dynamics are then extended to the quantum-classical case.

4.5.1 Quantum-Classical Nosé-Hoover Chains

In this section the procedure outlined in [7] is followed to give a brief overview of how the generalisation of the NHC thermostat scheme may be achieved. To this end, the NHC Hamiltonian operator is defined as,

$$\hat{H}^{NHC} = H^{NHC} + \hat{h}\left(R\right)$$
$$= \frac{\hat{p}^2}{2m} + \frac{P^2}{2M} + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P^2_{\eta_2}}{2M_{\eta_2}} + \hat{V}\left(\hat{q}, R\right) + gk_bT\left(\eta_1 + \eta_2\right) \ .$$

In the above equation, $\hat{q}$ and $\hat{p}$ represent the quantum position and momentum operators respectively, while H^{NHC} is defined in Eqn. (2.23). The classical phase space point for this system is $X = (R, \eta_1, \eta_2, P_{\eta_1}.P_{\eta_2})$. For this scheme, the antisymmetric matrix used is

the one defined in Eqn. (2.25), this matrix is given by

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

One then begins the generalisation of this scheme by substituting this matrix into the antisymmetric matrix super-operator $\mathcal{D}$, in place of the $\mathcal{B}^c$ matrix which appears in Eqn. (4.31). In so doing one obtains the NHC matrix super-operator

$$
\mathcal{D}^{NHC} =
\begin{bmatrix}
0 & 1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j \\
- \left(1 + \frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j \right) & 0
\end{bmatrix} . \tag{4.42}
$$

The quantum-classical Heisenberg equation of motion may then be expressed in matrix form as

$$
\frac{\partial \hat{\chi}}{\partial t} = \frac{i}{\hbar} \begin{bmatrix} \hat{H}_W^{NHC} & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D}^{NHC} \cdot \begin{bmatrix} \hat{H}_W^{NHC} \\ \hat{\chi}_W \end{bmatrix} , \tag{4.43}
$$

while it may be given in terms of the Liouville super-operator as

$$
\frac{\partial \chi^{\alpha\alpha'}}{\partial t} = \sum_{\beta\beta'} i\mathcal{L}_{\alpha\alpha',\beta\beta'}^{NHC} \chi^{\beta\beta'} , \tag{4.44}
$$

where the NHC Liouville super-operator is

$$
i\mathcal{L}_{\alpha\alpha',\beta\beta'}^{NHC} = \left(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}^{NHC} \right) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} , \tag{4.45}
$$

while the classical-like NHC Liouville operator is

$$
iL_{\alpha\alpha'}^{NHC} = \frac{P}{M} \frac{\partial}{\partial R} + \frac{1}{2} \left(F^\alpha + F^{\alpha'} \right) \frac{\partial}{\partial P} + \frac{P_{\eta_1}}{M_{\eta_1}} \frac{\partial}{\partial \eta_1} + F_{P_{\eta_1}} \frac{\partial}{\partial P_{\eta_1}}
$$
$$
+ \frac{P_{\eta_2}}{M_{\eta_2}} \frac{\partial}{\partial \eta_2} + F_{P_{\eta_2}} \frac{\partial}{\partial P_{\eta_2}} - \frac{P_{\eta_2}}{M_{\eta_2}} P_{\eta_1} \frac{\partial}{\partial P_{\eta_1}} . \tag{4.46}
$$

In defining this classical-like operator the system forces

$$F_{P_{\eta_1}} = \frac{P_{\eta_1}^2}{M_{\eta_1}} - gK_bT \ , \tag{4.47}$$

and

$$F_{P_{\eta_2}} = \frac{P_{\eta_2}^2}{M_{\eta_2}} - gK_bT \ . \tag{4.48}$$

have been used

4.5.2 Extending the Nosé-Hoover Power Thermostat to the Quantum-Classical Case

Having extended the NHC thermostat to the quantum-classical case, the same procedure is now applied to the NHP thermostat scheme. Since the extension of this scheme had not been performed in the literature, the derivation is given in greater detail than that of the NHC case in the preceding section. The NHP Hamiltonian operator is given by

$$\hat{H}^{NHP} = \frac{\hat{p}^2}{2m} + \frac{P^2}{2M} + \frac{P_\eta^2}{2M_\eta} + \hat{V}(\hat{q}, R) + gk_bT\eta \ , \tag{4.49}$$

where $\hat{q}$ and $\hat{p}$ represent the quantum position and momentum operators respectively. The classical phase space point is defined as $X = (R, \eta, P, P_\eta)$, while the antisymmetric matrix for this scheme is defined in Eqn. (2.29) as

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

The antisymmetric matrix super-operator associated with this scheme, $\mathcal{D}^{NHP}$, may be written as

$$\mathcal{D}^{NHP} = \begin{bmatrix} 0 & 1 + \frac{i\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHP}\overrightarrow{\partial}_j \\ -\left(1 + \frac{i\hbar}{2}\overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHP}\overrightarrow{\partial}_j\right) & 0 \end{bmatrix} , \tag{4.50}$$

where the symplectic matrix $\mathcal{B}^c$ in Eqn. (4.31), has been replaced by the antisymmetric matrix for the NHP scheme. This allows one to express the equation of motion in matrix

form as

$$\frac{\partial \hat{\chi}}{\partial t} = \frac{i}{\hbar} \begin{bmatrix} \hat{H}_W^{NHP} & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D}^{NHP} \cdot \begin{bmatrix} \hat{H}_W^{NHP} \\ \\ \hat{\chi}_W \end{bmatrix} , \tag{4.51}$$

which may in turn be expressed as

$$\frac{\partial \hat{\chi}}{\partial t} = \frac{i}{\hbar} \left[\hat{H}^{NHP}, \hat{\chi} \right] - \frac{1}{2} \left(\hat{H}^{NHP} \overleftarrow{\partial} \cdot \mathcal{B}^{NHP} \cdot \overrightarrow{\partial} \hat{\chi} - \hat{\chi} \overleftarrow{\partial} \cdot \mathcal{B}^{NHP} \cdot \overrightarrow{\partial} \hat{H}^{NHP} \right) .$$

Evaluating the terms in the round brackets, one finds that they are equivalent to

$$\frac{\partial \hat{V}}{\partial R} \frac{\partial \hat{\chi}}{\partial P} + \frac{\partial \hat{\chi}}{\partial P} \frac{\partial \hat{V}}{\partial R} - 2 F_p \frac{\partial \hat{\chi}}{\partial P_\eta} + \frac{\partial \hat{V}}{\partial R} \frac{\tau P}{M} \frac{\partial \hat{\chi}}{\partial P_\eta}$$

$$+ \frac{\partial \hat{\chi}}{\partial P_\eta} \frac{\tau P}{M} \frac{\partial \hat{V}}{\partial R} - 2 \left(\frac{P}{M} + \frac{P_\eta}{M_\eta} \frac{\tau P}{M} \right) \frac{\partial \hat{\chi}}{\partial R}$$

$$- 2 \frac{P_\eta}{M_\eta} \frac{\partial \hat{\chi}}{\partial \eta} + 2 \frac{P_\eta}{M_\eta} P \frac{\partial \hat{\chi}}{\partial P} ,$$

where the force acting on the system is given by Eqn. (3.26). Using this result allows one to express the equation of motion as

$$\frac{\partial \hat{\chi}}{\partial t} = \frac{i}{\hbar} \left[\hat{H}, \hat{\chi} \right] - \frac{1}{2} \left(\frac{\partial \hat{V}}{\partial R} \frac{\partial \hat{\chi}}{\partial P} + \frac{\partial \hat{\chi}}{\partial P} \frac{\partial \hat{V}}{\partial R} \right) + \left(\frac{P}{M} + \frac{P_\eta}{M_\eta} \frac{\tau P}{M} \right) \frac{\partial \hat{\chi}}{\partial R}$$

$$+ \frac{P_\eta}{M_\eta} \frac{\partial \hat{\chi}}{\partial \eta} - \frac{P_\eta}{M_\eta} P \frac{\partial \hat{\chi}}{\partial P} + F_p \frac{\partial \hat{\chi}}{\partial P_\eta} - \frac{1}{2} \frac{\partial \hat{V}}{\partial R} \frac{\tau P}{M} \frac{\partial \hat{\chi}}{\partial P_\eta}$$

$$- \frac{1}{2} \frac{\partial \hat{\chi}}{\partial P_\eta} \frac{\tau P}{M} \frac{\partial \hat{V}}{\partial R} . \tag{4.52}$$

Before using this equation of motion to perform simulations, it first needs to be represented in a basis. For reasons already given the adiabatic basis will be used.

Representation in the adiabatic basis

To represent the equation of motion in this basis one begins by rewriting the Hamiltonian operator as

$$\hat{H}^{NHP} = \frac{P^2}{2M} + \frac{P_\eta^2}{2M_\eta} + g k_b T \eta + \hat{h}_S(R) , \tag{4.53}$$

where the quantum subsystems Hamiltonian operator has been introduced previously. This operator is defined as $\hat{h}_s(R) = \hat{K} + \hat{V}(\hat{\chi}, R)$. In this operator $\hat{K}$ represents the quantum kinetic operator while $\hat{V}$ represents the potential operator coupling, the classical bath and quantum subsystem. Recalling that the adiabatic states are defined by the

eigenvalue equation

$$\hat{h}_W(R)\,|\alpha; R\rangle = E_\alpha\,|\alpha; R\rangle \tag{4.54}$$

one finds that Eqn. (4.52) may be expressed in this basis as

$$
\begin{aligned}
\frac{\partial \chi^{\alpha\alpha'}}{\partial t} = {} & \left(i\omega_{\alpha\alpha'} + L_1^{NHP} + L_2^{NHP} + L_3^{NHP} \right) \chi^{\alpha\alpha'} \\
& + \frac{1}{2} \sum_\beta F^{\alpha\beta} \frac{\partial \chi^{\beta\alpha'}}{\partial P} + \frac{1}{2} \sum_\beta \frac{\partial \chi^{\alpha\beta}}{\partial P} F^{\beta\alpha'} \\
& + \frac{\tau P}{2M} \sum_\beta F^{\alpha\beta} \frac{\partial \chi^{\beta\alpha'}}{\partial P_\eta} + \frac{\tau P}{2M} \sum_\beta \frac{\partial \chi^{\alpha\beta}}{\partial P_\eta} F^{\beta\alpha'} \\
& + \left(\frac{P}{M} + \frac{P_\eta}{M_\eta} \frac{\tau P}{M} \right) \left(-\sum_\beta \left(-d_{\alpha\beta} \chi^{\beta\alpha'} + \chi^{\alpha\beta} d_{\beta\alpha'} \right) \right) ,
\end{aligned}
$$

where $F^{\alpha\beta} = -\langle \alpha \,|\, [(\partial\phi)/(\partial R)] \,|\, \beta \rangle$ and the non-adiabatic coupling vector is given by $d_{\alpha\beta} = \langle \alpha \,|\, [\partial/(\partial R)] \,|\, \beta \rangle$. The Liouville operators are defined in the equation set (3.51). This equation may be rewritten through the introduction of the Liouville super-operator such that

$$\frac{\partial \chi^{\alpha\alpha'}}{\partial t} = \sum_{\beta\beta'} i\mathcal{L}^{NHP}_{\alpha\alpha',\beta\beta'} \chi^{\beta\beta'} , \tag{4.55}$$

where the NHP Liouville super-operator is

$$i\mathcal{L}^{NHP}_{\alpha\alpha',\beta\beta'} = \left(i\omega_{\alpha\alpha'} + iL^{NHP}_{\alpha\alpha'} \right) \delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'} , \tag{4.56}$$

while the classical-like NHP Liouville operator is

$$iL^{NHP}_{\alpha\alpha'} = \left(L_1^{NHP} + L_2^{NHP} + L_3^{NHP} \right) + \frac{F^\alpha + F^{\alpha'}}{2} \left[\frac{P}{\partial P} + \tau \frac{P}{M} \frac{\partial}{\partial P_\eta} \right] . \tag{4.57}$$

The mathematical details involved with the extension of the NHP thermostat to the quantum-classical case may be found in Appendix F.

Chapter 5

Numerical Studies

In this chapter a discussion of the model used to test the integration schemes obtained in the previous chapter is discussed. This discussion is accompanied by a description of the dimensionless units used for the simulations. The simulation procedures are then discussed. Here the calculated observable, $\hat{\sigma}_z$, is also introduced. Finally, the obtained results are given for a range of parameters followed by a brief discussion

5.1 Spin-Boson Model

The simulation results presented in this chapter were obtained 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 a way to check the efficiency and accuracy of any new algorithms. The spin-boson model itself 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 bosons. The Hamiltonian operator for this model is

$$\hat{H}^{sb} = -\hbar\Omega\hat{\sigma}_x + \sum_{j=1}^{N_b}\left(\frac{\hat{P}_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2\hat{R}_j^2 - c_j\hat{R}_j\hat{\sigma}_z\right) , \qquad (5.1)$$

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 represents the splitting between the two levels of the system. The summation which appears is over all the bath oscillators. M_j, ω_j and c_j represent the mass, frequency and coupling strength between the system and the jth oscillator respectively. These parameters are fixed, by requiring that the harmonic bath

be described by an Ohmic spectral density [8]. To ensure this the coupling strength and frequencies were chosen to be the same as those introduced in [47, 48] namely

$$c_j = \omega_j \sqrt{\xi \hbar \omega_0 M_j} \ , \tag{5.2}$$

and

$$\omega_j = -\omega_c \ln \left(1 - j \frac{\omega_0}{\omega_c} \right) \ , \tag{5.3}$$

where

$$\omega_0 = \frac{\omega_c}{N_b} \left(1 - e^{-\omega_{max}/\omega_c} \right) \ . \tag{5.4}$$

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 [45].

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

$$\hat{H}_W^{sb} = -\hbar \Omega \hat{\sigma}_x + \sum_{j=1}^{N_b} \left(\frac{P_j^2}{2M_j} + \frac{1}{2} M_j \omega_j^2 R_j^2 - c_j R_j \hat{\sigma}_z \right) \ , \tag{5.5}$$

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

$$\hat{H}_W^{sb} = \hat{h}_s + H_b + \hat{V}_c(R) \ , \tag{5.6}$$

where $\hat{h}_s$ represents the quantum subsystem Hamiltonian

$$\hat{h}_s = -\hbar \Omega \hat{\sigma}_x \ . \tag{5.7}$$

The bath Hamiltonian, H_b, is given by

$$H_b = \sum_{j=1}^{N_b} \left(\frac{P_j^2}{2M_j} + \frac{1}{2} M_j \omega_j^2 R_j^2 \right) \ , \tag{5.8}$$

while the coupling potential energy, $\hat{V}_c(R)$, is defined as

$$\hat{V}_c(R) = -\sum_{j=1}^{N_b} c_j R_j \hat{\sigma}_z \ . \tag{5.9}$$

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 $N_b = 200$ oscillators. The reason this many oscillators are used is that this is the number required to ensure that the obtained results are in agreement with those predicted by linear response theory [49]. The results of these NVE dynamics will be 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 $N_b = 1$.

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

$$\hat{H}_W^{NHC} = \hat{H}_W^{sb} + \frac{P_{\eta_1}^2}{2M_{\eta_1}} + \frac{P_{\eta_2}^2}{2M_{\eta_2}} + N_b k_b T \eta_1 + k_b T \eta_2 \ , \tag{5.10}$$

while the NHP Hamiltonian operator for the same model is

$$\hat{H}_W^{NHP} = \hat{H}_W^{sb} + \frac{P_\eta^2}{2M_\eta} + N_b k_b T \eta \ . \tag{5.11}$$

5.1.1 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 are avoided since after the scaling is performed all values in the calculation are of roughly the same order.

These scaled units are obtained through scaling the phase space variables (R, P) as [45]

$$R_j' = \left(\frac{M_j \omega_c}{\hbar} \right)^{\frac{1}{2}} \quad \text{and} \quad P_j' = (\hbar M_j \omega_c)^{-\frac{1}{2}} P_j \ . \tag{5.12}$$

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

$$\hat{H}_W^{sb'} = -\Omega' \hat{\sigma}_x + \sum_{j=1}^{N_b} \left(\frac{P_j'^2}{2} + \frac{1}{2}\omega_j'^2 R_j'^2 - c_j'^2 \hat{\sigma}_z R_j' \right) , \tag{5.13}$$

where

$$\Omega' = \frac{\Omega}{\omega_c} , \quad \omega_j = \frac{\omega_j}{\omega_c} , \quad c_j = \omega_j \sqrt{\xi \frac{\omega_0}{\omega_c}} . \tag{5.14}$$

While the dimensionless inverse temperature and time may be expressed as [45]

$$\beta' = \frac{\hbar \omega_c}{k_b T} \quad \text{and} \quad t' = t\omega_c , \tag{5.15}$$

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.

5.2 Simulation Procedures

For the simulations performed, the systems phase space points were propagated forward in time from some initial state (R, P) at $t = 0$ to a final state (R', P') at $t = t'$. The observable of interest was then calculated at the new phase space point after each time step. The initial phase space point is obtained by sampling from the bath distribution function. It was assumed that the system was initially in an uncorrelated sate, with the quantum subsystem in state $|\uparrow\rangle$, while the bath was in thermal equilibrium. The initial density matrix for this case is then simply given by the product of the subsystem density matrix and the bath distribution function,

$$\hat{\rho}(0) = \hat{\rho}_s(0) \rho_b(R, P) , \tag{5.16}$$

where

$$\hat{\rho}_s = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} . \tag{5.17}$$

The bath distribution function is given by

$$\rho_b(R, P) = \frac{e^{-\beta \hat{H}_b}}{Z_b} \tag{5.18}$$

where, H_b, denotes the bath Hamiltonian, while Z_b is its partition function. The partial Wigner transform of the initial density operator is

$$\hat{\rho}_W(0) = \hat{\rho}_s(0)\,\rho_{bW}(R, P) \; , \tag{5.19}$$

where the bath distribution function in dimensionless variables is given by [45]

$$\rho_{bW}(R, P) = \prod_{j=1}^{N_b} \frac{\tanh(\beta\omega_j/2)}{\pi} \times \left[-\frac{2\tanh(\beta\omega_j/2)}{\omega_j} H_b \right] \; . \tag{5.20}$$

5.2.1 Calculation of the Observable

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

$$\langle \chi \rangle = Tr(\hat{\rho}\hat{\chi}) \; . \tag{5.21}$$

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

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \; . \tag{5.22}$$

This particular observable was chosen, as it makes it be possible to compare the results we obtain with those found in the literature.

The expectation value of this operator represents the population difference of the two energy levels of the quantum subsystem. To demonstrate this the expectation value of this observable is calculated.

$$\begin{aligned}
\langle \sigma_z \rangle &= Tr(\hat{\rho}\hat{\sigma}_z) \\
&= Tr\left(\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right) \\
&= Tr\begin{pmatrix} \rho_{11} & -\rho_{12} \\ \rho_{21} & -\rho_{22} \end{pmatrix} \\
&= \rho_{11} - \rho_{22} \; .
\end{aligned} \tag{5.23}$$

From this one sees that in Eqn. (5.23) the expectation value of the operator $\hat{\sigma}_z$ is the

population difference between the two energy levels.

5.3 Results

In this section the results of the quantum-classical simulations are presented. All simulations of the spin-boson model were performed making use of the dimensionless coordinates. The system parameters used for the simulations were $\omega_{max} = 3$ and $\Omega = 1/3$. The Kondo parameter and temperature values were varied between simulations and took on four different sets of values. The first two sets ($\xi = 0.007$, $\beta = 0.3$) and ($\xi = 0.1$, $\beta = 3.0$) are the same as those found in [8]. These two sets were used as a way to check if the code would reproduce the published results. Once this was done, simulations were then also run for the two sets of values ($\xi = 0.002$, $\beta = 0.1$) and ($\xi = 0.1$, $\beta = 2.0$).

For all the simulations run the results of the NHP dynamics were compared with those obtained via the use of the well established NHC and NVE dynamics. These simulations were first performed using the adiabatic approximation. This approximation allows no exchange of energy between the thermal bath and the subsystem of interest. This amounts to setting the J-operator which appears in the quantum-classical equation of motion to zero. As such the system dynamics propagate adiabatically without any non-adiabatic quantum transitions.

Having obtained the results within the adiabatic approximation, further simulations were performed to try and simulate the non-adiabatic dynamics of the spin-boson model. In these simulations the quantum subsystem was allowed to exchange energy with the thermal bath, as such the J-operator was no longer set to zero. For all the simulations run under these conditions, the quantum subsystem was allowed to undergo a maximum of six non-adiabatic quantum transitions.

Figure 5.1: The adiabatic dynamics of the spin-boson model with the parameters: $\Omega = 1/3$, $\xi = 0.007$, $\omega_{max} = 3$, $\beta = 0.3$. The white circles represent the NHP results with $N_b = 1$; The black line represents the NVE results with $N_b = 200$; The black circles represent the NHC results with $N_b = 1$; .

Figure 5.2: The adiabatic dynamics of the spin-boson model with the parameters: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{max} = 3$, $\beta = 3.0$. The white circles represent the NHP results with $N_b = 1$; The black line represents the NVE results with $N_b = 200$; The black circles represent the NHC results with $N_b = 1$.

Figure 5.3: The adiabatic dynamics of the spin-boson model with the parameters: $\Omega = 1/3$, $\xi = 0.002$, $\omega_{max} = 3$, $\beta = 0.1$. The white circles represent the NHP results with $N_b = 1$; The black line represents the NVE results with $N_b = 200$; The black circles represent the NHC results with $N_b = 1$.
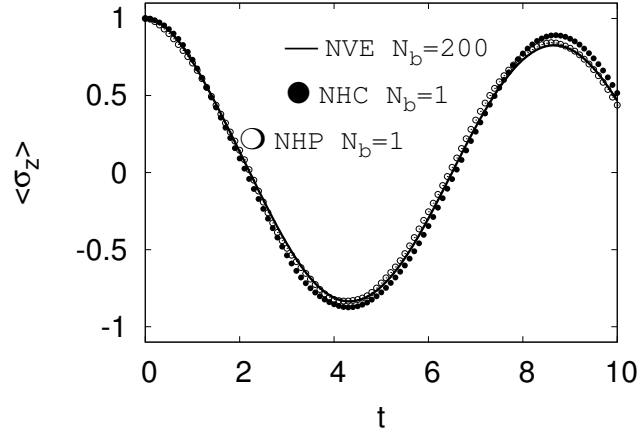

Figure 5.4: The adiabatic dynamics of the spin-boson model with the parameters: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{max} = 3$, $\beta = 2.0$. The white circles represent the NHP results with $N_b = 1$; The black line represents the NVE results with $N_b = 200$; The black circles represent the NHC results with $N_b = 1$.
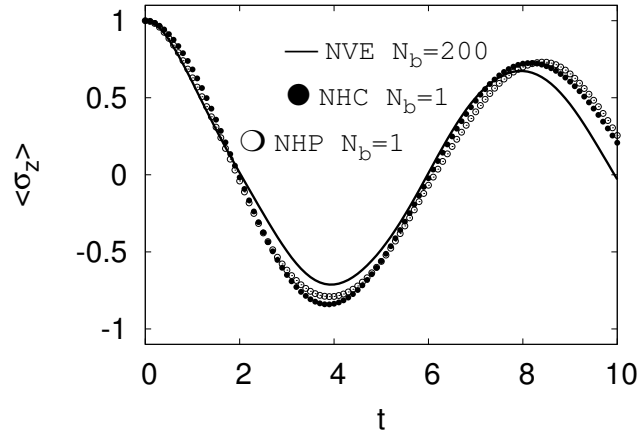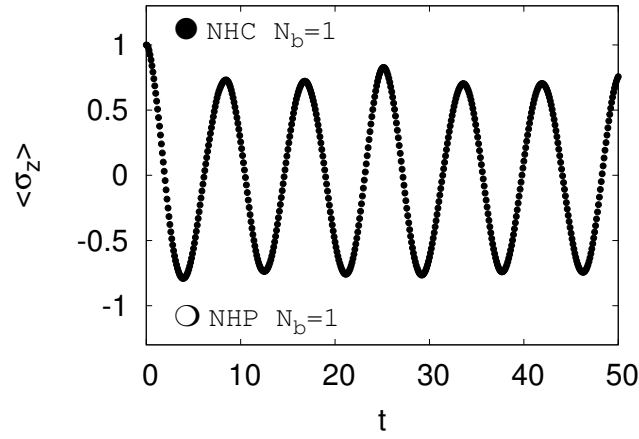
Figure 5.5: Long time adiabatic dynamics of the spin boson model. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{max} = 3$, $\beta = 3.0$. The white circles represent the NHP dynamics with $N_b = 1$; The black circles represent the NHC dynamics with $N_b = 1$.
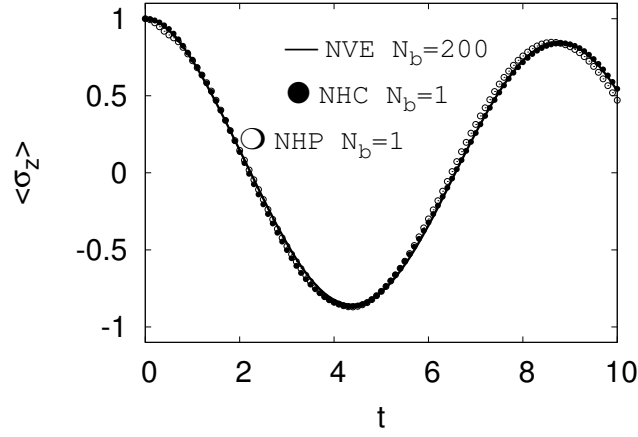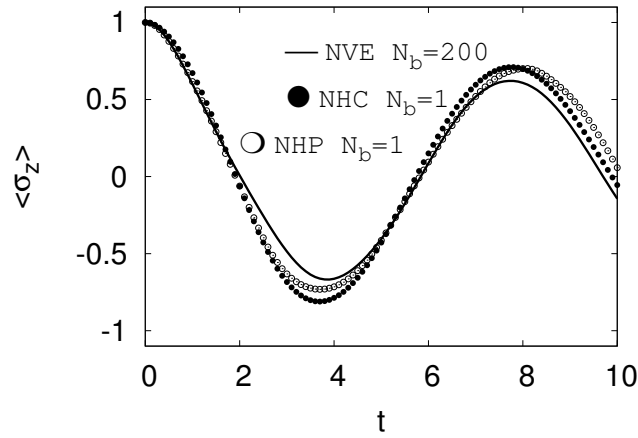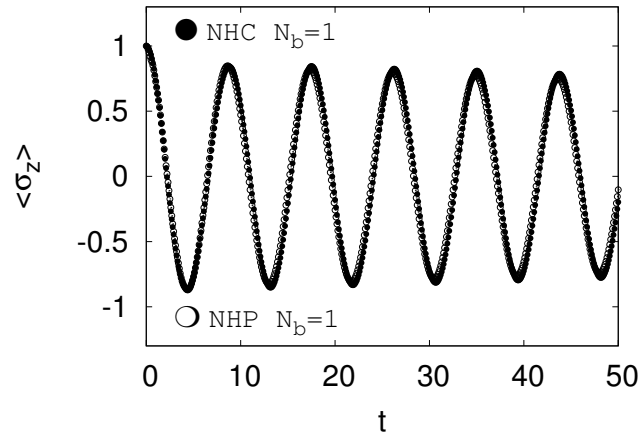

Figure 5.6: Long time adiabatic dynamics of the spin boson model. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{max} = 3$, $\beta = 2.0$. The white circles represent the NHP dynamics with $N_b = 1$; The black circles represent the NHC dynamics with $N_b = 1$.
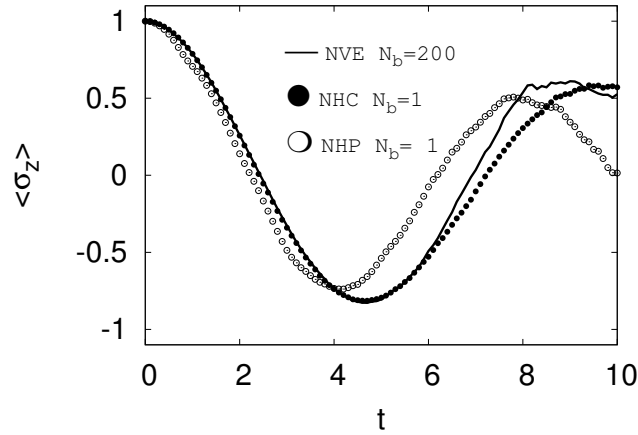
Figure 5.7: Non-adiabatic dynamics of the spin-boson model including up to six quantum transitions. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.007$, $\omega_{max} = 3$, $\beta = 0.3$. The white circles represent the results obtained with use of the NHP dynamics with $N_b = 1$. The continuous black line represents the NVE dynamics with $N_b = 200$. The black circles represent the NHC dynamics with $N_b = 1$.
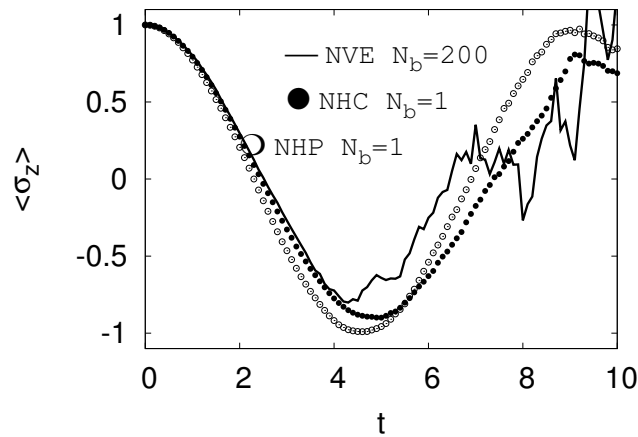
Figure 5.8: Non-adiabatic dynamics of the spin-boson model including up to six quantum transitions. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.1$, $\omega_{max} = 3$, $\beta = 3.0$. The white circles represent the results obtained with use of the NHP dynamics with $N_b = 1$. The continuous black line represents the NVE dynamics with $N_b = 200$. The black circles represent the NHC dynamics with $N_b = 1$.
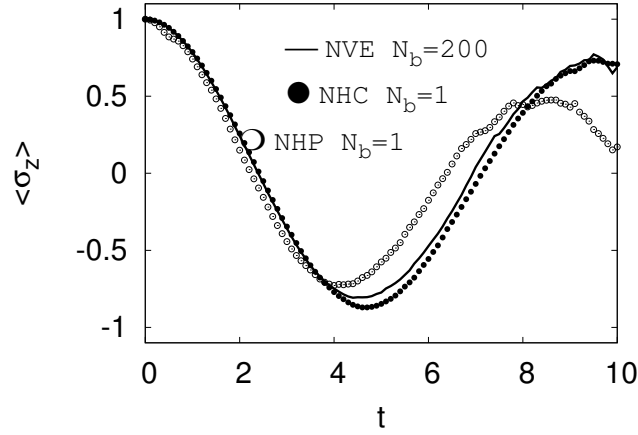
Figure 5.9: Non-adiabatic dynamics of the spin-boson model including up to six quantum transitions. The simulation parameters were: $\Omega = 1/3$, $\xi = 0.002$, $\omega_{max} = 3$, $\beta = 0.1$. The white circles represent the results obtained with use of the NHP dynamics with $N_b = 1$. The continuous black line represents the NVE dynamics with $N_b = 200$. The black circles represent the NHC dynamics with $N_b = 1$.

Figure 5.10: 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 continuous black line represents the NVE dynamics with $N_b = 200$. The black circles represent the NHC dynamics with $N_b = 1$.

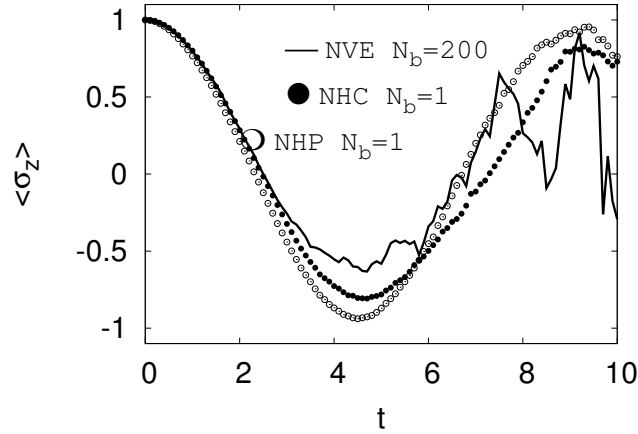In order to show how the NHP dynamics describes the dissipative evolution of the quantum subsystem within the adiabatic approximation, Figs. 5.1, 5.2, 5.3 and 5.4 have been presented. From these four figures one sees that the results produced by the NHP dynamics are in good agreement with those obtained using the well established NHC and NVE dynamics. In the presented results, Figs. 5.1 and 5.2, show the adiabatic calculations for the set of parameters ($\beta = 0.3$, $\xi = 0.007$) and ($\beta = 3.0$, $\xi = 0.1$) respectively. These were the same parameters used for the results shown in [8]. Simulations were also run for the new parameter sets with the obtained results shown in Figs. 5.3 and 5.4. These correspond to the parameter sets ($\beta = 0.1$, $\xi = 0.002$) and ($\beta = 2.0$, $\xi = 0.1$) respectively. The simulation run time for the parameter sets ($\beta = 3.0$, $\xi = 0.007$) and ($\beta = 2.0$, $\xi = 0.1$) was then extended, for the NHC and NHP dynamics. The obtained results may be found in Figs. 5.5 and 5.6 respectively. From these simulation results one sees that even after long time runs, the NHP dynamics are still in good agreement with the NHC dynamics.

In order to show how the NHP dynamics describe the dissipative evolution of the quantum subsystem, simulations were run for non-adiabatic dynamics. This meant that energy exchanges, were allowed to take place between the bath and quantum subsystem. These energy exchanges in turn lead to non-adiabatic quantum transitions taking place within the quantum subsystem. For the results presented here the quantum subsystem was allowed to undergo a maximum of six quantum transitions. In Figs. 5.7 and 5.9 the results obtained for these non-adiabatic calculations with the set of parameters ($\beta = 0.3$, $\xi = 0.007$) and ($\beta = 0.1$, $\xi = 0.002$) respectively are shown. These parameters correspond to the high temperature low coupling regime of the system dynamics. As the plots show there were some discrepancies between the results of the NHP dynamics and those of the NHC and NVE dynamics. A possible cause of these might have been the way in which the momentum shifts associated with the non-adiabatic transitions were calculated. It should be noted that this problem is not just limited to the NHP dynamics, but is rather a more common problem one comes across, when performing numerical simulations of non-adiabatic quantum dynamics [8]. The results shown in Figs. 5.8 and 5.10 correspond to the parameter sets ($\beta = 3.0$, $\xi = 0.1$) and ($\beta = 2.0$, $\xi = 0.1$) respectively. These parameter sets represent the low temperature high coupling regime of the dynamics. Within this regime the NHP dynamics were in fairly good agreement with the results produced via the NHC dynamics, with only slight discrepancies between the two. However, the NHP dynamics outperformed the NVE dynamics in this regime.

Although only these parameter sets are presented in this dissertation, it should be noted that simulations were run for various other parameters. The results obtained were in accord with the ones displayed here, and as such have not been reported in this dissertation.

Chapter 6

Conclusion

In this chapter a summary of the work performed in this dissertation is given. Having accomplished this the original contributions to the body of work found in the literature are then explicitly given. Finally possible future projects are discussed.

This dissertation started by differentiating between Hamiltonian and non-Hamiltonian theories. This was followed by a discussion about the underlying algebraic bracket formulation for non-Hamiltonian systems, ahead of the introduction and discussion of three extended system schemes. These were the Nosé-Hoover (NH), Nosé-Hoover Chain (NHC) and Nosé-Hoover Power (NHP) thermostats.

Having done this it was then shown, that by using the underlying bracket structure of the dynamics it is possible to design efficient time-reversible algorithms, for integrating the equations of motion associated with the thermostat schemes. This was done by following the procedure outlined in [22]. It was also shown how to design algorithms that are not only time-reversible but also preserve the invariant measure of phase space. This was done following the procedure presented in [9]. The stability and ergodic properties of the measure-preserving schemes were then tested via the simulation of a one-dimensional harmonic oscillator coupled to the thermostats.

Following this a detailed discussion of the theory of quantum-classical dynamics was then presented. This included a brief recap of Heisenberg's formulation of quantum mechanics, which lead to a discussion about quantum statistical mechanics. Here the concept of the density matrix operator was introduced. The phase space representation of quantum mechanics was then introduced with a focus on the Wigner representation. The task of modelling quantum dynamics within classical baths was then presented. This included a derivation of the quantum-classical Liouville equation expressed in the adiabatic basis.

The NHC and NHP thermostat schemes were then extended to the quantum-classical case. Having performed the extension of these schemes, a model was required with which to test them. To this end the spin-boson model along with the dimensionless units used for the simulations was introduced.

The original contribution of this work have been to devise an integration scheme that allows one to represent a thermal bath through the use of the NHP dynamics. A way was found to improve upon the time-reversible integration scheme found in [5] for this thermostat. This was achieved by devising a measure-preserving time-reversible integration scheme based on the procedure outlined in [9]. This scheme was then tested by simulating the dynamics of a one-dimensional harmonic oscillator coupled to the NHP thermostat. The obtained results were compared with those obtained using the well established NHC thermostat. It was found that the integration schemes of both thermostats produced ergodic results while conserving the extended system Hamiltonians. The task of extending the measure-preserving NHP thermostat to the quantum-classical case was then undertaken, with a view to represent a dissipative bath with as few degrees of freedom as possible. Once this extension was obtained, the damping of a tunnelling spin coupled to a thermalised harmonic mode was simulated via the use of the spin-boson model. In these simulations the results for the adiabatic approximation were in very good agreement with those obtained using the previously developed approaches namely, the NHC and NVE dynamics discussed in the theory.

For the non-adiabatic simulations the results were found to be in fairly good agreement between the NHC and NHP dynamics, in the low temperature high coupling regime. Within this regime the NHP dynamics managed to outperform the NVE dynamics. For the high temperature low coupling regime there were some discrepancies found between the NHP results and those of the NHC and NVE dynamics. A possible cause of these discrepancies could be the way in which the momentum shifts associated with the non-adiabatic transitions were calculated. These transitions occur when the subsystem and thermal bath exchange energy. It should be noted that this problem is not just limited to the NHP dynamics, but is rather a common trouble spot for the simulation of non-adiabatic quantum dynamics in general.

In the future we plan on using the thermostat schemes discussed in this dissertation, to simulate the dynamics of various other quantum spin systems, in contact with thermal baths. A possible application under consideration is the simulation of nano-mechanical

oscillators. These oscillators are used in the detection and amplification of weak microwave and radio waves. Another possible application lies in the field of quantum biology with a study of the role of thermal baths on quantum transport.

Appendix A

Miscellaneous Proofs

A.1 Time-Translation Invariance of Hamiltonian Brackets

If the Liouville operator is defined as

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

then the equations of motion expressed in Eqn. (2.6) 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,

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

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

$$u(\epsilon) = e^{\epsilon L}u(0)$$
$$= [1 + \epsilon L]u(0)$$
$$= u(0) + \epsilon(u, H) \ , \tag{A.4}$$

similarly

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

If one considers,

$$e^{\epsilon L}(u, v) = [1 + \epsilon L](u, v)$$

$$= (u, v) + \epsilon L(u, v)$$

$$= (u, v) + \epsilon((u, v), H) \ , \tag{A.6}$$

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. (2.1), gives

$$((u, v), H) = (u, (v, H)) + ((u, H), v)$$

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

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,

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

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

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

$$= (u, v) + \epsilon(u, \dot{v}) + \epsilon(\dot{u}, v) + \epsilon^2(\dot{u}, \dot{v}) \ ,$$

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 Accuracy of Approximated Propagator

Through use of the Taylor expansion it shall now show that the approximate propagator $\tilde{U}(h)$, is accurate up to second order in time h^2. Recalling that the approximated is defined in Eqn. (3.18) as

$$\tilde{U}(h) \approx e^{\frac{iL_2 h}{2}} e^{iL_1 h} e^{\frac{iL_2 h}{2}} \ . \tag{A.10}$$

One begins by Taylor expanding the exponential terms, which appear on the right side to obtain

$$e^{\frac{iL_2 h}{2}} e^{iL_1 h} e^{\frac{iL_2 h}{2}} = \left[1 + \frac{h}{2} iL_2 + \frac{h^2}{8} (iL_1)^2 + \cdots \right] \times$$
$$\left[1 + h iL_1 + \frac{h^2}{2} (iL_1)^2 + \cdots \right] \times$$
$$\left[1 + \frac{h}{2} iL_2 + \frac{h^2}{8} (iL_1)^2 + \cdots \right] \ .$$

Multiplying out the brackets produces

$$e^{\frac{iL_2 h}{2}} e^{iL_1 h} e^{\frac{iL_2 h}{2}} = 1 + (iL_1 + iL_2) h + \frac{1}{2} \left[(iL_1)(iL_2) + (iL_2)(iL_1) + \frac{1}{2} (iL_2)^2 \right.$$
$$\left. + \frac{1}{4} (iL_2)^2 + (iL_1)^2 + \frac{1}{4} + (iL_2)^2 \right] h^2 + \cdots$$
$$= 1 + (iL_1 + iL_2) h + \frac{1}{2} \left[(iL_1)(iL_2) + (iL_2)(iL_1) + (iL_2)^2 + (iL_1)^2 \right] h^2 + \cdots$$
$$= 1 + (iL_1 + iL_2) h + \frac{1}{2} (iL_1 + iL_2)^2 h^2 + \cdots$$
$$= 1 + iLh + \frac{1}{2} (iL)^2 h^2 + \cdots$$
$$\approx e^{iLh} \ . \tag{A.11}$$

The last line shows that the approximate propagator is equivalent up second order in time to the exact propagator. As such one may write that

$$e^{iLh} = e^{\frac{iL_2 h}{2}} e^{iL_1 h} e^{\frac{iL_2 h}{2}} + \mathcal{O}\left(h^3\right) \tag{A.12}$$

A.3   Equivalence of Equations of Motion

In order to show the equivalence of Eqns. (4.29) and (4.30) one begins by recalling that Eqn. (4.30) is

$$\frac{\partial \hat{\chi}_W}{\partial t} = \frac{i}{\hbar} \begin{bmatrix} \hat{H}_W & \hat{\chi}_W \end{bmatrix} \cdot \mathcal{D} \cdot \begin{bmatrix} \hat{H}_W \\ \hat{\chi}_W \end{bmatrix} \tag{A.13}$$

Substituting in the matrix, $\mathcal{D}$, given by Eqn. (4.31) this evolution equation becomes

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

Evaluating this equation produces

$$\begin{aligned}
\frac{\partial \hat{\chi}_W}{\partial t} &= \frac{i}{\hbar} \begin{bmatrix} \hat{H}_W & \hat{\chi}_W \end{bmatrix} \cdot \begin{bmatrix} \left(1 + \frac{i\hbar}{2}\overleftarrow{\partial}_i \cdot \mathcal{B}_{ij}^c \overrightarrow{\partial}_j\right) \hat{\chi}_W \\ -\left(1 + \frac{i\hbar}{2}\overleftarrow{\partial}_i \cdot \mathcal{B}_{ij}^c \overrightarrow{\partial}_j\right) \hat{H}_W \end{bmatrix} \\
&= \frac{i}{\hbar} \left(\hat{H}_W \left(1 + \frac{i\hbar}{2}\overleftarrow{\partial}_i \cdot \mathcal{B}_{ij}^c \overrightarrow{\partial}_j\right) \hat{\chi}_W - \hat{\chi}_W \left(1 + \frac{i\hbar}{2}\overleftarrow{\partial}_i \cdot \mathcal{B}_{ij}^c \overrightarrow{\partial}_j\right) \hat{H}_W \right) \\
&= \frac{i}{\hbar} \left[\hat{H}_W, \hat{\chi}_W\right] - \frac{1}{2}\left\{\hat{H}_W, \hat{\chi}_W\right\} + -\frac{1}{2}\left\{\hat{H}_W, \hat{\chi}_W\right\} \\
&= \left(\hat{H}_W, \hat{\chi}_W\right) \\
&= i\mathcal{L}\hat{\chi}_W
\end{aligned} \tag{A.14}$$

The last line of the above equation is identical to Eqn. (4.29) 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

Time-Translation Rules for the Nosé-Hoover Power Dynamics

In this appendix the mathematical details associated with the NHP thermostat's time-translation rules are presented. This is done for both the time-reversible and measure preserving cases. The measure-preserving case contains more details than the time-reversible one, since these translation rules are not present in the literature.

B.1 Time-Translation Rules for the Time-Reversible Nosé-Hoover Power Dynamics

Action of $U_5(h)$

$$U_5(h) = e^{hL_5^{NHP}}$$
$$= e^{h\left(\frac{\tau P}{M} + F_P\right)\frac{\partial}{\partial P_\eta}}$$

The solution of the equation of motion with respect to P_η is given by

$$P_\eta(h) = e^{h\left(\frac{\tau P}{M} + F_P\right)\frac{\partial}{\partial P_\eta}} P_\eta(0) \ .$$

Since none of the terms in the exponential depend on P_η, one may use the identity given by Eqn. (3.21a) to obtain

$$P_\eta(h) = P_\eta(0) + h\left(\frac{\tau P}{M} + F_P\right) \ .$$

This translation rule may be expressed in pseudo-code form as

$$P_\eta \to P_\eta + h\left(\frac{\tau P}{M} + F_P\right) \ . \tag{B.1}$$

Action of $U_4(h)$

$$U_4(h) = e^{hL_4^{NHP}}$$
$$= e^{h\frac{P_\eta}{M_\eta}\frac{\partial}{\partial\eta}}$$

The solution of the equation of motion with respect to η is given by

$$\eta(h) = e^{h\frac{P_\eta}{M_\eta}\frac{\partial}{\partial\eta}}\eta(0) \ .$$

Since none of the terms in the exponential depend on η, one may use the identity given by Eqn. (3.21a) to obtain

$$\eta(h) = \eta(0) + h\frac{P_\eta}{M_\eta} \ .$$

This translation rule may be expressed in pseudo-code form as

$$\eta \to \eta + h\frac{P_\eta}{M_\eta} \ . \tag{B.2}$$

Action of $U_3(h)$

$$U_3(h) = e^{hL_3^{NHP}}$$
$$= e^{-hP\frac{P_\eta}{M_\eta}\frac{\partial}{\partial P}}$$

The solution of the equation of motion with respect to P is given by

$$P(h) = e^{-hP\frac{P_\eta}{M_\eta}\frac{\partial}{\partial P}}P(0) \ .$$

Since one of the terms in the exponential depends on P, one may use the identity given by Eqn. (3.21b) to obtain

$$P(h) = P(0)\, e^{-hP\frac{P_\eta}{M_\eta}} \ .$$

This translation rule may be expressed in pseudo-code form as

$$P \rightarrow P\, e^{-hP\frac{P_\eta}{M_\eta}} \ . \tag{B.3}$$

Action of $U_2\,(h)$

$$U_2(h) = e^{hL_2^{NHP}}$$
$$= e^{hF_R\frac{\partial}{\partial P}}$$

The solution of the equation of motion with respect to P is given by

$$P(h) = e^{hF_R\frac{\partial}{\partial P}}P(0) \ .$$

Since none of the terms in the exponential depend on P, one may use the identity given by Eqn. (3.21a) to obtain

$$P(h) = P(0) + hF_R \ .$$

This translation rule may be expressed in pseudo-code form as

$$\eta \rightarrow \eta + h\frac{P_\eta}{M_\eta} \ . \tag{B.4}$$

Action of $U_1\,(h)$

$$U_1(h) = e^{hL_1^{NHP}}$$
$$= e^{h\left(\frac{\tau P}{M}\frac{P_\eta}{M_\eta} + \frac{P}{M}\right)\frac{\partial}{\partial R}}$$

The solution of the equation of motion with respect to R is given by

$$R(h) = e^{h\left(\frac{\tau P}{M}\frac{P_\eta}{M_\eta} + \frac{P}{M}\right)\frac{\partial}{\partial R}}R(0) \ .$$

Since none of the terms in the exponential depend on R, one may use the identity given by Eqn. (3.21a) to obtain

$$R(h) = R(0) + h\left(\frac{\tau P}{M}\frac{P_\eta}{M_\eta} + \frac{P}{M}\right) \ .$$

This translation rule may be expressed in pseudo-code form as

$$R \to R + h \left(\frac{\tau P}{M} \frac{P_\eta}{M_\eta} + \frac{P}{M} \right) \ . \tag{B.5}$$

B.2 Time-Translation Rules for the Measure-Preserving Nosé-Hoover Power Dynamics

Action of $U_A^{NHP}(h)$

The Liouville operator associated with this propagator is

$$L_A^{NHP} = \frac{P}{M} \frac{\partial}{\partial R} + F_p \frac{\partial}{\partial P_\eta} \ . \tag{B.6}$$

This Liouville operator corresponds to a set of two equations of motion. These equations have the formal solution

$$\begin{pmatrix} R(h) \\ P_\eta(h) \end{pmatrix} = U_A(h) \begin{pmatrix} R(0) \\ P_\eta(0) \end{pmatrix} \ . \tag{B.7}$$

The first of these equations may be written explicitly as,

$$\begin{aligned} R(h) &= e^{hL_A^{NHP}} R(0) \\ &= e^{h \left(\frac{P}{M} \frac{\partial}{\partial R} + F_p \frac{\partial}{\partial P_\eta} \right)} R(0) \ . \end{aligned} \tag{B.8}$$

Since the two terms in the propagator commute, one may simply disregard the $F_p \frac{\partial}{\partial P_\eta}$ term in the above equation, since its action on $R(0)$ is zero. As such Eqn. (B.8) becomes

$$R(h) = e^{h \frac{P}{M} \frac{\partial}{\partial R}} R(0). \tag{B.9}$$

Making use of the mathematical identity given by Eqn. (3.21a) one obtains that

$$R(h) = R(0) + h \frac{P}{M} \ .$$

This translation rule may be expressed in its pseudo code form as

$$R \to R + h \frac{P}{M} \ . \tag{B.10}$$

The second equation may be written as

$$P_\eta(h) = e^{hF_p \frac{\partial}{\partial P_\eta}} P_\eta(0) \ , \tag{B.11}$$

where the $\frac{P}{M} \frac{\partial}{\partial R}$ term has been disregarded. Making use of Eqn. (3.21a) one obtains that

$$P_\eta(h) = P_\eta(0) + hF_p \ . \tag{B.12}$$

This translation rule may be expressed in its pseudo code form as:

$$P_\eta \to P_\eta + hF_p \ . \tag{B.13}$$

Action of $U_B^{NHP}(h)$

The Liouville operator associated with this propagator is

$$L_B^{NHP} = F_R \left[\frac{\partial}{\partial P} + \frac{\tau P}{M} \frac{\partial}{\partial P_\eta} \right] \tag{B.14}$$

This Liouville operator corresponds to a set of two equations of motion. These equations have the formal solution

$$\begin{pmatrix} P(h) \\ P_\eta(h) \end{pmatrix} = U_B(h) \begin{pmatrix} P(0) \\ P_\eta(0) \end{pmatrix} \ . \tag{B.15}$$

The first of these may be explicitly written as

$$\begin{aligned} P(h) &= e^{hL_B^{NHP}} P(0) \\ &= e^{hF_R \left[\frac{\partial}{\partial P} + \frac{\tau P}{M} \frac{\partial}{\partial P_\eta} \right]} P(0) \ . \end{aligned} \tag{B.16}$$

Since the two operators do not commute a slightly different technique is required to obtain the translation rules associated with this propagator. To this end one begins by defining

$$\alpha = F_R \frac{\partial}{\partial P} \ ,$$

and

$$\beta = F_R \frac{\tau P}{M} \frac{\partial}{\partial P_\eta} \ .$$

Making use of the Taylor expansion one obtains

$$P(h) = e^{h(\alpha+\beta)}P(0)$$

$$= [1 + h\alpha + h\beta + \frac{h^2}{2!}\left(\alpha^2 + \alpha\beta + \beta\alpha + \beta^2\right)$$

$$+ \frac{h^3}{3!}\left(\alpha^3 + \alpha^2\beta + \alpha\beta\alpha + \alpha\beta^2 + \beta\alpha^2 + \beta\alpha\beta\right.$$

$$+ \beta^2\alpha + \beta^3 \left.\right) + \ldots]P(0) \ .$$

Eliminating the zero terms this reduces to

$$P(h) = (1 + h\alpha)P(0)$$

$$= P(0) + hF_R \ .$$

This translation rule may be expressed in its pseudo-code form as

$$P \to P + hF_R \ . \tag{B.17}$$

Applying a similar procedure to the second equation, and eliminating the non-zero terms from the subsequent expression one gets that

$$P_\eta(h) = \left(1 + h\beta + \frac{h^2}{2!}(\alpha\beta)\right)P_\eta(0)$$

$$= P_\eta(0) + \frac{h\tau}{M}F_R\left(P + \frac{h}{2}F_R\right)$$

This translation rule may be expressed in its pseudo-code form as

$$P_\eta \to P_\eta + \frac{h\tau}{M}F_R\left(P + \frac{h}{2}F_R\right) \ . \tag{B.18}$$

Action of $U_C^{NHP}(h)$

The Liouville operator associated with this propagator is

$$L_C^{NHP} = \frac{P_\eta}{M_\eta}\left[\tau\frac{P}{M}\frac{\partial}{\partial R} - P\frac{\partial}{\partial P} + \frac{\partial}{\partial \eta}\right] \ , \tag{B.19}$$

This Liouville operator corresponds to a set of two equations of motion. These equations have the formal solution

$$\begin{pmatrix} R\,(h) \\ P\,(h) \\ \eta\,(h) \end{pmatrix} = U_C(h) \begin{pmatrix} R\,(0) \\ P\,(0) \\ \eta\,(0) \end{pmatrix} . \tag{B.20}$$

Since the last term in the Liouville operator commutes with the other two, one may make use of identity given by Eqn. (3.21a) to integrate this equation of motion, in so doing one obtains

$$\eta(h) = \eta(0) + h\frac{P_\eta}{M_\eta} .$$

This translation rule may be expressed in its pseudo-code form as

$$\eta \rightarrow \eta + h\frac{P_\eta}{M_\eta} . \tag{B.21}$$

This leaves one with two equations to integrate, which may be expressed as

$$\begin{pmatrix} R\,(h) \\ P\,(h) \end{pmatrix} = e^{L_C^{NHP'}h} \begin{pmatrix} R\,(0) \\ P\,(0) \end{pmatrix} , \tag{B.22}$$

where,

$$L_C^{NHP'} = \frac{P_\eta}{M_\eta}\left[\tau\frac{P}{M}\frac{\partial}{\partial R} - P\frac{\partial}{\partial P}\right] . \tag{B.23}$$

This new Liouville operator corresponds to a set of two equations of motion. The solution to the first equation may be written out explicitly as

$$R\,(h) = e^{hL^{NHC'}_C}R\,(0)$$
$$= e^{\frac{P_\eta}{M_\eta}\left[\tau\frac{P}{M}\frac{\partial}{\partial R} - P\frac{\partial}{\partial P}\right]}R\,(0) .$$

Since the two terms in the square brackets do not commute one makes use of the Taylor series expansion approach, to integrate the equations of motion. To this end one begins by defining

$$\alpha = \frac{P_\eta}{M_\eta}\tau\frac{P}{M}\frac{\partial}{\partial R} ,$$

and

$$\beta = -\frac{P_\eta}{M_\eta}P\frac{\partial}{\partial P} .$$

Applying the Taylor series expansion, one obtains that,

$$
\begin{aligned}
e^{h(\alpha+\beta)}R\left(0\right) &= \left[1 + h\left(\alpha+\beta\right) + \frac{h^2}{2!}\beta\alpha + \frac{h^3}{3!}\beta^2\alpha + \ldots\right]R\left(0\right) \\
&= \left[1 + h\alpha + \frac{h^2}{2!}\beta\alpha + \frac{h^3}{3!}\beta^2\alpha + \ldots\right]R\left(0\right) \\
&= R\left(0\right) + h\tau\frac{P}{M}\frac{P_\eta}{M_\eta} - \frac{h^2}{2!}\left(\frac{P_\eta}{M_\eta}\right)^2\tau\frac{P}{M} + \frac{h^3}{3!}\left(\frac{P_\eta}{M_\eta}\right)^3\tau\frac{P}{M} + \ldots \\
&= R\left(0\right) + \tau\frac{P}{M}\left[1 - \left(1 - h\frac{P_\eta}{M_\eta} + \frac{h^2}{2!}\left(\frac{P_\eta}{M_\eta}\right)^2 - \frac{h^3}{3!}\left(\frac{P_\eta}{M_\eta}\right)^3 + \ldots\right)\right] \\
&= R\left(0\right) + \tau\frac{P}{M}\left[1 - e^{-h\frac{P_\eta}{M_\eta}}\right] .
\end{aligned}
$$

This translation rule may be expressed in its pseudo-code form as

$$
R \rightarrow R + \frac{\tau P}{M}\left[1 - e^{-h\frac{p_\eta}{M_\eta}}\right] . \tag{B.24}
$$

Following this same procedure on the equation

$$
P(h) = \frac{P_\eta}{M_\eta}\left[\tau\frac{P}{M}\frac{\partial}{\partial R} - P\frac{\partial}{\partial P}\right]P(0) ,
$$

one obtains that

$$
P(h) = P(0)e^{-h\frac{P_\eta}{M_\eta}} .
$$

This translation rule may be expressed in its pseudo-code form as

$$
P \rightarrow Pe^{-h\frac{p_\eta}{M_\eta}} . \tag{B.25}
$$

Appendix C

Time-Reversible Integration of the Nosé-Hoover and Nosé-Hoover Chain Thermostat Schemes

In the main text it has been shown how to obtain time-reversible algorithms, in particular the derivation for the NHP dynamics is given. For completeness the derivations of the time-reversible NH and NHC thermostat schemes which were performed as a part of my study of the theory are presented here.

C.1 Time-Reversible Integration of Nosé-Hoover Dynamics

The first integration scheme presented is based upon the NH dynamics. To achieve this the procedure outlined in section 3.1 was followed. To this end one begins by directly splitting the Liouville operator such that

$$L^{NH} = \sum_n L_n \, . \tag{C.1}$$

To find the L_n terms, one makes use of the Liouville operator definition given by Eqn. (3.4) along with the NH equations of motion given by Eqns. (2.22). From the Liouville operator definition combined, with Eqn. (2.22a) one obtains that

$$\dot{R} = L_1 R$$
$$= \frac{P}{M} \frac{\partial}{\partial R} R \, ,$$

from which it is possible to see that $L_1 = \frac{P}{M}\frac{\partial}{\partial R}$. Following a similar procedure with regards to the other equations which make up the equation set (2.22), one obtains the following set of explicit Liouville operators

$$L_1 = \frac{P}{M}\frac{\partial}{\partial R} , \tag{C.2a}$$

$$L_2 = F_R\frac{\partial}{\partial P} , \tag{C.2b}$$

$$L_3 = -P\frac{P_\eta}{M_\eta}\frac{\partial}{\partial P} , \tag{C.2c}$$

$$L_4 = \frac{P_\eta}{M_\eta}\frac{\partial}{\partial \eta} , \tag{C.2d}$$

$$L_5 = F_P\frac{\partial}{\partial P_\eta} . \tag{C.2e}$$

The forces acting on the system have been defined as

$$F_R = -\frac{\partial V(R)}{\partial R} , \tag{C.3}$$

and

$$F_p = \frac{P^2}{M} - gk_BT . \tag{C.4}$$

Combining commuting Liouville operators, allows one to rewrite this set of Liouville operators as:

$$L_1^{NH} = L_1 , \tag{C.5a}$$

$$L_2^{NH} = L_2 + L_3 , \tag{C.5b}$$

$$L_3^{NH} = L_4 , \tag{C.5c}$$

$$L_4^{NH} = L_5 . \tag{C.5d}$$

If a small time step, h, along with a Liouville Trotter factorisation is considered then one may express the propagator as

$$e^{hL^{NH}} \approx e^{\frac{h}{2}L_4^{NH}}e^{\frac{h}{2}L_3^{NH}}e^{\frac{h}{2}L_2^{NH}}e^{hL_1^{NH}} \times$$
$$e^{\frac{h}{2}L_2^{NH}}e^{\frac{h}{2}L_3^{NH}}e^{\frac{h}{2}L_4^{NH}} . \tag{C.6}$$

A possible integration scheme may be obtained by using the direct translation technique applied to the following propagator

$$U^{NH}(h) = U_4\left(\frac{h}{2}\right) U_3\left(\frac{h}{2}\right) U_2\left(\frac{h}{2}\right) U_1(h)$$
$$\times U_2\left(\frac{h}{2}\right) U_3\left(\frac{h}{2}\right) U_4\left(\frac{h}{2}\right) , \tag{C.7}$$

where $U_\alpha^{NH}(h) = exp\left[hL_\alpha^{NH}\right]$. This leads to the following pseudo-code structure for the NH integration scheme

$$P_\eta \rightarrow P_\eta + \tfrac{h}{2}F_P \ \bigg\} : U_4\left(\frac{h}{2}\right)$$

$$\eta \rightarrow \eta + \tfrac{h}{2}\tfrac{P_\eta}{M_\eta} \ \bigg\} : U_3\left(\frac{h}{2}\right)$$

$$\left.\begin{array}{ccc} P & \rightarrow & P exp\left[-\tfrac{h}{2}\tfrac{P_\eta}{M_\eta}\right] \\ \\ P & \rightarrow & P + \tfrac{h}{2}F_R \end{array}\right\} \ U_2(h)$$

$$R \rightarrow R + h\tfrac{P}{M} \ \Big\} \ U_1(h)$$

$$\text{Calculate } F_R$$

$$\left.\begin{array}{ccc} P & \rightarrow & P exp\left[-\tfrac{h}{2}\tfrac{P_\eta}{M_\eta}\right] \\ \\ P & \rightarrow & P + \tfrac{h}{2}F_R \end{array}\right\} \ U_2(h)$$

$$\text{Calculate } F_P$$

$$\eta \rightarrow \eta + \tfrac{h}{2}\tfrac{P_\eta}{M_\eta} \ \bigg\} : U_3\left(\frac{h}{2}\right)$$

$$P_\eta \rightarrow P_\eta + \tfrac{h}{2}F_P \ \bigg\} : U_4\left(\frac{h}{2}\right)$$

Where the mathematical identities given the equation set (3.21) have been used.

C.2 Time-Reversible Integration of Nosé-Hoover Chain Dynamics

The integration scheme presented here is based on the NHC dynamics. In order to obtain this scheme one follows the procedure outlined in section 3.1 and begins by directly

splitting the Liouville operator such that

$$L^{NHC} = \sum_n L_n \, . \tag{C.8}$$

In order to find the L_n terms, one makes use of the Liouville operator definition given by Eqn. (3.4), along with the NHC equations of motion given by Eqns. (2.26). For the Liouville operator definition combined with Eqn. (2.26a) one obtains that

$$\dot{R} = L_1 R$$
$$= \frac{P}{M} \frac{\partial}{\partial R} R \, ,$$

from which it can clearly be see that $L_1 = \frac{P}{M} \frac{\partial}{\partial R}$. Following a similar procedure with regards to the other equations which make up the equation set (2.26), one obtains the following set of explicit Liouville operators

$$L_1 = \frac{P}{M} \frac{\partial}{\partial R} \tag{C.9a}$$

$$L_2 = \frac{P_{\eta_1}}{M_{\eta_1}} \frac{\partial}{\partial \eta_1} \tag{C.9b}$$

$$L_3 = \frac{P_{\eta_2}}{M_{\eta_2}} \frac{\partial}{\partial \eta_2} \tag{C.9c}$$

$$L_4 = F_R \frac{\partial}{\partial P} \tag{C.9d}$$

$$L_5 = -\frac{P_{\eta_1}}{M_{\eta_1}} P \frac{\partial}{\partial P} \tag{C.9e}$$

$$L_6 = F_p \frac{\partial}{\partial P_{\eta_1}} \tag{C.9f}$$

$$L_7 = -P_{\eta_1} \frac{P_{\eta_2}}{M_{\eta_2}} \frac{\partial}{\partial P_{\eta_1}} \tag{C.9g}$$

$$L_8 = F_{p_{\eta_1}} \frac{\partial}{\partial P_{\eta_2}} \tag{C.9h}$$

Where the forces acting on the system have been defined as

$$F_R = -\frac{\partial V(R)}{\partial R} \, , \tag{C.10}$$

$$F_p = \frac{P^2}{M} - g k_B T \, , \tag{C.11}$$

and

$$F_{p_{\eta_1}} = \frac{P_{\eta_1}^2}{M_{\eta_1}} - g k_B T \, . \tag{C.12}$$

Making use of the fact that one may combine commuting Liouville operators. It then becomes possible to rewrite this set of Liouville operators as:

$$L_1^{NHC} = L_1 + L_2 + L_3 \ , \tag{C.13a}$$

$$L_2^{NHC} = L_4 \ , \tag{C.13b}$$

$$L_3^{NHC} = L_5 \ , \tag{C.13c}$$

$$L_4^{NHC} = L_6 + L_7 \ , \tag{C.13d}$$

$$L_5^{NHC} = L_8 \ . \tag{C.13e}$$

By Considering a small time step, h, along with a Liouville Trotter factorisation one is able to express the propagator as

$$e^{hL^{NHC}} \approx e^{\frac{h}{2}L_5^{NHC}} e^{\frac{h}{2}L_4^{NHC}} e^{\frac{h}{2}L_3^{NHC}} e^{\frac{h}{2}L_2^{NHC}} e^{hL_1^{NHC}} \times$$
$$e^{\frac{h}{2}L_2^{NHC}} e^{\frac{h}{2}L_3^{NHC}} e^{\frac{h}{2}L_4^{NHC}} e^{\frac{h}{2}L_5^{NHC}} \ . \tag{C.14}$$

A possible integration scheme may then be obtained, using the direct translation technique applied to the following propagator,

$$U^{NHC}(h) = U_5\left(\frac{h}{2}\right) U_4\left(\frac{h}{2}\right) U_3\left(\frac{h}{2}\right) U_2\left(\frac{h}{2}\right) U_1(h)$$
$$\times U_2\left(\frac{h}{2}\right) U_3\left(\frac{h}{2}\right) U_4\left(\frac{h}{2}\right) U_5\left(\frac{h}{2}\right) \ , \tag{C.15}$$

where $U_\alpha^{NHC}(h) = exp\left[hL_\alpha^{NHC}\right]$. It then becomes straight forward to obtain the pseudo-code structure for the NHC integration scheme. This may be written as:

$$P_{\eta_2} \quad \rightarrow \quad P_{\eta_2} + \frac{h}{2}F_{P_{\eta_1}} \ \left.\right\} : U_5\left(\frac{h}{2}\right)$$

$$P_{\eta_1} \quad \rightarrow \quad P_{\eta_1} \, exp\left[-\frac{h}{2}\frac{P_{\eta_2}}{M_{\eta_2}}\right] + \frac{h}{2}F_p \, exp\left[-\frac{h}{4}\frac{P_{\eta_2}}{M_{\eta_2}}\right] sinh\left[-\frac{h}{4}\frac{P_{\eta_2}}{M_{\eta_2}}\right] \ \left.\right\} : U_4\left(\frac{h}{2}\right)$$

$$P \quad \rightarrow \quad P \, exp\left[-\frac{h}{2}\frac{P_{\eta_1}}{M_{\eta_1}}\right] \ \left.\right\} U_3\left(\frac{h}{2}\right)$$

$$P \quad \rightarrow \quad P + \frac{h}{2}F_R \ \left.\right\} U_2\left(\frac{h}{2}\right)$$

$$\left.\begin{array}{rcl} R & \rightarrow & R + h\frac{P}{M} \\\\ \eta_1 & \rightarrow & \eta_1 + h\frac{P_{\eta_1}}{M_{\eta_1}} \\\\ \eta_2 & \rightarrow & \eta_2 + h\frac{P_{\eta_1}}{M_{\eta_2}} \end{array}\right\} U_1\left(h\right)$$

Calculate F_R

$$\left.\begin{array}{rcl} P & \rightarrow & P + \frac{h}{2}F_R \end{array}\right\} U_2\left(\frac{h}{2}\right)$$

$$\left.\begin{array}{rcl} P & \rightarrow & P\,exp\left[-\frac{h}{2}\frac{P_{\eta_1}}{M_{\eta_1}}\right] \end{array}\right\} U_3\left(\frac{h}{2}\right)$$

Calculate F_P

$$\left.\begin{array}{rcl} P_{\eta_1} & \rightarrow & P_{\eta_1}\,exp\left[-\frac{h}{2}\frac{P_{\eta_2}}{M_{\eta_2}}\right] + \frac{h}{2}F_p\,exp\left[-\frac{h}{4}\frac{P_{\eta_2}}{M_{\eta_2}}\right]sinh\left[-\frac{h}{4}\frac{P_{\eta_2}}{M_{\eta_2}}\right] \end{array}\right\} : U_4\left(\frac{h}{2}\right)$$

Calculate $F_{P_{\eta_1}}$

$$\left.\begin{array}{rcl} P_{\eta_2} & \rightarrow & P_{\eta_2} + \frac{h}{2} \end{array}\right\} : U_5\left(\frac{h}{2}F_{P_{\eta_1}}\right)$$

Where the mathematical identities given by Eqns. (3.21a) - (3.21c) have been used. The hyperbolic sine function that appears in the above has the potential to be singular. However it has been shown, in [25], that this may be treated via a Maclaurin series taken to some arbitrarily high order without effecting the accuracy.

Appendix D

Measure-Preserving Integration of the Nosé-Hoover and Nosé-Hoover Chain Thermostat Schemes

In the main text it has been shown how to obtain measure-preserving time-reversible algorithms, in particular the derivation for the NHP dynamics is given. For completeness the derivation of the time-reversible measure-preserving NH and NHC thermostat schemes, which was performed as a part of my study of the theory is presented here.

D.1   Measure-Preserving Integration of Nosé-Hoover dynamics

In order to derive a measure preserving integration scheme for the Nosé-Hoover thermostat one begins by splitting the Liouville operator as,

$$L^{NH} = \sum_{\alpha=1}^{4} L_{\alpha}^{NH} \, , \tag{D.1}$$

where each L_{α}^{NH} is defined as,

$$L_{\alpha}^{NH} = \mathcal{B}_{jk}^{NH} \frac{\partial H_{\alpha}^{NH}}{\partial X_k} \frac{\partial}{\partial X_j} \tag{D.2}$$

and preserves the invariant measure of the phase space [9]. H_{α}^{NH} represents the splitting of the NHP Hamiltonian such that $H^{NHP} = \sum_{\alpha=1}^{4} H_{\alpha}^{NH}$. The most natural way to split

the NH Hamiltonian leads to the following components

$$H_1 = \frac{P^2}{2M} \, , \tag{D.3a}$$

$$H_2 = V\left(R\right) \, , \tag{D.3b}$$

$$H_3 = \frac{P_\eta^2}{2M_\eta} \, , \tag{D.3c}$$

$$H_4 = gk_bT\eta \, . \tag{D.3d}$$

Making use of Eqn. (D.1), along with Eqns. (D.3a)-(D.3d) one obtains the following explicit form of the Liouville operators:

$$L_1^{NH} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{P^2}{M}\frac{\partial}{\partial P_\eta} \tag{D.4a}$$

$$L_2^{NH} = -\frac{\partial V\left(R\right)}{\partial R}\frac{\partial}{\partial P} \tag{D.4b}$$

$$L_3^{NH} = \frac{P_\eta}{M_\eta}\left[\frac{\partial}{\partial \eta} + P\frac{\partial}{\partial P}\right] \tag{D.4c}$$

$$L_4^{NH} = -gk_BT\frac{\partial}{\partial P_\eta} \, . \tag{D.4d}$$

For convenience, these may be defined as

$$L_A^{NH} = L_2^{NH} \tag{D.5a}$$

$$L_B^{NH} = L_1^{NH} + L_4^{NH} \tag{D.5b}$$

$$L_C^{NH} = L_3^{NH} \, , \tag{D.5c}$$

where the combined commuting Liouville operators have been added to obtain L_B^{NH} along with renaming L_2 and L_3 to keep the notation consistent. The propagator associated with the nth Liouville operator, L_n^{NH}, is defined as

$$U_\alpha^{NH}\left(h\right) = exp\left[hL_\alpha^{NH}\right] \, ,$$

where $\alpha = A, B, C$ and h represents a single numerical time step. A possible measure-preserving time-integration scheme for the NHP dynamics may then be obtained through

the use of the Trotter factorisation, and may be approximated by the propagator

$$U^{NH}\left(h\right) = U_B^{NH}\left(h/4\right) U_C^{NH}\left(h/2\right) U_B^{NH}\left(h/4\right) U_A^{NH}\left(h\right)$$

$$\times\, U_B^{NH}\left(h/4\right) U_C^{NH}\left(h/2\right) U_B^{NH}\left(h/4\right)\;. \tag{D.6}$$

By using the direct translation technique to evaluate the action of this propagator one obtains the following pseudo-code structure:

$$\left.\begin{array}{ll} R & \to R + \frac{h}{4}\frac{P}{M} \\ P_\eta & \to P_\eta + \frac{h}{4}F_P \end{array}\right\} : U_B\left(h/4\right), \tag{D.7}$$

$$\left.\begin{array}{ll} P & \to P \,\exp\left[-\frac{h}{2}\frac{P_\eta}{M_\eta}\right] \\ \eta & \to \eta + \frac{h}{2}\frac{P_\eta}{M_\eta} \end{array}\right\} : U_C\left(h/2\right), \tag{D.8}$$

$$\left.\begin{array}{ll} R & \to R + \frac{h}{4}\frac{P}{M} \\ P_\eta & \to P_\eta + \frac{h}{4}F_P \end{array}\right\} : U_B\left(h/4\right), \tag{D.9}$$

$$\left.\begin{array}{ll} P & \to\; P + hF_R \end{array}\right\} : U_A\left(h\right), \tag{D.10}$$

$$\left.\begin{array}{ll} R & \to R + \frac{h}{4}\frac{P}{M} \\ P_\eta & \to P_\eta + \frac{h}{4}F_P \end{array}\right\} : U_B\left(h/4\right), \tag{D.11}$$

$$\left.\begin{array}{ll} P & \to P \,\exp\left[-\frac{h}{2}\frac{P_\eta}{M_\eta}\right] \\ \eta & \to \eta + \frac{h}{2}\frac{P_\eta}{M_\eta} \end{array}\right\} : U_C\left(h/2\right), \tag{D.12}$$

$$\left.\begin{array}{ll} R & \to R + \frac{h}{4}\frac{P}{M} \\ P_\eta & \to P_\eta + \frac{h}{4}F_P \end{array}\right\} : U_B\left(h/4\right), \tag{D.13}$$

Where the forces acting on the system have been defined as

$$F_R = -\frac{\partial V\left(R\right)}{\partial R}\,, \tag{D.14}$$

and

$$F_p = \frac{P^2}{M} - gk_BT\,, \tag{D.15}$$

along with making use of the identities defined in the equation set (3.21).

D.2 Measure Preserving Integration of Nosé-Hoover Chain dynamics

In order to derive a measure preserving NHC integration scheme, one begins by directly splitting the Liouville operator such that

$$L^{NHC} = \sum_{\alpha=1}^{6} L_\alpha^{NHC} \ , \tag{D.16}$$

where each L_α^{NHC} is defined as,

$$L_\alpha^{NHC} = \mathcal{B}_{jk}^{NHC} \frac{\partial H_\alpha^{NHC}}{\partial X_k} \frac{\partial}{\partial X_j} \ . \tag{D.17}$$

H_α^{NHC} represents the split NHC Hamiltonian terms, such that $H^{NHC} = \sum_{\alpha=1}^{6} H_\alpha$, these components may be explicitly written as,

$$H_1 = \frac{P^2}{2M} \ , \tag{D.18a}$$

$$H_2 = \frac{P_{\eta_1}^2}{2M_{\eta_1}} \ , \tag{D.18b}$$

$$H_3 = \frac{P_{\eta_2}^2}{2M_{\eta_2}} \ , \tag{D.18c}$$

$$H_4 = V(R) \ , \tag{D.18d}$$

$$H_5 = gk_bT\eta_1 \ , \tag{D.18e}$$

$$H_6 = gk_bT\eta_2 \ . \tag{D.18f}$$

Combining Eqns. (D.16) and (D.18) allows us to obtain the following explicit forms of the Liouville operators:

$$L_1^{NHC} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{P^2}{M}\frac{\partial}{\partial P_{\eta_1}} \,, \tag{D.19a}$$

$$L_2^{NHC} = \frac{P_{\eta_1}}{M_{\eta_1}}\frac{\partial}{\partial \eta_1} - P\frac{P_{\eta_1}}{M_{\eta_1}}\frac{\partial}{\partial P} + \frac{P_{\eta_1}^2}{M_{\eta_1}}\frac{\partial}{\partial P_{\eta_2}} \,, \tag{D.19b}$$

$$L_3^{NHC} = \frac{P_{\eta_2}}{M_{\eta_2}}\frac{\partial}{\partial \eta_2} - P_{\eta_1}\frac{P_{\eta_2}}{M_{\eta_2}}\frac{\partial}{\partial P_{\eta_1}} \,, \tag{D.19c}$$

$$L_4^{NHC} = F_R\frac{\partial}{\partial P} \,, \tag{D.19d}$$

$$L_5^{NHC} = -gk_bT\frac{\partial}{\partial P_{\eta_1}} \,, \tag{D.19e}$$

$$L_6^{NHC} = -gk_bT\frac{\partial}{\partial P_{\eta_2}} \,. \tag{D.19f}$$

In order to derive a more efficient algorithm, one combines the Liouville operators which commute, thereby obtaining the following set of Liouville operators which are associated with the NHC thermostat:

$$L_A^{NHC} = L_4^{NHC} + L_3^{NHC} \,, \tag{D.20a}$$

$$L_B^{NHC} = L_1^{NHC} + L_5^{NHC} \,, \tag{D.20b}$$

$$L_C^{NHC} = L_2^{NHC} + L_6^{NHC} \,. \tag{D.20c}$$

If a small time step, h, is considered along with a direct Trotter factorisation one obtains:

$$e^{hL^{NHC}} \approx e^{\frac{h}{4}L_B^{NHC}} e^{\frac{h}{2}L_C^{NHC}} e^{\frac{h}{4}L_B^{NHC}} e^{hL_A^{NHC}} \times$$
$$e^{\frac{h}{4}L_B^{NHC}} e^{\frac{h}{2}L_C^{NHC}} e^{\frac{h}{4}L_B^{NHC}} \,. \tag{D.21}$$

Defining the propagator associated with the nth Liouville operator L_n^{NHC} as

$$U_\alpha^{NHC}(h) = exp\left[hL_\alpha^{NHC}\right] \tag{D.22}$$

where $\alpha = A, B, C$. A possible measure-preserving time-reversible integration scheme for the NHC dynamics may then be obtained through the use of the symmetric Trotter

factorisation, and may be approximated by the propagator

$$U^{NHC}(h) = U_B^{NHC}\left(\frac{h}{4}\right) U_C^{NHC}\left(\frac{h}{2}\right) U_B^{NHC}\left(\frac{h}{4}\right) U_A^{NHC}(h)$$
$$\times U_B^{NHC}\left(\frac{h}{4}\right) U_C^{NHC}\left(\frac{h}{2}\right) U_B^{NHC}\left(\frac{h}{4}\right). \tag{D.23}$$

Making use of the direct translation technique to evaluate the action of this propagator leads to the following pseudo-code structure:

$$\left.\begin{array}{rcl} R & \to & R + \frac{h}{4}\frac{P}{M} \\[2ex] P_{\eta_1} & \to & P_{\eta_1} + \frac{h}{4}F_p \end{array}\right\} : U_B\left(\frac{h}{4}\right), \tag{D.24}$$

Calculate $F_{P_{\eta_1}}$

$$\left.\begin{array}{rcl} \eta_1 & \to & \eta_1 + \frac{h}{2}\frac{P_{\eta_1}}{M_{\eta_1}} \\[2ex] P & \to & P\,exp\left[-\frac{h}{2}\frac{P_{\eta_1}}{M_{\eta_1}}\right] \\[2ex] P_{\eta_2} & \to & P_{\eta_2} + \frac{h}{2}F_{p_{\eta_1}} \end{array}\right\} : U_C\left(\frac{h}{2}\right) \tag{D.25}$$

Calculate F_p

$$\left.\begin{array}{rcl} R & \to & R + \frac{h}{4}\frac{P}{M} \\[2ex] P_{\eta_1} & \to & P_{\eta_1} + \frac{h}{4}F_p \end{array}\right\} : U_B\left(\frac{h}{4}\right) \tag{D.26}$$

Calculate F_R

$$\left.\begin{array}{rcl} P & \to & P + hF_R \\[2ex] \eta_2 & \to & \eta_2 + h\frac{P_{\eta_2}}{M_{\eta_2}} \\[2ex] P_{\eta_1} & \to & P_{\eta_1}\,exp\left[-h\frac{P_{\eta_2}}{M_{\eta_2}}\right] \end{array}\right\} : U_A(h) \tag{D.27}$$

Calculate F_p

$$\left.\begin{array}{rcl} R & \to & R + \frac{h}{4}\frac{P}{M} \\[2ex] P_{\eta_1} & \to & P_{\eta_1} + \frac{h}{4}F_p \end{array}\right\} : U_B\left(\frac{h}{4}\right), \tag{D.28}$$

$$\text{Calculate } F_{P_{\eta_1}}$$

$$\left.\begin{array}{rcl} \eta_1 & \rightarrow & \eta_1 + \frac{h}{2}\frac{P_{\eta_1}}{M_{\eta_1}} \\[2em] P & \rightarrow & P exp\left[-\frac{h}{2}\frac{P_{\eta_1}}{M_{\eta_1}}\right] \\[2em] P_{\eta_2} & \rightarrow & P_{\eta_2} + \frac{h}{2}F_{p_{\eta_1}} \end{array}\right\} : U_C\left(\frac{h}{2}\right) \qquad (D.29)$$

$$\text{Calculate } F_p$$

$$\left.\begin{array}{rcl} R & \rightarrow & R + \frac{h}{4}\frac{P}{M} \\[2em] P_{\eta_1} & \rightarrow & P_{\eta_1} + \frac{h}{4}F_p \end{array}\right\} : U_B\left(\frac{h}{4}\right) \qquad (D.30)$$

Where the forces acting on the system have been defined as

$$F_R = -\frac{\partial V(R)}{\partial R} , \qquad (D.31)$$

$$F_p = \frac{P^2}{M} - gk_BT , \qquad (D.32)$$

and

$$F_{p_{\eta_1}} = \frac{P_{\eta_1}^2}{M_{\eta_1}} - gk_BT . \qquad (D.33)$$

along with making use of the identities defined in the equation set (3.21).

Appendix E

Representation of the 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:

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

Expand the first term on the right hand side

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

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

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

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

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

Using the completness relation, this becomes

$$\left\langle\alpha\left|\left\{\hat{H}_W, \hat{\chi}_W\right\}\right|\alpha'\right\rangle = \left\langle\alpha\left|\frac{\partial\hat{H}_W}{\partial R}\sum_\beta|\beta\rangle\langle\beta|\frac{\partial\hat{\chi}_W}{\partial P}\right|\alpha'\right\rangle - \left\langle\alpha\left|\frac{\partial\hat{H}_W}{\partial P}\sum_\beta|\beta\rangle\langle\beta|\frac{\partial\hat{\chi}_W}{\partial R}\right|\alpha'\right\rangle$$

$$= -\sum_\beta F_W^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P} - \sum_\beta\frac{P}{M}\delta_{\alpha\beta}\left\langle\beta\left|\frac{\partial\hat{\chi}_W}{\partial R}\right|\alpha'\right\rangle , \qquad (E.5)$$

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 [4] $F_W^{\alpha\beta} = -\left\langle\alpha\left|\frac{\partial\hat{V}_W}{\partial R}\right|\beta\right\rangle$. The third term in Eqn. (E.1) can be similarly expanded to get

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

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

$$\frac{\partial\chi_W^{\alpha\alpha'}}{\partial t} = i\omega_{\alpha\alpha'}\chi_W^{\alpha\alpha'} + \frac{1}{2}\left(\sum_\beta F_W^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P} + \sum_{\beta'}\frac{\partial\chi_W^{\alpha\beta'}}{\partial P}F_W^{\beta'\alpha'}\right)$$

$$+ \frac{1}{2}\left(\sum_\beta\frac{P}{M}\delta_{\alpha\beta}\left\langle\beta\left|\frac{\partial\hat{\chi}_W}{\partial R}\right|\alpha'\right\rangle + \sum_{\beta'}\left\langle\alpha\left|\frac{\partial\hat{\chi}_W}{\partial R}\right|\beta'\right\rangle\frac{P}{M}\delta_{\beta'\alpha'}\right) . $$

$$(E.7)$$

The quantum-classical Liouville equation may thus be written as

$$\frac{\partial\chi_W^{\alpha\alpha'}}{\partial t} = i\omega_{\alpha\alpha'}\chi_W^{\alpha\alpha'} + \frac{1}{2}\left(\sum_\beta F_W^{\alpha\beta}\frac{\partial\chi_W^{\beta\alpha'}}{\partial P} + \sum_{\beta'}\frac{\partial\chi_W^{\alpha\beta'}}{\partial P}F_W^{\beta'\alpha'}\right)$$

$$+ \frac{P}{M}\left\langle\alpha\left|\frac{\partial\chi_W}{\partial R}\right|\alpha'\right\rangle . \qquad (E.8)$$

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 $|\alpha\rangle$. In order to find a way to express the last term in a more suitable form one starts by considering $\frac{\partial}{\partial R}\chi_W^{\alpha\alpha'}$

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

where the completness relation has once again been used. By definition [4], $d_{\beta'\alpha'} = \left\langle \beta' \,\middle|\, \frac{\partial}{\partial R} \,\middle|\, \alpha'\right\rangle$. It is possible to simplify $\left\langle \frac{\partial\alpha}{\partial R} \,\middle|\, \beta\right\rangle$ by considering the following

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

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

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

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

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

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

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

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

In writing Eqn. (E.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. (4.36). In order to accomplish this one adds and subtracts the term [7],

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

to the Liouville super-operator. This term involves the average of the Hellman-Feynman forces for two states α and α' [4]. Performing this addition and subtraction, gives us

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

The classical Liouville operator is defined as [13]

$$
iL_{\alpha\alpha'} = \frac{P}{M} \frac{\partial}{\partial R} + \frac{1}{2} \left(F_W^\alpha + F_W^{\alpha'} \right) \frac{\partial}{\partial P} \; , \tag{E.16}
$$

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

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

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. (4.39)

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

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

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

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

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

By defining

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

and making use of the relation [4, 7]

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

one obtains that

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

Similarly one may also define

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

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

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

which is the form of the jump operator given in Eqn. (4.39) .

Appendix F

Representing the Nosé-Hoover Power Thermostat's Quantum-Classical Liouville Super-Operator in the Adiabatic Basis

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

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

Expand the first term on the right hand side

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

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

$$\frac{i}{\hbar} \left(\langle\alpha|\hat{H}_W \hat{\chi}_W |\alpha'\rangle - \langle\alpha|\hat{\chi}_W \hat{H}_W |\alpha'\rangle \right) = \frac{i}{\hbar} \left(E_\alpha \langle\alpha|\hat{\chi}_W|\alpha'\rangle - E_{\alpha'} \langle\alpha|\hat{\chi}_W|\alpha'\rangle \right)$$

$$= i\omega_{\alpha\alpha'} \chi_W^{\alpha\alpha'} \, , \tag{F.3}$$

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:

$$-\frac{1}{2} \left\langle \alpha \left| \frac{\partial \hat{V}_W}{\partial R} \frac{\partial \hat{\chi}_W}{\partial P} \right| \alpha' \right\rangle = -\frac{1}{2} \sum_\beta \left\langle \alpha \left| \frac{\partial \hat{V}_W}{\partial R} \right| \beta \right\rangle \langle\beta| \frac{\partial \hat{\chi}_W}{\partial P} |\alpha'\rangle$$

$$= \frac{1}{2} \sum_\beta F^{\alpha\beta} \frac{\partial \chi_W^{\beta\alpha'}}{\partial P} \, , \tag{F.4}$$

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

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

The next term may be expanded to obtain

$$\left\langle \alpha \left| F_p \frac{\partial \hat{\chi}_W}{\partial P_\eta} \right| \alpha' \right\rangle = F_p \frac{\partial}{\partial P_\eta} \langle\alpha|\hat{\chi}_W|\alpha'\rangle$$

$$= F_p \frac{\partial \chi_W^{\alpha\alpha'}}{\partial P_\eta} \, , \tag{F.6}$$

while

$$-\frac{1}{2} \left\langle \alpha \left| \frac{\partial \hat{V}_W}{\partial R} \frac{\tau P}{M} \frac{\partial \hat{\chi}_W}{\partial P_\eta} \right| \alpha' \right\rangle = -\frac{1}{2} \frac{\tau P}{M} \left\langle \alpha \left| \frac{\partial \hat{V}_W}{\partial R} \frac{\partial \hat{\chi}_W}{\partial P_\eta} \right| \alpha' \right\rangle$$

$$= \frac{\tau P}{2M} \sum_\beta F^{\alpha\beta} \frac{\partial \chi_W^{\beta\alpha'}}{\partial P_\eta} \, . \tag{F.7}$$

Similarity

$$-\frac{1}{2}\left\langle\alpha\left|\frac{\partial\hat{\chi}_W}{\partial P_\eta}\frac{\tau P}{M}\frac{\partial\hat{V}_W}{\partial R}\right|\alpha'\right\rangle=-\frac{1}{2}\frac{\tau P}{M}\left\langle\alpha\left|\frac{\partial\hat{\chi}_W}{\partial P_\eta}\frac{\partial\hat{V}_W}{\partial R}\right|\alpha'\right\rangle$$

$$=\frac{\tau P}{2M}\sum_\beta\frac{\partial\chi_W^{\alpha\beta}}{\partial P_\eta}F^{\beta\alpha'}\;. \tag{F.8}$$

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 $|\alpha'\rangle$. In order to express this term in a more suitable form one first considers

$$\frac{\partial}{\partial R}\left\langle\alpha\left|\hat{\chi}_W\right|\alpha'\right\rangle=\left\langle\frac{\partial\alpha}{\partial R}\left|\hat{\chi}_W\right|\alpha'\right\rangle+\left\langle\alpha\left|\frac{\partial\hat{\chi}_W}{\partial R}\right|\alpha'\right\rangle+\left\langle\alpha\left|\hat{\chi}_W\right|\frac{\partial\alpha'}{\partial R}\right\rangle$$

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

where the completeness relation has again been used. By definition the non-adiabatic coupling matrix element may be expressed as $d_{\beta\alpha'}=\left\langle\beta\left|\frac{\partial}{\partial R}\right|\alpha'\right\rangle=\left\langle\beta\left|\frac{\partial\alpha'}{\partial R}\right\rangle$ [4, 7]. In order to find simplify $\left\langle\frac{\partial\alpha}{\partial R}\big|\beta\right\rangle$ one considers the following

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

using the orthonormal condition produces the identity

$$\left\langle\frac{\partial\alpha}{\partial R}\bigg|\beta\right\rangle=-\left\langle\alpha\left|\frac{\partial\beta}{\partial R}\right\rangle$$

$$=-d_{\alpha\beta}\;.$$

As such

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

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

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

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

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

The second to last term may be expanded to obtain

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

while the final term produces

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

As such the equation of motion may thus be expressed as

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

Making use of Liouville operators defined in the equation set (3.51) the above equation may be written as

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

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

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

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 E to obtain the J-operator into its traditional form. Doing this allows one to express the Liouville super-operator as

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

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 [13].

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