Quantum Statistical Mechanics. II. Stochastic Schrödinger Equation

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Abstract

The stochastic dissipative Schrödinger equation is derived for an open quantum system consisting of a sub-system able to exchange energy with a thermal reservoir. The resultant evolution of the wave function also gives the evolution of the density matrix, which is an explicit, stochastic form of the Lindblad master equation. A quantum fluctuation-dissipation theorem is also derived. The time correlation function is discussed.

1 Introduction

Quantum mechanics is often portrayed as synonymous with randomness and unpredictability, as opposed to the deterministic nature of the classical world. However this distinction is overly simplistic since Schrödinger's equation is completely deterministic and it gives the evolution of the wave function of an isolated system with complete certainty. Conversely the classical evolution of a sub-system that can exchange energy with a thermal reservoir has a random character such that the future can only be predicted from the present state of the sub-system with statistical probability rather than deterministic certainty.[1,2] In this latter case Hamilton's equations of motion for the isolated system must be augmented with dissipative and stochastic terms that arise from the probabilistic treatment of the reservoir.[2,3] This raises the question of whether one might similarly modify Schrödinger's equation in the quantum case in order to incorporate the reservoir or the environment probabilistically.

The main result obtained in the present paper is the stochastic dissipative Schrödinger equation for a sub-system able to exchange energy with a thermal reservoir. This is a direct analogue of the stochastic dissipative Hamilton's equation that has recently been derived for classical equilibrium statistical mechanics.[2,3] The stochastic dissipative Schrödinger equation derived here provides a new way to treat equilibrium quantum systems. One possible application is as a thermostat for computer simulation algorithms for quantum statistical mechanics. In addition, since it gives the evolution of an open quantum system, it will likely play a role in the development of a theory for non-equilibrium quantum statistical mechanics.

The origin of the stochastic Schrödinger equation in the present formulation

of quantum statistical mechanics differs from the literature (e.g. Refs [4?10]). Also called Belavkin equations, stochastic Schrödinger equations conventionally describe the evolution of the quantum state of a continuously measured system. In this interpretation, the stochastic character of the quantum trajectories result from the measurement process.

A second, related field of study concerns quantum dissipative systems, which modify the Schrödinger equation with Langevin-type dissipative and fluctuation terms.[11,12] This approach is related to that taken here in that it deals with an open quantum system with the extra terms accounting for the interactions with the reservoir beyond the sub-system of direct interest. In the literature one finds three main approaches:[12] modification of the procedure of quantization, such as using complex variables, or a non-linear Schrödinger equation,[13-16] the postulation of a heuristic stochastic form of the Schrödinger equation,[6,11,17,18] and the projection from the reservoir onto the sub-system of the density matrix,1[9,20] or operator.[21,22] In the projection category one can note the quantum Langevin equation,[23,24] which can be derived from an harmonic oscillator bath with linear coupling, the so-called Caldeira-Leggett model.[25]

The stochastic Schrödinger equation developed here also arises from the projection of the reservoir onto the sub-system. Here the emphasis on the statistical origin of the equation and the exact symmetry requirements that the equation must obey. The derivation follows closely that given in the classical case of the stochastic Hamilton's equations of motion.[2,3] The present equation allows the computation of the time evolution of the wave function of a sub-system of a thermal reservoir, with the reservoir accounted for in a macroscopic probabilistic sense rather than in a molecular mechanical sense. The stochastic and deterministic terms that arise are shown to be related by a quantum fluctuation-dissipation theorem.

2 Static Properties

2.1 Background

In Paper I,[26] two results were established that provide the starting point for the present paper. For a canonical equilibrium system (i.e., a sub-system that can exchange energy with a thermal reservoir of temperature T), it was

shown that the probability operator had Maxwell-Boltzmann form

$$\hat{\wp} = \frac{1}{Z(T)} e^{-\hat{\mathcal{H}}/k_B T} \tag{2.1}$$

Here $\hat{\mathcal{H}}$ is the Hamiltonian or energy operator of the sub-system and k_B is Boltzmann's constant. This result is the same as the conventional expression that is postulated for the canonical quantum probability operator.[27-30]

For future reference the entropy operator is $\hat{S} = -\hat{\mathcal{H}}/T$. The normalized energy eigenfunctions ζ_n^E, $\hat{\mathcal{H}}\,|\zeta_n^E\rangle = E_n\,|\zeta_n^E\rangle$, are also entropy eigenfunctions, $\zeta_n^S = \zeta_n^E$, $\hat{S}\,|\zeta_n^S\rangle = S_n\,|\zeta_n^S\rangle$, with $S_n \equiv S_{nn}^S = -E_n/T$. Here the degeneracy is not shown explicitly.

The second result invoked here from Paper I[26] is that the statistical average of an operator has the conventional von Neumann form,[27-30]

$$\langle \hat{O} \rangle_{stat} = \mathrm{Tr}\hat{\wp}\hat{O} \tag{2.2}$$

It is worth reiterating that these two results followed from the conservation law for energy, which implied that the sub-system wave function and the reservoir wave function are entangled.[26] This in turn implied that the principle energy quantum states collapsed. The degenerate reservoir energy quantum states were shown to sum to give the Maxwell-Boltzmann form for the probability operator. Whilst superposition states with a given energy can be composed from the degenerate sub-system energy quantum states, it was shown that these cancel and that there is no contribution to the statistical average of an operator from the non-diagonal terms in the energy representation. Since the statistical average contains only diagonal terms in either the energy or the operator representation, it may be interpreted as resulting from the collapse of the wave function (c.f., Eqs (2.6) and (2.7) below).

The primary goal of this paper is to derive a stochastic dissipative form of the Schrödinger equation that represents the evolution of the wave function of the sub-system in the presence of the reservoir. Accordingly an expression will be required for the average of an operator that invokes the resultant wave function and its trajectory. The focus therefore is not so much on pure quantum states, as in the von Neumann expression, Eq. (2.2), but in expressing the average as an expectation value of a wave function state. The

two approaches of course have to be consistent.

Toward this end, and to illustrate the underlying philosophy of the present approach, it is now shown that the von Neumann statistical average, Eq. (2.2), can be written as an integral of an expectation value over wave space. Making an expansion in entropy eigenfunctions, one has

$$\begin{aligned}
\int d\psi \, \frac{\langle\psi|\hat{\wp}\hat{O}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} &= \int d\underline{\psi}^S \frac{1}{N(\psi)} \sum_{lmn} \psi_l^{S*}\psi_n^S \wp_{lm}^S O_{mn}^S \\
&= \sum_{mn} \wp_{mm}^S O_{mn}^S \int d\underline{\psi}^S \frac{1}{N(\psi)} \psi_m^{S*}\psi_n^S \\
&= \sum_{n} \wp_{nn}^S O_{nn}^S \int d\underline{\psi}^S \frac{1}{N(\psi)} \psi_n^{S*}\psi_n^S \\
&= \text{constant} \sum_{mn} \wp_{mn}^S O_{nm}^S \\
&= \text{Tr}\,\hat{\wp}\hat{O}
\end{aligned} \tag{2.3}$$

The third equality follows because the integrand for the terms $m \neq n$ is odd, and so they vanish upon integration. The fourth equality follows because the value of the integral does not depend upon n, and because $\wp_{mn}^S = \wp_{nn}^S \delta_{mn}$. The constant is incorporated into the normalization factor.

Continuing the focus on wave space, one can explore the possible utility of a probability density. For the present canonical equilibrium case, for which the Maxwell-Boltzmann distribution holds, there are two plausible definitions namely

$$\wp(\psi) = \frac{1}{Z(T)} \frac{\langle\psi|\, e^{-\hat{\mathcal{H}}/k_B T}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \tag{2.4}$$

or

$$\wp(\psi) = \frac{1}{Z(T)} e^{-E(\psi)/k_B T} \;,\; E(\psi) = \frac{\langle\psi|\,\hat{\mathcal{H}}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \tag{2.5}$$

However, such a probability density does not give the statistical average of an operator,

$$\langle\hat{O}\rangle_{stat} \neq \int d\psi \, \wp(\psi) O(\psi) \tag{2.6}$$

where the expectation value of the operator is $O(\psi) = \langle\psi|\,\hat{O}\,|\psi\rangle \,/\, \langle\psi\,|\,\psi\rangle$. The reason that this fails is that this expression always contains contributions from the superposition states and never reduces to a sum over pure quantum

states of either the observable operator or of the entropy operator.

However, the collapse of the wave function into entropy eigenstates yields

$$\begin{aligned}\langle\hat{O}\rangle_{stat} &= \int_{coll.} d\psi\, \wp(\psi) O(\psi) \\ &= \sum_n \wp(\zeta_n^S) O(\zeta_n^S) \\ &= \frac{1}{Z(T)} \sum_n e^{-E_n/k_B T} O_{nn}^S \\ &= \mathrm{Tr}\hat{\wp}\hat{O} \end{aligned} \tag{2.7}$$

For a pure energy state (equivalently pure entropy state), the two definitions of the probability density are equal.

In order give some indication of the direction in which the present paper is heading, the relationship between these expressions for the statistical average and the one obtained in the text below is now discussed. Suppose that $\psi(t)$ is a stochastic trajectory that has been generated such that the time average (equivalently stochastic average, or statistical average) of the density operator formed from it equals the canonical equilibrium probability operator,

$$\hat{\wp} = \frac{1}{t} \int_0^t dt' \, \frac{1}{N(\psi(t'))} \, |\psi(t')\rangle \langle\psi(t')| \tag{2.8}$$

Here and below, $N \equiv \langle\psi\,|\,\psi\rangle$ is the norm of the wave function. In this case the canonical equilibrium statistical average can be written as a time average of the expectation value,

$$\begin{aligned}\langle\hat{O}\rangle_{stat} &= \mathrm{Tr}\hat{\wp}\hat{O} \\ &= \sum_{mn} \langle\zeta_m|\,\hat{\wp}\,|\zeta_n\rangle \langle\zeta_n|\,\hat{O}\,|\zeta_m\rangle \\ &= \frac{1}{t} \int_0^t dt' \, \sum_{mn} \frac{\langle\zeta_m\,|\,\psi(t')\rangle \langle\psi(t')\,|\,\zeta_n\rangle \, O_{nm}}{N(\psi(t'))} \\ &= \frac{1}{t} \int_0^t dt' \, \sum_{mn} \frac{\psi_m(t')\psi_n(t')^* O_{nm}}{N(\psi(t'))} \\ &= \frac{1}{t} \int_0^t dt' \, \frac{\langle\psi(t')|\,\hat{O}\,|\psi(t')\rangle}{\langle\psi(t')\,|\,\psi(t')\rangle} \end{aligned} \tag{2.9}$$

The final equality has the appearance that superposition states contribute to the average, but the first equality makes it clear that these must average to zero.

A direct consequence of the density matrix averaged over the stochastic trajectory equalling the probability operator, Eq. (2.8), is that different entropy modes are uncorrelated,

$$\frac{1}{t}\int_0^t dt' \, \frac{\psi_m^S(t')\psi_n^S(t')^*}{N(\psi(t'))} = \delta_{mn}\wp_{mm}^S \tag{2.10}$$

This reduces the average to a single sum in the entropy basis, as it must.

2.2 First Entropy

2.2.1 Definition

In the classical case, the exponential of the entropy is essentially the probability.[1,2] A similar definition may be invoked in the quantum case for the entropy operator,

$$\hat{\wp} = \frac{1}{Z}e^{\hat{S}/k_B} \tag{2.11}$$

where k_B is Boltzmann's constant. In view of the form of the Maxwell-Boltzmann probability operator, Eq. (2.1), one can identify the entropy operator for the canonical equilibrium system as

$$\hat{S} = -\frac{1}{T}\hat{\mathcal{H}} \tag{2.12}$$

The expectation value of this is the reservoir entropy,

$$\begin{aligned} S_r(\psi) &= \frac{\langle\psi|\,\hat{S}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \\ &= -\frac{1}{T}\frac{\langle\psi|\,\hat{\mathcal{H}}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \\ &= -\frac{1}{T}\frac{\underline{\underline{\mathcal{H}}} : \underline{\psi\psi}^*}{\underline{\psi\psi}^*} \end{aligned} \tag{2.13}$$

The absence of superscripts, as in the final equality, indicate that the basis is arbitrary. This gives the reservoir entropy for the given wave state of the

sub-system. This is the same as the total entropy, $S_{tot}(\psi) \equiv S_r(\psi) + S_s(\psi) = S_r(\psi)$, since the sub-system entropy of a wave state vanishes (see Appendix B of Ref. 26). Because the total entropy and the reservoir entropy for a sub-system wave state are equal, the subscript will usually be dropped below.

2.2.2 Most Likely Wave Function

The total entropy is now maximized to obtain the most likely wave function. The gradient is $\nabla \equiv \{\underline{\partial}_{\psi}, \underline{\partial}_{\psi^*}\}$. The gradient of the entropy is

$$\nabla S(\psi) = -\frac{1}{TN(\psi)}\{\underline{\underline{\mathcal{H}}} \cdot \underline{\psi}^* - E(\psi)\underline{\psi}^*, \underline{\underline{\mathcal{H}}} \cdot \underline{\psi} - E(\psi)\underline{\psi}\} \tag{2.14}$$

One gets the same result if one takes the gradient parallel to the hypersurface of constant norm of the entropy with the norm fixed. The two terms in the braces are the complex conjugate of each other. The first term represents the components of the gradient in the direction $\underline{\psi}$, and the second term represents the components in the direction $\underline{\psi}^*$.

The sub-system wave function that maximizes the total entropy (sub-system plus reservoir), $\overline{\psi}$, is given by the vanishing of this gradient. Clearly this is an eigenfunction of the Hamiltonian,

$$\underline{\underline{\mathcal{H}}} \cdot \underline{\overline{\psi}} = E(\overline{\psi})\underline{\overline{\psi}} \tag{2.15}$$

This holds equally for the complex conjugate. The overline denotes the most likely wave function. This result only depends upon the isolated sub-system and not upon the temperature of the reservoir.

The energy eigenvalues are given by the solutions to the characteristic equation,

$$\mathrm{Det}\{\underline{\underline{\mathcal{H}}} - E\underline{\underline{I}}\} = 0 \tag{2.16}$$

The matrix inside the braces is real and symmetric. There are presumably a countably infinite number of solutions to this, $E_n, n = 0, 1, ...$ The quantum states may be ordered in terms of increasing energy, as usual. For a given energy eigenvalue, an eigenfunction $\underline{\zeta}^E_{ng}, g = 1, 2, ..., G_n$ satisfies the eigenfunction equation $\underline{\underline{\mathcal{H}}} \cdot \underline{\zeta}^E_{ng} = E_n \underline{\zeta}^E_{ng}$, and hence it also satisfies $E(\zeta^E_{ng}) = E_n$. For simplicity, below the degeneracy label g will often not be shown. The chosen energy level will be written $E_0 \equiv E(\overline{\psi})$, even though the formal analysis is

not restricted to the ground state. Obviously if $\underline{\psi}$ is an eigenfunction, then so is its conjugate $\underline{\psi}^*$. Without loss of generality, the most likely wave function may be taken to be normalized $\overline{N} = N(\overline{\psi}) = 1$.

It is important to appreciate the difference between the most likely microstate and the most likely macrostate. In particular, the most likely energy of the sub-system is *not* equal to the energy in the most likely microstate. In fact, $\overline{E} > E(\overline{\psi})$. Of course the most likely energy is given by $\partial S_{tot}(\underline{E}/T) = S_s(E) - E/T$ (see next). (Caution: despite this point, the notation $\overline{S} \equiv S(\overline{\psi})$ is used below.)

This point in general, and the explicit result for $\overline{\psi}$ in particular, are identical to the result for the classical canonical system.[2] In the latter case the most likely point in phase space is the point of lowest energy of the isolated system. The most likely (classical) energy of the sub-system is greater than this because there are many more points of higher energy.

A solution of the characteristic equation obviously has adiabatic velocity

$$\underline{\dot{\overline{\psi}}}^0 \equiv \frac{1}{i\hbar}\underline{\underline{\mathcal{H}}} \cdot \underline{\overline{\psi}} = \frac{1}{i\hbar} E(\overline{\psi})\underline{\overline{\psi}} \tag{2.17}$$

Here and below, *adiabatic* means evolution by Schrödinger's equation for an isolated sub-system.

2.2.3 Fluctuation Form

The most likely wave function for a canonical equilibrium system was just shown to be an eigenfunction of the energy operator, Eq. (2.15),

$$\hat{\mathcal{H}} \left|\overline{\psi}\right\rangle = E_0 \left|\overline{\psi}\right\rangle \tag{2.18}$$

The eigenenergy is $E_0 \equiv E(\overline{\psi})$. There are of course multiple solutions of this eigenvalue equation (because of the degeneracy within each level), and $\overline{\psi}$ is fixed as one of them. It will turn out that most of the final results do not depend explicitly on $\overline{\psi}$, but they do depend upon the choice of E_0. If E_0 is not the ground state energy, then there may be problems with the fluctuation expression for the entropy that is now given.

The total entropy when the sub-system is in the wave state ψ, which is equal

to the reservoir entropy, was obtained in Eq. (2.12),

$$S^{(1)}(\psi|T) = -\frac{1}{T}E(\psi) = -\frac{1}{T}\frac{\langle\psi|\,\hat{\mathcal{H}}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \tag{2.19}$$

This is here called the first entropy in order to distinguish it from the second entropy that will be introduced shortly.

One may define the fluctuation of a wave function as its departure from the most likely value, $\Delta\psi \equiv \psi - \overline{\psi}$, or $|\Delta\psi\rangle \equiv |\psi\rangle - \left|\overline{\psi}\right\rangle$. In terms of this, one carries out a second order expansion about the most likely wave function and writes the first entropy in fluctuation approximation as

$$S^{(1)}(\psi|T) = \langle\Delta\psi|\,\hat{S}''\,|\Delta\psi\rangle + \overline{S}^{(1)} \tag{2.20}$$

where the value in the most likely state is $\overline{S}^{(1)} \equiv S^{(1)}(\overline{\psi}|T) = -E_)/T$. Because the most likely state maximizes the first entropy, the entropy fluctuation operator is negative definite. Equating the two expressions for the first entropy, and multiplying both sides by the magnitude $N(\psi) \equiv \langle\psi\,|\,\psi\rangle$, on e obtains

$$-\frac{1}{T}\,\langle\psi|\,\hat{\mathcal{H}}\,|\psi\rangle = N(\psi)\,\langle\Delta\psi|\,\hat{S}''\,|\Delta\psi\rangle + N(\psi)\overline{S}^{(1)} \tag{2.21}$$

Taking the cross second derivative and evaluating it at $\left|\overline{\psi}\right\rangle$ one obtains

$$-\frac{1}{T}\hat{\mathcal{H}} = N(\overline{\psi})\hat{S}'' + \overline{S}^{(1)}\,\hat{I} \tag{2.22}$$

the remaining terms vanishing. Hence the entropy fluctuation operator is

$$\hat{S}'' = -\frac{1}{T\overline{N}}[\hat{\mathcal{H}} - E_0\hat{I}] \tag{2.23}$$

In order for this to be a negative definite operator, as required for the stability of the fluctuations, E_0 must be the lowest possible energy. It is not clear how to proceed if this condition is violated.

This procedure that relates the fluctuation operator to the entropy operator will be used below to obtain the second entropy operator from the second entropy fluctuation operator.

2.3 Helmholtz Free Energy

The total unconstrained entropy is the logarithm of the partition function, and it may be rewritten as

$$\begin{aligned} S_{tot}(T) &= k_B \ln Z(T) \\ &= k_B \mathrm{Tr}\{\hat{\wp}(T) \ln Z(T)\} \\ &= k_B \mathrm{Tr}\left\{\hat{\wp}(T)\left[-\ln \hat{\wp}(T) + \ln e^{-\hat{\mathcal{H}}/k_B T}\right]\right\} \\ &= -\frac{1}{T}\mathrm{Tr}\{\hat{\wp}(T)\hat{\mathcal{H}}\} \\ &\quad - k_B \mathrm{Tr}\{\hat{\wp}(T) \ln \hat{\wp}(T)\} \end{aligned} \tag{2.24}$$

This is written in the form of a sum over quantum states. It can be equivalently written as an integral over the Hilbert space,

$$\begin{aligned} S_{tot}(T) &= k_B \ln Z(T) \\ &= k_B \int d\psi \, \frac{\langle\psi|\hat{\wp}(T) \ln Z(T)\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \\ &= k_B \int d\psi \left[-\frac{-\langle\psi|\hat{\wp}(T) \ln \hat{\wp}(T)\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle}\right. \\ &\quad \left. + \frac{\langle\psi|\hat{\wp}(T) \ln e^{-\hat{\mathcal{H}}/k_B T}\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle}\right] \\ &= -\frac{\langle\hat{\mathcal{H}}\rangle_T}{T} - k_B \int d\psi \, \frac{\langle\psi|\hat{\wp}(T) \ln \hat{\wp}(T)\,|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \end{aligned} \tag{2.25}$$

The equivalence of these expressions follows from the collapse of the wave function, Eq. (2.3): the trace can be formulated equivalently as a sum over quantum states or as an integral over Hilbert space.

The first term is evidently the unconstrained reservoir entropy (c.f., Eq. (2.12), averaged over the sub-system microstates),

$$S_r(T) = -\frac{\langle\hat{\mathcal{H}}\rangle_T}{T} \tag{2.26}$$

Because the probabilities are sharply peaked, canonical equilibrium averages are equal to micro-canonical or isolated equilibrium averages. Accordingly,

the remaining term is the unconstrained sub-system entropy,

$$\begin{aligned} S_s(T) &= -k_B \langle \ln \hat{\wp}(T) \rangle_T \\ &= -k_B \mathrm{Tr}\{\hat{\wp}(T) \ln \hat{\wp}(T)\} \\ &= -k_B \int d\psi \, \frac{\langle \psi | \hat{\wp}(T) \ln \hat{\wp}(T) | \psi \rangle}{\langle \psi | \psi \rangle} \end{aligned} \tag{2.27}$$

This formula for the sub-system entropy is of the form $S = -k_B \sum_\alpha \wp_\alpha \ln \wp_\alpha$, which is commonly called the information entropy. In the classical case it is variously attributed to Boltzmann, Gibbs, and Shannon, and it was popularized by Jaynes. In quantum mechanics it is called the von Neumann entropy, and it is written in terms of the density matrix, $S = -k_B \mathrm{Tr} \rho \ln \rho$.[28-30] It is commonly called *the* entropy of the system, which implies that it is the entropy of the total system, when in fact it is only the sub-system part of the total entropy. Because most workers mistake this for the total entropy, it is commonly maximized to obtain equilibrium properties including the equilibrium probability distribution (e.g., Jaynes' maxent approach to statistical mechanics). The consequences and problems with this common mis- interpretation are detailed elsewhere.[31]

One has to distinguish between the statistical mechanical and the thermodynamic definitions of the free energy.[1] In statistical mechanics, the free energy corresponds to the unconstrained total entropy, whereas in thermodynamics the free energy corresponds to the maximal constrained total entropy. In the thermodynamic limit of an infinitely large sub-system and relatively negligible fluctuations, the two are equal. In statistical mechanics, in general the free energy is minus the temperature times the total entropy. For the present canonical case of a sub-system exchanging energy with a thermal reservoir the statistical mechanical Helmholtz free energy is

$$\begin{aligned} F_{SM}(T) &= -T S_{tot}(T) \\ &= -k_B T \ln Z(T) \\ &= \langle \hat{\mathcal{H}} \rangle_T - T S_s(T) \end{aligned} \tag{2.28}$$

This is the obvious analogue of the classical form for the Helmholtz free energy that one sees in standard thermodynamic texts. The main point to note is that it is the sub-system entropy that appears explicitly. All text books apart from the author's[1,2] call this term *the* entropy, and imply that

it is the entropy of the total system, which it clearly isn't. The sub-system entropy that appears here is that of an unconstrained isolated system, Eq. (2.27). The second point to note that it is the average of the normalized energy that appears; this is extensive with the sub-system size, as is the sub-system entropy.

The thermodynamic free energy is minus the temperature times the maximum value of the constrained total entropy. By definition the most likely state maximizes the constrained total entropy. The most likely values of the energy and norm may be denoted by an overbar. In so far as the fluctuations are Gaussian, these are equal to the average values.

For the present canonical case, the thermodynamic Helmholtz free energy is

$$\begin{aligned} F_{TD}(T) &= -TS_{tot}(\overline{E}|T) \\ &= \overline{E}(T) - TS_s(\overline{E}(T)) \end{aligned} \tag{2.29}$$

The sub-system entropy that appears here is the con- strained one given by the isolated system with specified values of energy. There is an obvious identity between the functional forms for the thermodynamic and statistical mechanical Helmholtz free energies. The free energy is negative, assuming that the constant has been chosen to make the total entropy positive. The thermodynamic free energy is strictly greater (i.e., strictly smaller in magnitude) than the statistical mechanical free energy. In the thermodynamic limit of an infinitely large sub-system and relatively negligible fluctuations, the two are equal to a very good approximation.

3 Transition Probability and the Stochastic Dissapative Schrödinger Equation

The aim of this section is to derive the transition probability operator for a canonical equilibrium system, and from this to derive the stochastic dissipative Schrödinger equation. The strategy will follow closely the analogous derivation for the classical case.[2]

This section is primarily concerned with the wave state transition, $|\psi_1\rangle \xrightarrow{\tau} |\psi_2\rangle$. The time interval τ can be positive or negative and is initially of arbitrary duration; rather quickly a small τ expansion will be performed. One

can consider the initial and final sub-system wave functions of the transition as belonging to distinct Hilbert spaces and form the direct product $\mathsf{H}_1 \otimes \mathsf{H}_2$, with the total wave function written as $|\psi_1\rangle |\psi_2\rangle \equiv |\psi_1, \psi_2\rangle$.

The analysis is based upon the second entropy operator, which may also be called the transition entropy operator, or the two-time entropy operator. For the transition in time τ, the unconditional transition probability operator is related to the second entropy operator by

$$\hat{\wp}^{(2)}(\tau) = \frac{e^{\hat{S}^{(2)}(\tau)/k_B}}{Z^{(2)}(\tau, T)} \tag{3.1}$$

A detailed analysis of the second entropy in fluctuation approximation follows. Eventually, the second entropy operator $\hat{S}^{(2)}$ will be related to the second entropy fluctuation operator $\hat{\mathscr{A}}^{(2)}$.

3.1 Second Entropy Fluctuation Operator

3.2 Fluctuation Form

Recall that the fluctuation of the sub-system wave function is $\Delta\psi \equiv \psi - \overline{\psi}$. Assume that the second entropy for the transition has the quadratic fluctuation form

$$\begin{aligned} & S^{(2)}(\psi_2, \psi_1; \tau) \\ & \quad = \langle \Delta\psi_2, \Delta\psi_1 | \, \hat{\mathscr{A}}^{(2)}(\tau) \, | \Delta\psi_2, \Delta\psi_1 \rangle + \overline{S}^{(1)} \\ & \quad = \langle \Delta\psi_2 | \, \hat{a}(\tau) \, | \Delta\psi_2 \rangle + \langle \Delta\psi_1 | \, \hat{c}(\tau) \, | \Delta\psi_1 \rangle \\ & \qquad + \langle \Delta\psi_2 | \, \hat{b}(\tau) | \Delta \rangle \, \psi_1 + \langle \Delta\psi_1 | \, \hat{b}(\tau)^\dagger \, | \Delta\psi_2 \rangle + \overline{S}^{(1)} \end{aligned} \tag{3.2}$$

Note that the order of the arguments of the second entropy defines the time interval as the time of the first argument minus the time of the second argument, $S^{(2)}(\psi_2, \psi_1; \tau) \Rightarrow \tau \equiv t_2 - t_1$. The various operators are also a function of temperature, which is generally not shown. The final (immaterial) constant makes the maximum value of the second entropy equal to that of the first entropy $\overline{S}^{(1)}$ when the two termini are the most likely state, $\psi_1 = \psi_2 = \overline{\psi}$, which is related the reduction condition discussed further below.[2,32] The negative definite operator $\hat{\mathscr{A}}^{(2)}(\tau)$ (equivalently its component operators $\hat{a}(\tau)$, $\hat{b}(\tau)$, and $\hat{c}(\tau)$) is the second entropy fluctuation operator, and, after its properties

have been established, it will be used to give the second entropy operator itself, and hence the transition probability operator.

Three symmetries must hold: statistical symmetry,

$$S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_1, \psi_2; -\tau) \tag{3.3}$$

reality,

$$S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_2, \psi_1; \tau)^* \tag{3.4}$$

and microscopic reversibility,

$$S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_1^*, \psi_2^*; \tau) \tag{3.5}$$

(Note that this means the conjugate of the fluctuation, $\Delta\psi^* \equiv \psi^* - \overline{\psi}^*$.

Statistical symmetry simply reflects the ordering of the arguments of the second entropy discussed above. It can also be called time homogeneity symmetry, since it follows by first shifting the time origin by t, $t_2 = t+\tau$ and $t_1 = t$, and then setting $t \Rightarrow -\tau$. The second entropy is real for the same reasons that the first entropy is real: because it is a physical observable (more precisely, a linear combination of physical observables with real coefficients), and also because its exponential gives the transition probability density, which is taken to be real. Microscopic reversibility is non-trivial and relies upon two facts: First, Schrödinger?s equation for the total isolated system (subsystem plus reservoir) obeys microscopic reversibility. And second, for an equilibrium system, a wave state of the reservoir ψ_r and its conjugate ψ_r^* are equally probable, since conjugation represents velocity reversal.

Statistical symmetry implies that

$$\hat{a}(-\tau) = \hat{c}(\tau) \text{ and } \hat{b}(-\tau) = \hat{b}(\tau)^\dagger \tag{3.6}$$

Reality implies that

$$\hat{a}(\tau)^\dagger = \hat{a}(\tau) \text{ and } \hat{c}(\tau)^* = \hat{c}(\tau) \tag{3.7}$$

The form of the two cross terms in the second entropy guarantees reality for the contribution from these two terms. Microscopic reversibility implies that

$$\hat{a}(\tau)^* = \hat{c}(\tau) \text{ and } \hat{b}(\tau)^* = \hat{b}(\tau)^\dagger \tag{3.8}$$

Hence $\hat{a}(\tau) = \hat{a}(\tau)^\dagger = \hat{a}(-\tau)^*$, and $\hat{b}(\tau) = \hat{b}(\tau)^{*\dagger} = \hat{b}(-\tau)^*$

3.2.1 Most Likely Terminus

The derivative of the second entropy with respect to $\langle\psi_2|$ is

$$\frac{\partial S^{(2)}(\psi_2,\psi_1;\tau)}{\partial\langle\psi_2|} = \hat{a}(\tau)\,|\Delta\psi_2\rangle + \hat{b}(\tau)\,|\Delta\psi_1\rangle \tag{3.9}$$

The most likely terminus of the transition, $\overline{\psi}_2 \equiv \overline{\psi}(\tau|\psi_1)$, follows by setting this derivative to zero,

$$\left|\Delta\overline{\psi}_2\right\rangle = -\hat{a}(\tau)^{-1}\hat{b}(\tau)\,|\Delta\psi_1\rangle \tag{3.10}$$

3.2.2 Reduction Condition

The second entropy may be re-written in terms of the departure from the most likely terminus, $\Delta\psi_2 - \Delta\overline{\psi}_2 = \psi_2 - \overline{\psi}_2$,

$$\begin{aligned} S^{(2)}(\psi_2,\psi_1;\tau) = {} & \left\langle\psi_2 - \overline{\psi}_2\right|\hat{a}(\tau)\left|\psi_2 - \overline{\psi}_2\right\rangle \\ & + \langle\Delta\psi_1|\,\{\hat{c}(\tau) - \hat{b}(\tau)^\dagger\hat{a}(\tau)^{-1}\hat{b}(\tau)\}\,|\Delta\psi_1\rangle + \overline{S}^{(1)} \end{aligned} \tag{3.11}$$

The reduction condition is that in the most likely state, the second entropy reduces to the first entropy,[2,32]

$$\begin{aligned} S^{(2)}(\overline{\psi}_2,\psi_1;\tau) &= S^{91)}(\psi_1|T) \\ &= \langle\Delta\psi_1|\,\hat{S}''\,|\Delta\psi_1\rangle + \overline{S}^{(1)} \\ &= -\frac{1}{T\overline{N}}\,\langle\Delta\psi_1|\,\{\hat{\mathcal{H}}' - E_0\hat{I}\}\,|\Delta\psi_1\rangle + \overline{S}^{(1)} \end{aligned} \tag{3.12}$$

This uses the fluctuation form of the first entropy, Eqs (2.20) and (2.23). The reduction condition is equivalent to insisting that the transition probability must reduce to the probability of the initial state upon summing over all possible final states.2,32 The reduction condition therefore yields the requirement

$$\hat{c}(\tau) - \hat{b}(\tau)^\dagger\hat{a}(\tau)^{-1}\hat{b}(\tau) = -\frac{1}{T\overline{N}}\{\hat{\mathcal{H}}' - E_0\hat{I}\} \tag{3.13}$$

One could take $\overline{N} = 1$. This result must hold for each value of the time step τ.

3.2.3 Small Time Expansion

Since $\overline{\psi}_2 \to \psi_1$ as $\tau \to 0$, the second entropy must contain essentially a δ-function singularity. Hence the small-τ expansions must be of the form

$$\hat{a}(\tau) = \frac{1}{|\tau|}\hat{a}_{-1} + \frac{1}{\tau}\hat{a}'_{-1} + \hat{a}_0 + \hat{\tau}\hat{a}'_0 + \mathcal{O}(\tau) \tag{3.14}$$

$$\hat{b}(\tau) = \frac{1}{|\tau|}\hat{b}_{-1} + \frac{1}{\tau}\hat{b}'_{-1} + \hat{b}_0 + \hat{\tau}\hat{b}'_0 + \mathcal{O}(\tau) \tag{3.15}$$

and

$$\hat{c}(\tau) = \frac{1}{|\tau|}\hat{c}_{-1} + \frac{1}{\tau}\hat{c}'_{-1} + \hat{c}_0 + \hat{\tau}\hat{c}'_0 + \mathcal{O}(\tau) \tag{3.16}$$

with $\hat{\tau} \equiv \text{sign } \tau = \tau/|\tau|$.

The reason why the non-analytic terms appear (i.e., those containing $|\tau|$ and $\hat{\tau}$ is that these are necessary to yield the irreversible behavior that is characteristic of all thermodynamic evolution. One concludes that this is not a Taylor expansion for an infinitesimal time step, since this would only ever yield analytic terms, but rather an expansion for small but finite time steps that is a resummation of an infinite order Taylor expansion. The validity of beginning the expansion with terms $\mathcal{O}(\tau^{-1})$ can be judged by the consequences; amongst other things it yields a physically plausible stochastic Schrödinger equation with a conventional velocity for the wave function.

From the symmetries given above, $\hat{a}(\tau) = \hat{a}(\tau)^\dagger = \hat{a}(-\tau)^*$, and $\hat{a}(-\tau) = \hat{c}(\tau)$, one can see that the unprimed $\hat{a}$ are real and self-adjoint and equal the unprimed $\hat{c}$, and the primed $\hat{a}$ are imaginary and self-adjoint and equal the negative of the primed $\hat{c}$. Also, since $\hat{b}(\tau) = \hat{b}(\tau)^\dagger = \hat{b}(-\tau)^*$, the unprimed $\hat{b}$ are real and self-adjoint, and the primed $\hat{b}$ are imaginary and anti-self-adjoint.

Since $\overline{\psi}_2 \to \psi_1$ as $\tau \to 0$, to leading order $\hat{a})\tau) = -\hat{b}(\tau)$, which implies that

$$\hat{a}_{-1} = -\hat{b}_{-1} \equiv -\hat{\lambda}^{-1} \text{ and } \hat{a}'_{-1} = -\hat{b}'_{-1} = 0 \tag{3.17}$$

From the symmetry relations, $\hat{\lambda}$ is a real Hermitian operator that is positive definite (because the second entropy must be negative definite). The primed coefficients individually vanish because $\hat{a}'_{-1}$ is self-adjoint and $\hat{b}'_{-1}$ is anti-self-adjoint. With these, the small time expansions read

$$\hat{a}(\tau) = -\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{a}_0 + \hat{\tau}\hat{a}'_0 + \mathcal{O}(\tau) \tag{3.18}$$

$$\hat{b}(\tau) = \frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{b}_0 + \hat{\tau}\hat{b}'_0 + \mathcal{O}(\tau) \tag{3.19}$$

and

$$\hat{c}(\tau) = -\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{a}_0 - \hat{\tau}\hat{a}'_0 + \mathcal{O}(\tau) \tag{3.20}$$

Inserting these expansions in the reduction condition, to zeroth order in the time step one must have

$$\begin{aligned}
-\frac{1}{T\overline{N}}\{\hat{\mathcal{H}}' - E_0\hat{I}\} &= \hat{c}(\tau) - \hat{b}(\tau)^\dagger \hat{a}(\tau)^{-1}\hat{b}(\tau) \\
&= -\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{a}_0 - \hat{\tau}\hat{a}'_0 - \left[\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{b}_0 - \hat{\tau}\hat{b}'_0\right] \\
&\quad \times \left[-\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{a}_0 + \hat{\tau}\hat{a}'_0\right]^{-1}\left[\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{b}_0 + \hat{\tau}\hat{b}'_0\right] \\
&= -\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{a}_0 - \hat{\tau}\hat{a}'_0 + \left[\frac{1}{|\tau|}\hat{\lambda}_{-1} + \hat{b}_0 - \hat{\tau}\hat{b}'_0\right] \\
&\quad \times \left[\hat{I} + |\tau|\hat{\lambda}\hat{a}_0 + \tau\hat{\lambda}\hat{a}'_0\right]\left[\hat{I} + |\tau|\hat{\lambda}\hat{b}_0 + \tau\hat{\lambda}\hat{b}'_0\right] \\
&= \hat{a}_0 - \hat{\tau}\hat{a}'_0 + \hat{b}_0 - \hat{\tau}\hat{b}'_0 + \hat{a}_0 + \hat{\tau}\hat{a}'_0 + \hat{b}_0 + \hat{\tau}\hat{b}'_0 \\
&= 2[\hat{a}_0 + \hat{b}_0] + \mathcal{O}(\tau)
\end{aligned} \tag{3.21}$$

In short,

$$\hat{a}_0 + \hat{b}_0 = -\frac{1}{T\overline{N}}\{\hat{\mathcal{H}}' - E_0\hat{I}\} = \frac{1}{2}\hat{S}'' \tag{3.22}$$

This is formally the same as the result for classical fluctuations in macrostates or microstates given in Ref. 2.

Using this, the expansion for the most likely terminal wave function becomes

$$\begin{aligned}
\left|\Delta\overline{\psi}_2\right\rangle &= -\hat{a}(\tau)^{-1}\hat{b}(\tau)\left|\Delta\psi_1\right\rangle \\
&= \left[\hat{I} + |\tau|\hat{\lambda}\hat{a}_0 + \tau\hat{\lambda}\hat{a}'_0\right]\left[\hat{I} + |\tau|\hat{\lambda}\hat{b}_0 + \tau\hat{\lambda}\hat{b}'_0\right]\left|\Delta\psi_1\right\rangle \\
&= \left|\Delta\psi_1\right\rangle + \tau\hat{\lambda}[\hat{a}'_0 + \hat{b}'_0]\left|\Delta\psi_1\right\rangle \\
&\quad - \frac{|\tau|}{2T\overline{N}}\hat{\lambda}[\hat{\mathcal{H}} - E_0\hat{I}]\left|\Delta\psi_1\right\rangle + \mathcal{O}(\tau^2)
\end{aligned} \tag{3.23}$$

The adiabatic evolution must be contained in the term proportional to τ, $\left|\dot{\psi}_1^0\right\rangle = (1/i\hbar)\hat{\mathcal{H}}\left|\psi_1\right\rangle$. In addition there must be a reservoir contribution to

this term so that one has

$$\hat{\lambda}[\hat{a}_0' + \hat{b}_0'] = \frac{1}{i\hbar}[\hat{\mathcal{H}} - E_0\hat{I}] \tag{3.24}$$

This reversible reservoir contribution, in addition to the adiabatic contribution, is required in order for the deterministic evolution to be a linear homogeneous function of the initial wave function, as will be seen. Since $\hat{a}_0'$ is self-adjoint and $\hat{b}_0'$ is anti-self-adjoint, one can conclude that $\hat{b}_0' = 0$.

With this result, all of the small time expansion coefficients have been analyzed and the form of the second entropy fluctuation operator and its small time limit have been determined. There remains only one free coefficient that is not fixed in terms of known operators, namely $\hat{\lambda}$. This operator represents in essence the strength of the interaction between the sub-system and the reservoir, and its magnitude can be varied within relatively wide bounds. As will be seen in the following sub-sections, its form is constrained by certain requirements for the evolution of the wave function.

3.3 Stochastic, Dissipative Schrödinger Equation

3.3.1 Dissipation

Inserting the above result for reversible term, Eq. (3.24), into the small time expansion for the most likely terminal wave function $\left|\Delta\overline{\psi}_2\right\rangle$, and using the fact that $[\hat{\mathcal{H}} - E_0\hat{I}]\left|\overline{\psi}\right\rangle = |0\rangle$, one finds that to linear order in the time step the most likely evolution is

$$\begin{aligned}\left|\Delta\overline{\psi}_2\right\rangle = |\psi_1\rangle &+ \frac{\tau}{i\hbar}[\hat{\mathcal{H}} - E_0\hat{I}]\,|\psi_1\rangle \\ &- \frac{|\tau|}{2T\overline{N}}\hat{\lambda}[\hat{\mathcal{H}} - E_0\hat{I}]\,|\psi_1\rangle\end{aligned} \tag{3.25}$$

Notice that the most likely wave function $\overline{\psi}$ has been canceled from this expression (but it does depend upon the state energy E_0). This cancellation is necessary for it to be the required linear homogeneous function of the initial wave function. This is the dissipative Schrödinger equation. (Caution: do not use this equation without the stochastic term given below.)

The final term is essentially the gradient of the first entropy, $-[\hat{\mathcal{H}} - E_0\hat{I}]\,|\Delta\psi_1\rangle\,/T\overline{N} =$

$\hat{S}''|\Delta\psi_1\rangle = \partial S^{(1)}(\psi_1|T)/\partial|\psi_1\rangle$. This provides the thermodynamic driving force toward the most likely state. It is the exact analogue of the dissipative term in the classical Langevin equation. In that case the dissipation is linearly proportional to the velocity, which itself is proportional to the velocity gradient of the entropy.

The operator $\hat{\lambda}$ may be called the statistical drag operator. From the symmetry requirements it must be Hermitian and real. Apart from this its magnitude can be chosen within wide bounds. It reflects the exchange with the thermal reservoir, and, like all reservoirs, it is an abstraction of reality so that the final results are not sensitive to its precise value (see next).

3.3.2 Fluctuation

Since the evolution of the sub-system wave function is determined in part by the interactions with the reservoir, and since the wave function of the reservoir is unknown, there must be a random element to the evolution, which is to say that it is only determined in a probabilistic sense, and it may not be the same each time that the sub-system visits the same sub-system wave state. Therefore, one must add a stochastic operator to the above deterministic equation to give the stochastic dissipative Schrödinger equation,

$$\begin{aligned}|\psi_2\rangle &= |\psi_1\rangle + \frac{\tau}{i\hbar}[\hat{\mathcal{H}} - E_0\hat{I}]\,|\psi_1\rangle \\ &\qquad - \frac{|\tau|}{2T\overline{N}}\hat{\lambda}[\hat{\mathcal{H}} - E_0\hat{I}]\,|\psi_1\rangle + \hat{\mathcal{R}}\,|\psi_1\rangle \\ &\equiv [\hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}]\,|\psi_1\rangle \\ &\equiv \hat{\mathcal{U}}(\tau)\,|\psi_1\rangle \end{aligned} \tag{3.26}$$

The properties of the stochastic operator $\hat{\mathscr{R}}$ will be derived in the following sub-section. Briefly, here it may be stated that it has mean zero and variance $\mathcal{O}(\tau)$, and stochastic operators at different time steps are uncorrelated. The time integral below should be understood as discretized with time step τ.

For a trajectory, with $t_j \equiv j\tau$, this gives

$$\begin{aligned} |\psi_n\rangle &= [\hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}_{n-1}].....[\hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}_1] \\ &\quad \times [\hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}_0]\,|\psi_0\rangle \\ &\equiv \hat{\mathcal{U}}(t_n, t_0)\,|\psi_0\rangle \end{aligned} \tag{3.27}$$

One has to be careful to preserve the order of the products in the time propagator. Although the statistical distribution of the stochastic operator is independent of time, its realization at each time step is of course variable and is denoted here $\hat{\mathcal{R}}_j$. This is the only term that depends upon time in this equilibrium case. This Markovian expression for the trajectory is expected to be valid for the evolution of the wave function. The following analysis is carried through only to linear order in the time step,and $\hat{\mathcal{U}}(\tau) = \hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}$ will be used below.

3.3.3 Fluctuation Dissipation Theorem

The form of the drag operator and of the stochastic operator and their relationship is now established from the microscopic reversibility condition and from the stationarity of the probability operator condition.

Since in an equilibrium system microscopic reversibility holds (c.f., Eq. (3.5)), the propagator must be unitary on average,

$$\langle \hat{\mathcal{U}}(t_n, t_0)\hat{\mathcal{U}}(t_n, t_0)^\dagger \rangle_{stoch} = \hat{I} \tag{3.28}$$

(The stochastic average is also called the time average or the statistical average.) To see this directly,

$$|\psi_2\rangle = \hat{\mathcal{U}}(t_2, t_1)\,|\psi_1\rangle \tag{3.29}$$

has Hermitian conjugate

$$\langle \psi_2| = \langle \psi_1|\hat{\mathcal{U}}(t_2, t_1)^\dagger \tag{3.30}$$

Microscopic reversibility implies that

$$\langle \psi_1| = \langle \psi_2|\hat{\mathcal{U}}(t_2, t_1) \tag{3.31}$$

This holds after averaging over the stochastic operator. From this one concludes that for a general equilibrium system

$$\hat{\mathcal{U}}(t_2,t_1)^\dagger = \hat{\mathcal{U}}(t_2,t_1)^{-1} \tag{3.32}$$

which is to say that the time propagator is unitary. This is to be interpreted as being true after averaging over the stochastic terms.

Note that for this open system and its stochastic dissipative Schrödinger equation, the time reversed propagator is not equal to the inverse, $\hat{\mathcal{U}}(t_1,t_2)^\dagger \neq \hat{\mathcal{U}}(t_2,t_1)^{-1}$. This contrasts with an isolated system, where the explicit form for the adiabatic time propagator, $\hat{U}^0(t_2,t_1) \equiv \exp\left(-i(t_2-t_1)\hat{\mathcal{H}}/\hbar\right)$, shows that $\hat{U}^0(t_1,t_2) = \hat{U}^0(t_2,t_1)^{-1}$. The difference between the two cases is the presence of the irreversible terms, those proportional to $|\tau|$, in the stochastic dissipative Schrödinger equation.

In general, a unitary transformation preserves the norm,

$$\begin{aligned}\langle\psi(t)\,|\,\psi(t)\rangle &= \left\langle\hat{\mathcal{U}}(t)\psi(0)\,\middle|\,\hat{\mathcal{U}}(t)\psi(0)\right\rangle \\ &= \langle\psi(0)|\hat{\mathcal{U}}(t)^\dagger\hat{\mathcal{U}}(t)\,|\psi(0)\rangle \\ &= \langle\psi(0)\,|\,\psi(0)\rangle\end{aligned} \tag{3.33}$$

Here and often below, $\hat{\mathcal{U}}(t) \equiv \hat{\mathcal{U}}(t,0)$. Again this is true on average.

The unitary condition gives an expression for the variance of the stochastic operator. To linear order in τ one has

$$\begin{aligned}&[\hat{I}+\hat{u}(\tau)+\hat{\mathcal{R}}][\hat{I}+\hat{u}(\tau)+\hat{\mathcal{R}}]^\dagger \\ &\quad= \hat{I}+\hat{u}(\tau)+\hat{u}(\tau)^\dagger+\hat{\mathcal{R}}\hat{\mathcal{R}}^\dagger+\mathcal{O}(\tau^2) \\ &\quad= \hat{I}+\frac{|\tau|}{2}[\hat{\lambda}\hat{S}''+\hat{S}''^\dagger\hat{\lambda}^\dagger]+\langle\hat{\mathcal{R}}\hat{\mathcal{R}}^\dagger\rangle_{stoch}+\mathcal{O}(\tau^2)\end{aligned} \tag{3.34}$$

The final equality follows after the stochastic average and neglecting terms higher than linear order in τ. Hence one concludes that the drag operator and the variance of the stochastic operator must satisfy

$$\langle\hat{\mathcal{R}}\hat{\mathcal{R}}^\dagger\rangle_{stoch} = -\frac{|\tau|}{2}[\hat{\lambda}\hat{S}''+\hat{S}''^\dagger\hat{\lambda}^\dagger] \tag{3.35}$$

since both $\hat{S}''$ and $\hat{\lambda}$ are Hermitian operators. Since the former is negative definite, and the latter is positive definite, one can see that the variance of

the stochastic operator is Hermitian, positive definite, and proportional to the length of the time step.

A second condition can be derived from the time evolution of the probability operator,

$$\hat{\wp}(t) = \hat{\mathcal{U}}(t)\hat{\wp}(0)\hat{\mathcal{U}}(t)^{\dagger} \tag{3.36}$$

If this is stationary for the Maxwell-Boltzmann probability operator, then time averages over the stochastic dissipative Schrödinger equation equal canonical equilibrium averages.

In so far as the probability operator equals the density operator, this is like a stochastic form of the conventional Lindblad master equation in the Krauss representation. It should be noted that the present formula, in addition to being stochastic, has been derived with explicit terms that abstract from a specific model for the reservoir, and that it obeys the exact unitary and irreversibility symmetry rules that are derived from the underlying Schrödinger equation for the total isolated system and the equilibrium nature of the reservoir.

In view of the above, the evolution of the canonical equilibrium probability operator for a single time step is

$$\begin{aligned}\hat{\wp}(\tau) &= \frac{1}{Z(T)}[\hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}]e^{-\hat{\mathcal{H}}/k_BT}[\hat{I} + \hat{u}(\tau) + \hat{\mathcal{R}}]^{\dagger} \\ &= \hat{\rho}(0) + \frac{|\tau|}{2Z(T)}[\hat{\lambda}\hat{S}''e^{-\hat{\mathcal{H}}/k_BT} + e^{-\hat{\mathcal{H}}/k_BT}\hat{S}''\hat{\lambda}] \\ &\quad + \frac{1}{Z(T)}\hat{\mathcal{R}}e^{-\hat{\mathcal{H}}/k_BT}\hat{\mathcal{R}}^{\dagger} + \mathcal{O}(\tau^2)\end{aligned} \tag{3.37}$$

The reversible term cancels in the second equality be- cause it is pure imaginary and $\hat{\mathcal{H}}$ is self-adjoint. For an equilibrium system the probability operator must be stationary, $\hat{\wp}(t) = \hat{\wp}(0)$ (after stochastic averaging). Hence this yields the condition

$$\langle\hat{\mathcal{R}}e^{-\hat{\mathcal{H}}/k_BT}\hat{\mathcal{R}}^{\dagger}\rangle_{stoch} = -\frac{|\tau|}{2}[\hat{\lambda}\hat{S}''e^{-\hat{\mathcal{H}}/k_BT} + e^{-\hat{\mathcal{H}}/k_BT}\hat{S}''\hat{\lambda}] \tag{3.38}$$

If this holds then the Maxwell-Boltzmann probability operator for a canonical equilibrium system is stationary under the stochastic dissipative Schrödinger

equation. This is the second relationship that the drag operator and the variance of the stochastic operator have to satisfy.

This stationarity condition, as well as the unitary condition, Eq. (3.35), may be simultaneously satisfied if the drag operator and the stochastic operator have entropy states as their eigenstates. (For the present canonical equilibrium system, entropy eigenstates are the same as energy eigenstates, but since all of the analysis goes through for a general reservoir, one may as well deal with entropy eigenstates.) This is a reasonable ansatz as entropy provides the driving force for exchange between the sub-system and the reservoir. Recall that the entropy eigenfunctions are also eigenfunctions of the entropy fluctuation operator,

$$\hat{S}'' \left|\zeta_n^S\right\rangle = S_n'' \left|\zeta_n^S\right\rangle \tag{3.39}$$

with, in the canonical equilibrium case, the eigenvalues being $S_n'' \equiv -[E_n - E + 0]/\overline{N}T$.

These observations suggest that the drag operator should commute with the entropy operator, which in this case is the same as the energy operator. Accordingly, one ansatz for the drag operator is to construct it from the set of entropy eigenfunctions,

$$\hat{\lambda} \equiv \sum_n \lambda_n \left|\zeta_n^S\right\rangle \left\langle\zeta_n^S\right| \tag{3.40}$$

which gives $\hat{\lambda}\left|\zeta_n^S\right\rangle = \lambda_n \left|\zeta_n^S\right\rangle$. In other words, the drag operator is represented by a diagonal matrix in the basis of entropy eigenfunctions. Because $\hat{\lambda}$ is a real Hermitian operator, λ_n must be real. It may be called the drag coefficient for the state ζ_n^S. Similarly choose

$$\hat{\mathcal{R}} \equiv \sum_n r_n \left|\zeta_n^S\right\rangle \left\langle\zeta_n^S\right| \tag{3.41}$$

so that $\hat{\mathcal{R}}\left|\zeta_n^S\right\rangle = r_n \left|\zeta_n^S\right\rangle$, with r_n a random real number of zero mean and variance now to be determined.

Taking the scalar product of both sides of the unitary condition Eq. (3.35) one obtains

$$\begin{aligned} \left\langle\zeta_m^S\right| \hat{\mathcal{R}}\hat{\mathcal{R}}^\dagger \left|\zeta_m^S\right\rangle_{stoch} &= -\frac{|\tau|}{2} \left\langle\zeta_m^S\right| [\hat{\lambda}\hat{S}'' + \hat{S}''\hat{\lambda}] \left|\zeta_m^S\right\rangle \\ &= -|\tau| S_n'' \lambda_n \delta_{m,n} \end{aligned} \tag{3.42}$$

Inserting the ansatz for the stochastic operator one sees that the variance is

$$\langle r_m r_n \rangle_{stoch} = -|\tau| S_n'' \lambda_n \delta_{m,n} = \frac{|\tau|\{E_n - E_0\}}{T\overline{N}} \lambda_n \delta_{m,n} \tag{3.43}$$

One sees from this that the stochastic variables for different entropy modes are uncorrelated. This is a necessary condition for the stochastic trajectory, Eq. (2.10). One also sees that the λ_n, in addition to being real, should have the same sign as $E_n - E_0$. Apart from this the λ_n can be chosen as convenient.

Taking the scalar product of both sides of the stationarity condition, Eq. (3.38), one has

$$\begin{aligned} &\left\langle \zeta_m^S \right| \hat{\mathcal{R}} e^{-\hat{\mathcal{H}}/k_B T} \hat{\mathcal{R}}^\dagger \left| \zeta_m^S \right\rangle_{stoch} \\ &\quad = -\frac{|\tau|}{2} \left\langle \zeta_m^S \right| \left[\hat{\lambda} \hat{S}'' e^{-\hat{\mathcal{H}}/k_B T} + e^{-\hat{\mathcal{H}}/k_B T} \hat{S}'' \hat{\lambda} \right] \left| \zeta_m^S \right\rangle \\ &\quad = -|\tau| \lambda_n S_n'' e^{-E_n/k_B T} \delta_{m,n} \end{aligned} \tag{3.44}$$

Using the ansatz for the stochastic operator, the left hand side is just $e^{-E_n/k_B T} \langle r_m r_n^* \rangle_{stoch}$, and so one sees that this is the same as the covariance derived from the unitary condition, Eq. (3.43).

A second ansatz is to take both the drag operator and the stochastic operator to be proportional to the entropy fluctuation operator,

$$\hat{\lambda} = -\lambda \hat{S}'' \text{ and } \hat{R} = r \hat{S}'' \tag{3.45}$$

with λ real and positive. In this case also the unitary condition and the stationary condition yield the same variance, namely

$$\langle r^2 \rangle_{stoch} = |\tau| \lambda \tag{3.46}$$

Again this ansatz yields an operator that is diagonal in the entropy basis, as required by Eq. (2.10).

Equations (3.43) and Eq. (3.46) are forms of the quantum fluctuation dissipation theorem. They say that the variance of the stochastic operator, which controls the fluctuation, must be linearly proportional to the drag operator, which controls the dissipation. The variance is proportional to the duration

of the time step, so it is an irreversible contribution to the evolution of the wave function. It is positive, since $\lambda_n > 0$, provided that $E_n > E_0$, or, $S'' < 0$. In the various equations above, one typically sets $\overline{N} = 1$.

From the explicit expression for the stochastic dissipative time propagator, Eq. (3.26), and using the present result of the fluctuation-dissipation theorem that $\hat{\lambda}$ and $\hat{S}''$ commute, one sees that the time propagator has the symmetry

$$\hat{\mathcal{U}}(\tau)^\dagger = \hat{\mathcal{U}}(-\tau) \tag{3.47}$$

(This holds after averaging over the stochastic operator.) This is equivalent to the symmetry identified for the classical conditional transition probability density in Eq. (7.164) of Ref. 2, $\wp(\mathbf{\Gamma}_2|\mathbf{\Gamma}_1, \Delta_t) = \wp((\mathbf{\Gamma}_2^\dagger|\mathbf{\Gamma}_1^\dagger, -\Delta_t)$.

3.3.4 Time Average over a Trajectory

In the precis for the paper, 2.1, it was stated that one required the wave function generated by the stochastic propagator $\psi(t)$ to be such that the time average (equivalently stochastic average, or statistical average) of the density matrix operator formed from it equals the canonical equilibrium probability operator,

$$\hat{\wp} = \frac{1}{t}\int_0^t dt', \frac{1}{N(\psi(t'))} |\psi(t')\rangle \langle\psi(t')| \tag{3.48}$$

If this is the case then the time average of the expectation value of an operator equals that given by the conventional von Neumann form, as shown in Eq. (2.9),

$$\langle \hat{O} \rangle_{stat} = \mathrm{Tr}\hat{\wp}\hat{O} = \frac{1}{t}\int_0^t dt', \frac{1}{N(\psi(t'))} \frac{\langle\psi(t')|\hat{O}|\psi(t')\rangle}{\langle\psi(t')|\psi(t')\rangle} \tag{3.49}$$

Since the probability operator must be stationary, inserting the propagator into the density matrix gives

$$\begin{aligned}
\hat{\wp} &= \frac{1}{t}\int_0^t dt', \frac{1}{N(\psi(t'))} |\psi(t')\rangle \langle\psi(t')| \\
&= \frac{1}{t}\int_0^t dt', \frac{1}{N(\psi)} \hat{\mathcal{U}}(t')|\psi\rangle\langle\psi|\hat{\mathcal{U}}(t')^\dagger \\
&= \frac{1}{t}\int_0^t dt', \hat{\mathcal{U}}(t')\hat{\wp}\hat{\mathcal{U}}(t')^\dagger
\end{aligned} \tag{3.50}$$

(This assumes that the initial density matrix equals the Maxwell-Boltzmann operator.) This may be seen to be the same as the stationary condition invoked above, Eq. (3.36). Of course in addition to ensuring that the Maxwell-Boltzmann operator is stationary under the stochastic propagator, one should also investigate its stability and its independence from the initial conditions.

3.4 Transition Probability Operator and Time Correlation Function

3.4.1 Second Entropy Operator

The second entropy fluctuation operator appearing in Eq. (3.2) is $\hat{\mathcal{A}}^{(2)}(\tau, T)$. Its symmetries and small time expansion were obtained above. From this is readily obtained the second entropy operator, $\hat{S}^{(2)}(\tau, T)$, using the same method as for the first entropy, 2.2.3.

The second entropy can be written in terms of either operator,

$$\begin{aligned} S^{(2)}(\psi_2, \psi_1|\tau, T) &= \frac{\langle \psi_1, \psi_2| \hat{S}^{(2)}(\tau, T) |\psi_1, \psi_2\rangle}{\langle \psi_1, \psi_2 | \psi_1, \psi_2\rangle} \\ &= \langle \Delta\psi_1, \Delta\psi_2| \hat{\mathcal{A}}^{(2)}(\tau, T)(\tau, T) |\Delta\psi_1, \Delta\psi_2\rangle + \overline{S}^{(1)}(T) \end{aligned} \quad (3.51)$$

The equality holds to quadratic order. Multiplying both the right hand sides by the total magnitude, taking the cross second derivative, and evaluating it at $\psi_1 = \psi_2 = \overline{\psi}$, one obtains

$$\hat{S}^{(2)}(\tau, T) = \overline{N}^2 \hat{\mathcal{A}}^{(2)}(\tau, T) + \overline{S}^{(1)}(T)\hat{I}^{(2)} \quad (3.52)$$

the remaining terms vanishing. Recall $\overline{N} = \langle \overline{\psi}\ \overline{\psi} \rangle$, $E_0 = \langle \overline{\psi}| \hat{\mathcal{H}} |\overline{\psi}\rangle / \overline{N}$, $\overline{S}^{(1)}(T) = -E_0/T$, and $\hat{\mathcal{H}} |\overline{\psi}\rangle = E_0 |\overline{\psi}\rangle$.

Obviously the small time expansion of the second entropy operator follows directly from that obtained above for the second entropy fluctuation operator.

3.4.2 Time Correlation Function

The transition probability operator is just the exponential of the second entropy operator,

$$\hat{\wp}^{(2)}(\tau,T) = \frac{1}{Z^{(2)}(\tau,T)} e^{\hat{S}^{(2)}(\tau,T)/k_B} \tag{3.53}$$

With it, the statistical average of a two-time operator $\hat{O}^{(2)}$ is

$$\begin{aligned}
\langle \hat{O}^{(2)} \rangle_{\tau,T} &= \int d\psi_1 d\psi_2 \, \frac{\langle \psi_1, \psi_2 | \hat{\wp}^{(2)}(\tau,T) \hat{O}^{(2)} | \psi_1, \psi_2 \rangle}{\langle \psi_1, \psi_2 | \psi_1, \psi_2 \rangle} \\
&= \frac{1}{Z^{(2)}} \int d\underline{\psi}_1 d\underline{\psi}_2 \frac{1}{N(\psi_1) N(\psi_2)} \\
&\quad \times \sum_{\substack{m_2,n_2 \\ m_1,n_1}} \psi^*_{2,m_2} \psi_{2,n_2} \psi^*_{1,m_1} \psi_{1,n_1} \\
&\quad \times \left\{ e^{\hat{S}^{(2)}(\tau,T)/k_B} \hat{O}^{(2)} \right\}_{\substack{m_2,n_2 \\ m_1,n_1}} \\
&= \frac{\text{constant}}{Z^{(2)}} \sum_{m_2,m_1} \left\{ e^{\hat{S}^{(2)}(\tau,T)/k_B} \hat{O}^{(2)} \right\}_{\substack{m_2,n_2 \\ m_1,n_1}} \\
&= \mathrm{Tr}^{(2)} \left\{ \hat{\wp}^{(2)}(\tau,T) \hat{O}^{(2)} \right\}
\end{aligned} \tag{3.54}$$

In passing to the third equality, the same trick as in Eq. (2.3) has been used, namely that all the terms in the integrand are odd except those with $m_2 = n_2$ and $m_1 = n_1$. This is the dual collapse of the wave functions at the termini of the transition. Once the representation of the product of the operators has been taken outside of the integral, what remains is the same for all indices, and hence the integral is a constant that can be taken outside of the sum and incorporated into the partition function.

The transition probability operator is $\hat{\wp}^{(2)}(\tau,T) \equiv e^{\hat{S}^{(2)}(\tau,T)/k_B} / Z'^{(2)}$ with the partition function being

$$\begin{aligned}
Z'^{(2)}(\tau,T) &= \mathrm{Tr}^{(2)} e^{\hat{S}^{(2)}(\tau,T)/k_B} \\
&= \sum_{m_2,m_1} \langle \zeta_{m_2}, \zeta_{m_1} | \, e^{\hat{S}^{(2)}(\tau,T)/k_B} \, | \zeta_{n_1}, \zeta_{n_2} \rangle
\end{aligned} \tag{3.55}$$

with the ζ being an arbitrary orthonormal basis. The elements of the transition matrix are explicitly

$$\wp(2)^{m_2,n_2}_{m_1,n_1} = \langle \zeta_{m_2}, \zeta_{m_1} | \wp(2)(\tau,T) \, | \zeta_{n_1}, \zeta_{n_2} \rangle \tag{3.56}$$

and similarly for the operator matrix. Hence the two-time trace is explicitly

$$\mathrm{Tr}^{(2)}\left\{\hat{\wp}^{(2)}\hat{O}^{(2)}\right\} = \sum_{\substack{m_2,n_2\\m_1,n_1}} \wp^{(2)}_{\substack{m_2,n_2\\m_1,n_1}} O^{(2)}_{\substack{n_2,m_2\\n_1,m_1}} \tag{3.57}$$

A common quantity is the time correlation of two one-time operators. To obtain this one can introduce the diagonal two-time operator, $\hat{D}^{(2)}_{BA}$, which has the expectation

$$\frac{\langle\psi_2,\psi_1|\,\hat{D}^{(2)}_{BA}\,|\psi_2,\psi_1\rangle}{N(\psi_1)N(\psi_2)} = \frac{\langle\psi_2|\,\hat{B}\,|\psi_2\rangle}{N(\psi_2)}\frac{\langle\psi_1|\,\hat{A}\,|\psi_1\rangle}{N(\psi_1)} \tag{3.58}$$

The time correlation function will shortly be expressed in terms of this and the transition probability operator.

Choose $\langle\hat{A}\rangle_{stat} = \langle\hat{B}\rangle_{stat} = 0$. Define the time correlation function as

$$C_{BA}(\tau) = \langle\hat{B}(\tau)\hat{A}(0)\rangle_{stat} = \langle\hat{A}(0)\hat{B}(\tau)\rangle_{stat} \tag{3.59}$$

For a two-time average such as this, the positional order of the operators is irrelevant because the sign of τ gives the order of their application. This contrasts with a one-time average, where it is conventional that the position of the operators in the equation designates the time order of their application, which is to say that they are applied in order from right to left. The order of course is significant if the operators don't commute.

In view of the definitions of the two-time and one-time averages, in the zero time limit one has

$$C_{BA}(0^+) = \langle\hat{B}\hat{A}\rangle_{stat} \text{ and } C_{BA}(0^-) = \langle\hat{A}\hat{B}\rangle_{stat} \tag{3.60}$$

The right hand sides are one-time averages, which are here signified by the absence of a time argument. These expressions mean that if the operators don't commute, then there is a discontinuity at $\tau = 0$.

Time homogeneity means that the time correlation function must be invariant to a shift in the time origin. Hence first changing $\tau \Rightarrow t+\tau$, and then setting $t = -\tau$ such that $\hat{B}(\tau)\hat{A}(0) \Rightarrow \hat{B}(t+\tau)\hat{A}(t) \Rightarrow \hat{B}(0)\hat{A}(-\tau)$, must leave the time correlation function unchanged. From this one concludes that

$$C_{AB}(\tau) = C_{BA}(-\tau) \tag{3.61}$$

This can be called time homogeneity or statistical symmetry.

In view of the above, the small time expansion of the time correlation function must be of the form

$$C_{AB}(\tau) = C_{AB;0} + \hat{\tau} C'_{AB;0} + |\tau| C_{AB;1} + \tau C'_{AB;1} \tag{3.62}$$

with

$$C_{AB;0} = \frac{1}{2}\langle \hat{A}\hat{B} + \hat{B}\hat{A} \rangle_{stat} \tag{3.63}$$

and

$$C'_{AB;0} = \frac{1}{2}\langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle_{stat} \tag{3.64}$$

In terms of the diagonal two-time operator and the transition probability operator, and not explicitly showing the temperature dependence, the time correlation function is

$$\begin{aligned} C_{AB}(\tau) &= \langle \hat{D}^{(2)}_{BA} \rangle_{stat} \\ &= \mathrm{Tr}^{(2)} \left\{ \hat{\wp}^{(2)}(\tau) \hat{D}^{(2)}_{BA} \right\} \\ &= \sum_{\substack{m_2,n_2 \\ m_1,n_1}} \wp^{(2)}_{\substack{m_2,n_2 \\ m_1,n_1}}(\tau) B_{n_2,m_2} A_{n_1,m_1} \end{aligned} \tag{3.65}$$

If one uses the basis $\{\zeta^A_n\}$ for ψ_1 and $\{\zeta^B_n\}$ for ψ_2, then the operator matrices are diagonal and this becomes

$$\begin{aligned} C_{AB}(\tau) &= \sum_{\substack{n_2 \\ n_1}} \wp^{(2)}_{\substack{n_2,n_2 \\ n_1,n_1}}(\tau) B_{n_2,n_2} A_{n_1,n_1} \\ &= \sum_{n_2,n_1} \wp^{(2)}_{n_2,n_1}(\tau) B_{n_2,n_2} A_{n_1,n_1} \end{aligned} \tag{3.66}$$

One can therefore identify $\wp^{(2),BA}_{mn}(\tau)$ as the unconditional probability of the transition between states of the two operators,

$$\wp^{(2),BA}_{mn}(\tau) \equiv \wp^{(2),BA}_{\substack{m,m \\ n,n}}(\tau) = \left\langle \zeta^B_m, \zeta^A_n \middle| \wp^{(2)}(\tau) \middle| \zeta^B_m, \zeta^A_n \right\rangle \tag{3.67}$$

In view of the time homogeneity (statistical) symmetry, Eq. (3.61), the above representation of the time correlation function, Eq. (3.65), shows that

$$\wp^{(2)}_{\substack{m_2,n_2 \\ m_1,n_1}}(\tau) = \wp^{(2)}_{\substack{m_1,n_1 \\ m_2,n_2}}(-\tau) \tag{3.68}$$

One can see explicitly that this condition is guaranteed by the statistical symmetry of the second entropy, Eq. (3.3), $S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_1, \psi_2; -\tau)$, or, equivalently, $\hat{a}(-\tau) = \hat{c}(\tau)$ and $\hat{b}(-\tau) = \hat{b}(\tau)^\dagger$.

3.4.3 Time Correlation with Propagator

It is desired to write the time correlation function as a one time trace involving the stochastic time propagator. The most straightforward expression is

$$\begin{aligned} C_{BA}(\tau) &= \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(\tau)^\dagger\hat{B}\hat{\mathcal{U}}(\tau)\hat{A}\hat{\wp}\rangle_{stoch} \\ &= \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(-\tau)^\dagger\hat{A}\hat{\mathcal{U}}(-\tau)\hat{B}\hat{\wp}\rangle_{stoch} \end{aligned} \tag{3.69}$$

For non-zero $\tau > 0$, both forms unambiguously signify that the operator $\hat{A}$ is applied before the operator $\hat{B}$, and *vice versa* for $\tau < 0$. Unfortunately, due to the discontinuity in the time correlation function, there is an ambiguity in this expression at $\tau = 0$.

To circumvent this problem, and because of the convention that the operators are applied in order from right to left for one-time averages, one needs to define the operator

$$\begin{aligned} \hat{\eta}_{BA}(\tau) &= \frac{1+\hat{\tau}}{2}\hat{B} + \frac{1-\hat{\tau}}{2}\hat{A} \\ &= \begin{cases} \hat{B} & \tau > 0 \\ \hat{A} & \tau < 0 \end{cases} \end{aligned} \tag{3.70}$$

Recall that $\hat{\tau} \equiv \mathrm{sign}\ \tau$. With this the time correlation function in singlet form is

$$C_{BA}(\tau) = \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(|\tau|)^\dagger\hat{\eta}_{BA}(\tau)\hat{\mathcal{U}}(|\tau|)\hat{\eta}_{BA}(-\tau)\hat{\wp}\rangle_{stoch} \tag{3.71}$$

The definitions have the effect that the operator that is applied first in time always occupies the right hand position, which is the usual convention for non-commuting operators. In addition, the time propagator always proceeds in the positive time direction. Since $\hat{\eta}_{AB}(-\tau) = \hat{\eta}_{BA}(\tau)$, it is clear that $C_{BA}(-\tau) = C_{AB}(\tau)$, as required.

Explicitly the time correlation function is

$$\begin{aligned} C_{BA}(\tau) &= \begin{cases} \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(\tau)^\dagger\hat{B}\hat{\mathcal{U}}(\tau)\hat{A}\hat{\wp}\rangle_{stoch} & \tau > 0 \\ \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(-\tau)^\dagger\hat{A}\hat{\mathcal{U}}(-\tau)\hat{B}\hat{\wp}\rangle_{stoch} & \tau < 0 \end{cases} \\ &= \begin{cases} \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(\tau)^\dagger\hat{B}\hat{\mathcal{U}}(\tau)\hat{A}\hat{\wp}\rangle_{stoch} & \tau > 0 \\ \mathrm{Tr}^{(1)}\langle\hat{\mathcal{U}}(\tau)^\dagger\hat{B}\hat{\mathcal{U}}(\tau)\hat{\wp}\hat{A}\rangle_{stoch} & \tau < 0 \end{cases} \end{aligned} \tag{3.72}$$

The second equality uses the facts that the trace is invariant to cyclic permutations of the operators, that $\hat{\mathcal{U}}(-\tau) = \hat{\mathcal{U}}(\tau)^\dagger$, and that the equilibrium probability operator and the time propagator commute. In the limit $\tau \to 0$, $\hat{\mathcal{U}}(\tau) \to \hat{I}$, and

$$C_{BA}(0^+) = \mathrm{Tr}^{(1)} \hat{B}\hat{A}\hat{\wp} = \langle \hat{B}\hat{A} \rangle_{stat} \tag{3.73}$$

and

$$C_{BA}(0^-) = \mathrm{Tr}^{(1)} \hat{A}\hat{B}\hat{\wp} = \langle \hat{A}\hat{B} \rangle_{stat} \tag{3.74}$$

as required.

In a particular representation of the operators, the average that is the time correlation function for $\tau > 0$ is

$$\begin{aligned} C_{BA}(\tau) &= \mathrm{Tr}^{(1)} \langle \hat{\mathcal{U}}(\tau)^\dagger \hat{B} \hat{\mathcal{U}}(\tau) \hat{A}\hat{\wp} \rangle_{stoch} \quad , \ \tau > 0 \\ &= \sum_{\substack{m_2,n_2 \\ m_1,n_1}} \sum_l \langle \mathcal{U}_{m_1,n_2}(\tau)^\dagger \mathcal{U}_{m_2,l}(\tau) \wp_{n_1,m_1} \rangle_{stoch} B_{n_2,m_2} A_{l,n_1} \\ &= \mathrm{Tr}^{(1)} \langle \hat{\mathcal{U}}(\tau)^\dagger \hat{\wp} \hat{B} \hat{\mathcal{U}}(\tau) \hat{A} \rangle_{stoch} \\ &= \sum_{\substack{m_2,n_2 \\ m_1,n_1}} \sum_l \langle \mathcal{U}_{m_1,l}(\tau)^\dagger \mathcal{U}_{n_2,n_1}(\tau) \wp_{l,m_2} \rangle_{stoch} B_{m_2,n_2} A_{n_1,m_1} \end{aligned} \tag{3.75}$$

The third equality uses the fact that the time propagator and the probability operator commute. Comparing this to the third equality in Eq. (3.71), this implies that the representation of the transition probability operator in terms of time propagators is

$$\begin{aligned} &\wp^{(2)}_{\substack{m_2,n_2 \\ m_1,n_1}}(\tau) \\ &\quad = \sum_l \langle \mathcal{U}_{l,n_2}(\tau)^\dagger \mathcal{U}_{m_2,n_1}(\tau) \wp_{m_2,l} \rangle_{stoch} \ , \ \tau > 0 \\ &\quad = \sum_l \langle \mathcal{U}_{m_1,l}(\tau)^\dagger \mathcal{U}_{m_2,n_1}(\tau) \wp_{l,n_2} \rangle_{stoch} \ , \ \tau > 0 \end{aligned} \tag{3.76}$$

For $\tau < 0$, swap the upper and lower rows of subscripts on the left hand side, as in Eq. (3.68). In the double entropy basis this is

$$\wp^{(2),SS}_{\substack{m_2,n_2 \\ m_1,n_1}}(\tau) = \langle \mathcal{U}_{n_2,n_2}(\tau)^\dagger \mathcal{U}_{n_1,n_1}(\tau) \wp^S_{n_2,n_2} \rangle_{stoch} \delta_{m_2,n_1} \delta_{m_1,n_2} \ , \ \tau > 0 \tag{3.77}$$

Recall that the probability operator and the time propagator are diagonal in the entropy representation.

As a check that the time propagator expression for the time correlation function is correct, the leading order terms in the small τ expansion of both sides of Eq. (3.77) will now be obtained explicitly. The right hand side is

$$\mathrm{RHS}^{SS}_{\substack{m_2,n_2\\m_1,n_1}} = \frac{\delta_{m_2,n_1}\delta_{m_1,n_2}}{Z}\left\langle e^{S^S_{n_2,n_2}/k_B}\mathcal{U}^S_{n_2,n_2}(\tau)^\dagger \mathcal{U}^S_{n_1,n_1}\right\rangle_{stoch} \quad , \quad \tau > 0 \tag{3.78}$$

Now with $\hat{\lambda} \equiv \sum_n \lambda_n |\zeta^S_n\rangle\langle\zeta^S_n|$ and $\hat{\mathcal{R}} \equiv \sum_n r_n |\zeta^S_n\rangle\langle\zeta^S_n|$ the stochastic propagator is

$$\begin{aligned}\mathcal{U}^S_{m,n}(\tau) &= \left\{\hat{I} + \frac{\tau}{i\hbar}[\hat{\mathcal{H}} - E_0\hat{I}] - \frac{|\tau|}{2T\overline{N}}\hat{\lambda}[\hat{\mathcal{H}} - E_0\hat{I}] + \hat{\mathcal{R}}\right\}^S_{m,n}\\ &= \left\{1 + \frac{\tau}{i\hbar}[E_n - E_0] - \frac{|\tau|}{2T\overline{N}}\lambda_n[E_n - E_0] + r_n\right\}\delta_{m,n}\end{aligned} \tag{3.79}$$

Using this and the variance of the random operator, to linear order in the time step the right hand side of the transition probability, Eq. (3.77), is

$$\begin{aligned}&\mathrm{RHS}^{SS}_{\substack{m_2,n_2\\m_1,n_1}}\\ &= \frac{\delta_{m_1,n_2}\delta_{m_2,n_1}}{Z}e^{S^S_{n_1,n_1}/k_B}\\ &\quad\times\left\{1 + \frac{\tau}{i\hbar}[E_{n_1} - E_{n_2}]\right.\\ &\quad - \frac{|\tau|}{2T\overline{N}}(\lambda_{n_1}[E_{n_1} - E_0] + \lambda_{n_2}[E_{n_2} - E_0]\\ &\quad\left. + \frac{|\tau|\lambda_{n_1}[E_{n_1} - E_0]}{2T\overline{N}}\delta_{m_1,n_1}\right\}\end{aligned} \tag{3.80}$$

The double diagonal part of this is

$$\mathrm{RHS}^{SS}_{\substack{m,m\\m,m}} = \frac{1}{Z}e^{S^S_{m,m}/k_B} \tag{3.81}$$

This is just the singlet probability. These diagonal terms are independent of the choice of the λ_n. For these the time correlation function is independent of the specific model of the reservoir interactions with the sub-system.

The non-diagonal terms are the ones that depend upon the time step, and this means that the time correlation function as a function of τ will depend upon the drag coefficients. However, since the reservoir should represent a weak

perturbation of the sub-system (the boundary region should be much smaller than the sub-system itself), the magnitudes of the λ_n should be small enough that the irreversible term (the one proportional to $|\tau|$ should be dominated by the adiabatic, reversible term (the one proportional to τ).

In order to show that this is equal to the left hand side of Eq. (3.77), which are the coefficients of the transition probability matrix, the eigenfunctions of the second entropy operator are required. Recall that the domain is $\mathsf{H} \otimes \mathsf{H}$, and so one can invoke a basis of the form $\{|\zeta_{m_2}\rangle, |\zeta_{m_1}\rangle\}$. (One could normalize this by a factor of $\sqrt{2}$.) In quantum mechanics one can neglect an overall phase factor for the wave function. However in the present case there is the possibility of a phase difference between the two Hilbert spaces and this should be considered. In particular the basis $\{-|\zeta_{m_2}\rangle, |\zeta_{m_1}\rangle\}$ differs from the first basis by a phase of π and spans a space orthogonal to that spanned by the first one. In the following analysis wave functions will be projected onto the sub-space spanned by the first basis on the grounds that it is the dominant one. The first reason for this is that the small time step limit is being considered, in which case the phase of ψ_2 must be almost the same as that of ψ_1. The second reason is that it will be shown that the leading eigenfunction in the second basis is negative and diverges in the small time step limit. Because this appears in the exponent of the transition probability, it contributes negligibly to the transition.

The second entropy operator acting on a basis vector in the double entropy basis is

$$\begin{aligned}
&\hat{S}^{(2)}(\tau)\begin{pmatrix}|\zeta^S_{m_2}\rangle\\ |\zeta^S_{m_1}\rangle\end{pmatrix}\\
&\quad= \left[2\overline{N}\hat{\mathcal{A}}^{(2)}\overline{S}^{(1)}\hat{I}^{(2)}\right]\begin{pmatrix}|\zeta^S_{m_2}\rangle\\ |\zeta^S_{m_1}\rangle\end{pmatrix}\\
&\quad= 2\overline{N}\begin{pmatrix}\hat{a}(\tau) & \hat{b}(\tau)\\ \hat{b}(\tau)^\dagger & \hat{c}(\tau)\end{pmatrix}\begin{pmatrix}|\zeta^S_{m_2}\rangle\\ |\zeta^S_{m_1}\rangle\end{pmatrix} + \overline{S}^{(1)}\begin{pmatrix}|\zeta^S_{m_2}\rangle\\ |\zeta^S_{m_1}\rangle\end{pmatrix}\\
&\quad= 2\overline{N}\begin{pmatrix}-\frac{\hat{\lambda}^{-1}}{|\tau|} + \hat{a}_0 + \hat{\tau}\hat{a}'_0 & \frac{\hat{\lambda}^{-1}}{|\tau|} + \hat{b}_0\\ \frac{\hat{\lambda}^{-1}}{|\tau|} + \hat{b}_0 & -\frac{\hat{\lambda}^{-1}}{|\tau|} + \hat{a}_0 - \hat{\tau}\hat{a}'_0\end{pmatrix}\begin{pmatrix}|\zeta^S_{m_2}\rangle\\ |\zeta^S_{m_1}\rangle\end{pmatrix}\\
&\quad= \overline{S}^{(1)}\begin{pmatrix}|\zeta^S_{m_2}\rangle\\ |\zeta^S_{m_1}\rangle\end{pmatrix} + \mathcal{O}(\tau)
\end{aligned} \tag{3.82}$$

It is clear that to leading order the eigenfunctions are of the form $|\zeta_m^S, \zeta_m^S\rangle$ with eigenvalue $\overline{S}^{(1)}$, and $|-\zeta_m^S, \zeta_m^S\rangle$ with eigenvalue $-4\overline{N}\lambda_m^{-1}/|\tau|$. The latter is large and negative in the small time step limit, and eigenfunctions of this form can be neglected.

One needs to go to the first correction to the leading eigenvalue in order to obtain its dependence on the modes. The next order eigenfunction has the form

$$\begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + \tau \begin{pmatrix} -\hat{\beta}\,|\zeta_m^S\rangle \\ \hat{\beta}\,|\zeta_m^S\rangle \end{pmatrix} + |\tau| \begin{pmatrix} -\hat{\gamma}\,|\zeta_m^S\rangle \\ \hat{\gamma}\,|\zeta_m^S\rangle \end{pmatrix} \tag{3.83}$$

With this the second order term, $\mathcal{O}(\tau^0)$, for the right hand side of the eigenfunction equation is

$$\begin{aligned} \text{RHS} = 4\overline{N} \begin{pmatrix} (\hat{\tau}\hat{\beta} + \hat{\gamma})\hat{\lambda}^{-1}\,|\zeta_m^S\rangle \\ -(\hat{\tau}\hat{\beta} + \hat{\gamma})\hat{\lambda}^{-1}\,|\zeta_m^S\rangle \end{pmatrix} + \overline{S}^{(1)} \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} \\ + 2\overline{N} \begin{pmatrix} (\hat{a}_0 + \hat{b}_0 + \hat{\tau}\hat{a}_0')\,|\zeta_m^S\rangle \\ (\hat{a}_0 + \hat{b}_0 - \hat{\tau}\hat{a}_0')\,|\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau) \end{aligned} \tag{3.84}$$

In order for this to be an eigenfunction, $\hat{\gamma}$ must equal zero. The coefficient $\hat{\tau} \equiv \operatorname{sign}\tau$ vanishes when

$$\hat{\beta} = -\frac{1}{2}\hat{a}_0'\hat{\lambda} \tag{3.85}$$

One now has, to the two leading orders,

$$\begin{aligned} \text{RHS} &= \overline{S}^{(1)} \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + 2\overline{N} \begin{pmatrix} (\hat{a}_0 + \hat{b}_0)\,|\zeta_m^S\rangle \\ (\hat{a}_0 + \hat{b}_0)\,|\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau) \\ &= \overline{S}^{(1)} \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + \overline{N} \begin{pmatrix} \hat{S}''\,|\zeta_m^S\rangle \\ \hat{S}''\,|\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau) \\ &= \left[\overline{S}^{(1)} - \frac{E_m - E_0}{T}\right] \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau) \end{aligned} \tag{3.86}$$

The prefactor is the eigenvalue. The constant parts of this will be incorporated into the the normalizing partition function $Z^{(2)}(\tau)$, leaving the m-dependent part, which is just $S_{mm}^S = -E_m/T$. With this result, the double diagonal entries of the transition probability in the double entropy basis, the

left hand side of Eq. (3.77), are

$$\begin{aligned}\wp^{(2),SS}_{\substack{m,m\\m,m}} &= \frac{1}{Z^{(2)}(\tau)}\left\langle \zeta^S_m, \zeta^S_m\right| e^{\hat{S}^{(2)}/k_B}\left|\zeta^S_m, \zeta^S_m\right\rangle \\ &= \frac{1}{Z'^{(2)}(\tau)} e^{S^2_{mm}/k_B}\end{aligned} \tag{3.87}$$

One sees that this is equal to the right hand side, Eq. (3.81), which tends to confirm the validity of the propagator expression for the time correlation function, Eq. (3.71). Unfortunately it is not possible to carry out the check to $\mathcal{O}(\tau)$ because the expansion for the second entropy is only valid to $\mathcal{O}(\tau^0)$

3.4.4 Parity

Operators that represent physical observables are Hermitian, $\hat{A} = \hat{A}^\dagger$. Without loss of generality they may be taken to be either real or imaginary, since, if complex, they can be split into their real and imaginary parts. Let $\epsilon_A = \pm 1$ denote the parity of the operator, $\hat{A} = \epsilon_A \hat{A}^* = \epsilon_A \hat{A}^T$, and similarly for other operators.

The expectation value in the wave state ψ is

$$A(\psi) = \frac{\underline{\underline{A}} : \underline{\psi}\underline{\psi}^*}{\underline{\psi}^* \cdot \underline{\psi}} \tag{3.88}$$

and that in the wave state ψ^* is

$$A(\psi^*) = \frac{\underline{\underline{A}} : \underline{\psi}^*\underline{\psi}}{\underline{\psi} \cdot \underline{\psi}^*} = \frac{\underline{\underline{A}}^T : \underline{\psi}\underline{\psi}^*}{\underline{\psi}^* \cdot \underline{\psi}} = \epsilon_A A(\psi) \tag{3.89}$$

Since conjugation of the wave state represents velocity reversal, one sees from this that the parity of an operator signifies whether it is even or odd under time reversal.

An Hermitian operator has real expectation value. Hence $C_{BA}(0)$ is real if, and only if, $\hat{B}\hat{A}$ is Hermitian. Since the two operators are individually Hermitian, this implies that they must commute,

$$C_{BA}(0)^* = C_{BA}(0) \Leftrightarrow \hat{B}\hat{A} = \hat{A}\hat{B} \tag{3.90}$$

In this case $C_{BA}(0^+) = C_{BA}(0^-)$.

Explicitly one has

$$\begin{aligned} C_{BA}(0^+)^* &= \langle \hat{B}\hat{A} \rangle^*_{stat} \\ &= \int d\psi \, \frac{\langle \psi | \hat{\wp} \hat{B} \hat{A} | \psi \rangle}{\langle \psi \, | \, \psi \rangle^*} \\ &= \int d\underline{\psi} \, \frac{1}{N(\psi)} \underline{\psi} \cdot \underline{\underline{\wp}}^* \cdot \underline{\underline{B}}^* \cot \underline{\underline{A}}^* \cdot \underline{\psi}^* \\ &= \epsilon_A \epsilon_B \int d\underline{\psi} * \, \frac{1}{N(\psi)} \underline{\psi}^* \cdot \underline{\underline{\wp}} \cdot \underline{\underline{B}} \cot \underline{\underline{A}} \cdot \underline{\psi} \\ &= \epsilon_A \epsilon_B C_{BA}(0) \end{aligned} \tag{3.91}$$

The final equality follows because the integral is over all of Hilbert space, and so $\underline{\psi}^*$ is a dummy variable of integration. Since the time correlation function is real if the operators commute, this proves that

$$\langle \hat{B}(0) \hat{A}(0) \rangle_{stat} = 0 \text{ if } \epsilon_A \neq \epsilon_B \text{ and } \hat{B}\hat{A} = \hat{A}\hat{B} \tag{3.92}$$

In other words, commuting operators with opposite parity are instantaneously uncorrelated. If the operators do not commute and have opposite parity, then the time correlation function at $\tau = 0$ is imaginary, $C_{BA}(0^+)^* = -C_{BA}(0^+)$. Hence one can say that in general $\mathrm{Re}\, C_{BA}(0) = 0$ if $\epsilon_A \neq \epsilon_B$.

From the symmetry conditions for the second entropy given in §3.1.1, one sees that the complex conjugate of the transition probability operator has the symmetry

$$\hat{\wp}^{(2)}(\tau)^* = \hat{\wp}^{(2)}(-\tau) \tag{3.93}$$

Accordingly

$$\begin{aligned} C_{BA}(\tau)^* &= \mathrm{Tr}^{(2)} \hat{\wp}^{(2)}(\tau)^* \{ \hat{B}^*, \hat{A}^* \} \\ &= \epsilon_A \epsilon_B \mathrm{Tr}^{(2)} \hat{\wp}^{(2)}(-\tau) \{ \hat{B}^*, \hat{A}^* \} \\ &= \epsilon_A \epsilon_B C_{BA}(-\tau) \end{aligned} \tag{3.94}$$

If $\hat{A}(\tau)$ and $\hat{B}(\tau)$ commute, then their time correlation function is real, $C_{BA}(\tau)^* = C_{BA}(\tau)$. In this case

$$C_{BA}(\tau) = \epsilon_A \epsilon_B C_{BA}(-\tau) = \epsilon_A \epsilon_B C_{AB}(\tau) \tag{3.95}$$

This may also be seen from the propagator expression, Eq. (3.71). Noting that $\hat{\mathcal{U}}(\tau)^* = \hat{\mathcal{U}}(-\tau)$, and assuming that the time correlation function is real, one has

$$\begin{aligned} C_{BA}(\tau) &= C_{BA}(\tau)^* \\ &= \mathrm{Tr}^{(1)}\langle \hat{\mathcal{U}}(\tau)^\dagger \hat{B}\hat{\mathcal{U}}(\tau)\hat{A}\hat{\wp}\rangle^*_{stoch} \\ &= \mathrm{Tr}^{(1)}\langle \hat{\mathcal{U}}(\tau)^{\dagger *} \hat{B}^*\hat{\mathcal{U}}(\tau)^* \hat{A}^*\hat{\wp}^*\rangle_{stoch} \\ &= \epsilon_A\epsilon_B \mathrm{Tr}^{(1)}\langle \hat{\mathcal{U}}(-\tau)^\dagger \hat{B}\hat{\mathcal{U}}(-\tau)\hat{A}\hat{\wp}\rangle^*_{stoch} \\ &= \epsilon_A\epsilon_B C_{BA}(-\tau) \end{aligned} \tag{3.96}$$

This result is the analogue of the classical result given in §2.5.1 of Ref. 2.

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