Quantum Statistical Mechanics. III. Equilibrium Probability

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Given are a first principles derivation and formulation of the probabilistic concepts that underly equilibrium quantum statistical mechanics. The transition to non-equilibrium probability is traversed briefly.

Introduction

This paper continues a series that ultimately aims to establish the theory of non-equilibrium quantum statistical mechanics. The first two papers in the series dealt with the canonical equilibrium system, namely a sub-system able to exchange energy with a fixed temperature reservoir.\(^1\)

The first paper\(^1\) showed that the wave function collapsed into entropy pure quantum states, due to entanglement resulting from energy conservation, and that consequently the average of an operator observable could be written as the sum over quantum states of the product of the probability and observable operators. The probability operator was shown to be the usual Maxwell-Boltzmann operator. These three results —the wave function collapse, the von Neumann trace, and the Maxwell-Boltzmann probability operator—are well known (see Refs. [3–5] in general, and Refs. [6–13] for wave function collapse). It is the derivation given in Paper I that is of most interest.\(^1\)

The second paper\(^2\) derived the stochastic dissipative Schrödinger equation for an open quantum system, namely a sub-system of a thermal reservoir, the canonical equilibrium system. Other modified versions of the Schrödinger equation exist (e.g. Refs [14–20], and also Refs [21–22]). The novelty of the stochastic dissipative Schrödinger equation derived in Paper II\(^2\) was the first principles derivation based upon maximizing the transition entropy. Also, it was shown that the stochastic dissipative propagator had to obey a quantum fluctuation dissipation theorem that guaranteed the stationarity of the Maxwell-Boltzmann probability operator.

In a sense this, the third paper in the series, is an intermezzo between the equilibrium and the non-equilibrium theory. It addresses certain issues that are required for the formulation of the non-equilibrium theory, which necessitates returning to a first principles understanding of the set theoretic basis for probability theory itself in a way that is consistent with quantum theory. This paper performs the analysis in an equilibrium context. Three new results emerge beyond those already given in Papers I and II.\(^1,2\) First, in Paper II\(^2\) the stochastic dissipative time propagator was taken to be unitary, for reasons of sufficiency and convenience. Here it is shown that the unitary condition is a necessary consequence of the reduction condition on the second entropy. Second, the two-time operator product of the forward and backward time propagators is here shown to be equal to the conditional transition probability operator. Third, a more exact understanding of the approximate nature of the quadratic fluctuation form for the transition entropy operator is developed in the present paper compared to Paper II.\(^2\) Beyond these equilibrium results that revisit Paper II—three steps backward as it were—the set theoretic basis of non-equilibrium probability theory is summarized in IV. This is a small but necessary step toward the full non-equilibrium theory that is intended for the future.

I. NATURE OF PROBABILITY IN QUANTUM SYSTEMS

A. States

In modeling a quantum system, one has to specify the finest level of description that will be used, which comes down to choosing a basis for the wave function. Typically such a basis can be taken to be the set of eigenfunctions of some operator, or set of commuting operators. As far as the chosen level of description is concerned, the basis and the operator are complete. Of course in actual fact the real system may contain further degrees of freedom or levels of description, and one should have some reason for believing that these are not directly relevant to the problem at hand and can be neglected.

The finest level of description chosen will be called the microstates of the system, and these correspond to the eigenstates of an operator. Different operators yield different sets of eigenstates, and different sets of eigenfunctions that serve as the basis for the Hilbert space of the wave function. Hence there is more than one way to represent the microstates of a quantum system. A microstate of one representation is a superposition of microstates of another representation. A complete set of commuting operators (a complete operator, for short) yields non-degenerate eigenvalues, a distinct one for each microstate.

Macrostates may be defined by the principle quantum number of the states of an incomplete set of commuting operators (an incomplete operator, for short). Such incomplete operators still have a set of corresponding microstates or basis functions, but in this case the microstates are degenerate, with all microstates in each macrostate having the same principle quantum number.

Let \(A = A_a A_b \ldots\) be an operator composed of commuting operators that form a complete set.\(^4,5\) The case of most physical relevance is when the operators are Her-
mitian, although this is not essential for the formal development of the theory. The eigenvalue equation,
\[ \hat{A}|\zeta_n^A\rangle = A_n|\zeta_n^A\rangle, \]  
(1.1)
defines the quantum states of \( A \), \( n = 1, 2, \ldots \). The eigenfunctions form a complete orthonormal set, \( \langle \zeta_n^A | \zeta_m^A \rangle = \delta_{nm} \). An arbitrary wave function may be expanded as
\[ |\psi\rangle = \sum_n w_n^A|\zeta_n^A\rangle, \]  
with \( w_n^A = \langle \zeta_n^A | \psi \rangle \).

An important point is that for such a complete operator, the quantum states are non-degenerate: \( A_n = A_m \) if and only if \( n = m \). The quantum states of such a complete operator are the analogue of the classical microstates in the set theoretic formulation of probability for statistical mechanics.24,26

Let \( \hat{C} \) be an Hermitian operator that is not complete. The eigenvalue equation in this case may be written
\[ \hat{C}|\zeta_{nk}^C\rangle = C_\alpha|\zeta_{nk}^C\rangle. \]  
(1.2)
The Greek index is the principle quantum number and the Roman index labels the degeneracy. The eigenfunctions again form a complete orthonormal set, \( \langle \zeta_{nk}^C | \zeta_{mk}^C \rangle = \delta_{nk}\delta_{kl} \), and \( |\psi\rangle = \sum_{nk} w_{nk}^A|\zeta_{nk}^C\rangle \), with \( w_{nk}^A = \langle \zeta_{nk}^C | \psi \rangle \). In this form the principle quantum number uniquely specifies the eigenvalue: \( C_\alpha = C_\beta \) if and only if \( \alpha = \beta \).

For brevity, it is sometimes convenient not to label the degeneracy explicitly and to instead write,
\[ \hat{C}|\zeta_\alpha^C\rangle = C_\alpha|\zeta_\alpha^C\rangle. \]  
(1.3)
In this form the convention invoked here is that the principle quantum number still uniquely specifies the eigenvalue, \( C_\alpha = C_\beta \iff \alpha = \beta \). This means that the eigenfunction \( |\zeta_\alpha^C\rangle \) belongs to the sub-space spanned by the degenerate eigenfunctions of the principle quantum number, \( \langle \zeta_{\alpha}^C \rangle \). The size of the sub-space is the degeneracy of the macrostate, which is the number of microstates it contains; it is denoted \( N_\alpha^c \). The quantum states of such an incomplete operator labeled by the principle quantum number are the analogue of the classical macrostates in the set theoretic formulation of probability for statistical mechanics.24,26

### B. Weight

The set theoretic formulation of probability in statistical mechanics is based the existence of a weight for each microstate.24,26 The physical origin and value of such a weight is a question separate to the formal development of the probability theory. Here it can be mentioned that in Paper I it was shown that for an isolated quantum system, the energy microstate weights are all equal, and that without loss of generality their value can be set to unity. It was further shown that the weight operator was diagonal in the basis of the complete energy operator. From this one can conclude that the weight operator of an isolated quantum system is the identity operator.

However, the most useful application of quantum statistical mechanics is to open quantum systems, which is to say that one seeks to describe in microscopic detail the behavior of a sub-system that is interacting with a reservoir or environment that enters only through some macroscopic thermodynamic parameters. In this case the microstates of the sub-system do not have equal weight. For this reason the probability theory for quantum statistical mechanics is formulated in a general way without assuming anything about the microstate weights other than that they are real and positive.

Suppose that there is a weight operator \( \hat{\omega} \) that is Hermitian, \( \hat{\omega}^\dagger = \hat{\omega} \). In the equilibrium case, which is the focus of the present analysis, the weight operator is also real, \( \hat{\omega}^* = \hat{\omega} \) (see Table I). The matrix elements of the weight in the representation of the complete operator \( \hat{A} \) are
\[ w_{mn}^A = \frac{\langle \zeta_n^A | \hat{\omega} | \zeta_m^A \rangle}{\sqrt{\langle \zeta_n^A | \zeta_n^A \rangle \langle \zeta_m^A | \zeta_m^A \rangle}}. \]  
(1.4)

In this case the denominator is redundant because the eigenfunctions are normalized. The matrix is Hermitian, \( w_{mn}^{A*} = w_{nm}^A \).

The diagonal elements are the weight of the quantum states of the operator \( \hat{A} \),
\[ w_n^A \equiv w_{nn}^A = \frac{\langle \zeta_n^A | \hat{\omega} | \zeta_n^A \rangle}{\langle \zeta_n^A | \zeta_n^A \rangle}. \]  
(1.5)

Since the weight matrix is Hermitian, these diagonal elements are real. They are also non-negative. These diagonal elements of the representation of the weight of a complete operator are the quantum analogue of the weight of classical microstates.24,26 The off-diagonal elements have no classical analogue.

The total weight of the quantum system is the sum of the weights of the quantum states,
\[ W = \sum_n w_n^A = \sum_n \frac{\langle \zeta_n^A | \hat{\omega} | \zeta_n^A \rangle}{\langle \zeta_n^A | \zeta_n^A \rangle} = Tr \hat{\omega}. \]  
(1.6)

It will now be justified that this is indeed independent of the operator \( \hat{A} \).

Suppose that \( \hat{B} \) is also a complete operator. In this representation the elements of the weight operator matrix are
\[ w_{kl}^B = \langle \zeta_k^B | \hat{\omega} | \zeta_l^B \rangle = \sum_{mn} \langle \zeta_k^B | \zeta_m^B \rangle w_{mn}^A \langle \zeta_m^A | \zeta_l^B \rangle. \]  
(1.7)
The weight of the quantum states of \( \hat{B} \) are
\[ w_k^B \equiv w_{kk}^B = \sum_{mn} \langle \zeta_k^B | \zeta_m^B \rangle w_{mn}^A \langle \zeta_m^A | \zeta_k^B \rangle. \]  
(1.8)
The scalar product \( \langle \zeta_n^A | \zeta_k^B \rangle \) represents the proportion of the quantum state \( \{n, A\} \) that appears in the quantum
state \{k, B\}, and analogously for \(\langle \zeta^B_n | \zeta^A_n \rangle\). Hence this equation may be interpreted as redistributing the weight from one representation to another.

The total weight in the representation \(\hat{B}\) is

\[
W = \sum_k w_k^B = \sum_k \sum_m \langle \zeta^B_k | \zeta^A_m \rangle w_m^A \langle \zeta^A_n | \zeta^B_k \rangle = \sum_m \langle \zeta^A_n | \zeta^A_m \rangle w_m^A = \sum_m w_m^A = \text{Tr} \hat{w}.
\]

This confirms that the total weight is independent of the representation.

As above, \(\hat{C}\) is an incomplete Hermitian operator \(\hat{C}|\zeta^C_n\rangle = C_\alpha|\zeta^C_n\rangle\). One could represent the weight operator in the basis of \(\hat{C}\), with the matrix indexed by the principle quantum number and the matrix elements defined as usual,

\[
w^C_{\alpha\beta} \equiv \frac{\langle \zeta^C_\alpha | \hat{w} | \zeta^C_\beta \rangle}{\sqrt{\langle \zeta^C_\alpha | \zeta^C_\alpha \rangle \langle \zeta^C_\beta | \zeta^C_\beta \rangle}}.
\]

However this is of no direct use. Alternatively, one could index the matrix by the microstates,

\[
w^C_{\alpha k, \beta l} \equiv \frac{\langle \zeta^C_\alpha | \hat{w} | \zeta^C_\beta \rangle}{\sqrt{\langle \zeta^C_{\alpha k} | \zeta^C_{\alpha k} \rangle \langle \zeta^C_{\beta l} | \zeta^C_{\beta l} \rangle}}.
\]

This is more reasonable, and one may say that the weight of the microstates of the operator \(\hat{C}\) are \(w^C_{\alpha k} \equiv w^C_{\alpha k, \alpha k}\).

It is essential that the weight of a principle quantum state of such an incomplete operator is equal to the sum of the weight of the degenerate quantum states that it contains,

\[
w^C_{\alpha k} \equiv \sum_{\beta l} w^C_{\alpha k, \beta l} = \sum_{\beta l} \frac{\langle \zeta^C_{\alpha k} | \hat{w} | \zeta^C_{\beta l} \rangle}{\sqrt{\langle \zeta^C_{\alpha k} | \zeta^C_{\alpha k} \rangle \langle \zeta^C_{\beta l} | \zeta^C_{\beta l} \rangle}}.
\]

Note that \(w^C_{\alpha k} \neq w^C_{\alpha \alpha k}\), where the right hand side is given by the diagonal terms in Eq. (1.10). In general the macrostate weight \(w^C_{\alpha k}\) cannot be written as a single expectation value of the weight operator.

The total weight of the quantum system is the sum of the above,

\[
W = \sum_\alpha w^C_\alpha = \sum_{\alpha, k} w^C_{\alpha k, \alpha k} = \text{Tr} \hat{w}.
\]

This is the total weight expressed as a sum over principle quantum states (macrostates). Again, \(W \neq \sum_\alpha w^C_{\alpha \alpha}\), using the diagonal terms in Eq. (1.10). The second equality that expresses this as a sum over microstates confirms that the same total weight results whether it is expressed in terms of microstates or macrostates. For the total weight to be independent of whether it invokes the weight associated with a complete or an incomplete operator (i.e. whether it is summed over microstates or macrostates), it is necessary that the definition of principle quantum number weight, Eq. (1.13) be used.

### C. Probability

One can define a probability operator in terms of the weight operator,

\[
\hat{\phi} = \frac{1}{W} \hat{w}.
\]

with normalization \(\text{Tr} \hat{\phi} = 1\). This, the weight operator above, and the entropy operator that follows are one-time operators. On occasion the superscript ‘(1)’ will be appended in order to distinguish them more clearly from the two-time operators that are introduced below for transitions.

The probability of a quantum state of a complete operator (microstate) is its weight divided by the total weight,

\[
\varphi^A_n = \frac{w^A_n}{W}.
\]

This is the same as the expectation value of the probability operator,

\[
\varphi^A_n = \frac{\langle \zeta^A_n | \hat{\phi} | \zeta^A_n \rangle}{\langle \zeta^A_n | \zeta^A_n \rangle} = \frac{\langle \zeta^A_n | \hat{w} | \zeta^A_n \rangle}{\sum_n \langle \zeta^A_n | \zeta^A_n \rangle}.
\]

By design, the microstate probability is normalized, \(\sum_n \varphi^A_n = 1\). An alternative notation is \(\varphi^A(n)\) or \(\varphi(n^A)\).

The probability of a principle quantum state of an incomplete operator is

\[
\varphi^C_\alpha = \frac{w^C_\alpha}{W}.
\]

With the usual matrix representation, \(\varphi^C_{\alpha k, \beta l} = \langle \zeta^C_{\alpha k} | \hat{\phi} | \zeta^C_{\beta l} \rangle\), this can be written

\[
\varphi^C_\alpha = \sum_{k \in \alpha} \varphi^C_{\alpha k, \alpha k} = \sum_{k \in \alpha} \frac{\langle \zeta^C_{\alpha k} | \hat{\phi} | \zeta^C_{\alpha k} \rangle}{\langle \zeta^C_{\alpha k} | \zeta^C_{\alpha k} \rangle} = \frac{\sum_{k \in \alpha} \langle \zeta^C_{\alpha k} | \hat{w} | \zeta^C_{\alpha k} \rangle}{\sum_{\alpha, k} \langle \zeta^C_{\alpha k} | \hat{w} | \zeta^C_{\alpha k} \rangle}.
\]

Note that the probability of the principle quantum states of an incomplete operator is not the expectation
value of the probability operator in that state,

\[
\psi_C = \frac{\langle C | \hat{\psi} | C \rangle}{\langle C | C \rangle}
\]

This is erroneous because the non-diagonal elements (superposition states) contribute to this.

Suppose that one has two incomplete operators, \( \hat{C}|\alpha_k\rangle = C_\alpha|\alpha_k\rangle \) and \( \hat{D}|\beta_l\rangle = D_\beta|\beta_l\rangle \), and that these commute, \( \hat{C}\hat{D} = \hat{D}\hat{C} \). They therefore share eigenfunctions and one can write

\[
\hat{C}|\alpha\beta,k\rangle = C_\alpha|\alpha\beta,k\rangle \quad \text{and} \quad \hat{D}|\alpha\beta,k\rangle = D_\beta|\alpha\beta,k\rangle.
\]

Since the two operators commute, the system can be in the state \( \{C,\alpha\} \) in the state \( \{D,\beta\} \) simultaneously. In this case the system is in the common sub-space \( \{C,\alpha\} \cap \{D,\beta\} \). The weight of such a simultaneous state is

\[
w_{\alpha\beta}^{CD} = \sum_{k=\alpha\cap\beta} (CD) w_{\alpha\beta,k}\alpha\beta,k,
\]

An alternative notation for the left hand side is \( w(\alpha^\beta) \).

The principle quantum number labels a complete set. Hence \( \sum_\beta \alpha \cap \beta = \alpha \), and \( \sum_\alpha \alpha \cap \beta = \beta \). This means that one has what might be called a conservation law for weight,

\[
\sum_\beta (D) w_{\alpha\beta}^{CD} = w_\alpha^C, \quad \text{and} \quad \sum_\alpha (C) w_{\alpha\beta}^{CD} = w_\beta^D.
\]

Evidently then, the sum of the joint weight over all pairs of principle quantum numbers gives the total weight of the system,

\[
\sum_{\alpha,\beta} (CD) w_{\alpha\beta}^{CD} = W.
\]

The unconditional probability that the quantum system is simultaneously in the principle quantum states \( \{C,\alpha\} \) and \( \{D,\beta\} \) is

\[
\psi^{CD}(\alpha\beta) = \frac{w_{\alpha\beta}^{CD}}{W},
\]

which can alternatively be written \( \psi(\alpha^\beta) \). If the system is in the principle quantum state \( \{D,\beta\} \), then the conditional probability that it is also in the state \( \{C,\alpha\} \) is

\[
\psi^{CD}(\alpha|\beta) = \frac{1}{w_\beta^D} \sum_{k=\alpha\cap\beta} (CD) w_{\alpha\beta,k}\alpha\beta,k
\]

This is usually written in the form of Bayes’ theorem,

\[
\psi^{CD}(\alpha\beta) = \frac{\psi^{CD}(\alpha|\beta) \psi_\beta^D}{\psi_\beta^D},
\]

or

\[
\psi(\alpha^\beta) = \frac{\psi(\alpha^\beta) \psi_\beta^D}{\psi_\beta^D}.
\]

\[\textbf{D. Entropy}\]

The entropy of the total quantum system is

\[
S = k_B \ln W,
\]

where \( k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \) is Boltzmann’s constant.

Similarly, the entropy of a microstate of a complete operator is \( S_n^A = k_B \ln w_n^A \), and that of a microstate of an incomplete operator is \( S_n^{C,\alpha} = k_B \ln w_n^{\alpha} \). In the same way, the entropy of a macrostate, which is the principle quantum state of an incomplete operator, is

\[
S_C^\alpha = k_B \ln \sum_{k} w_{\alpha,k}^{\alpha}.
\]

One can relate the entropy operator to the weight operator by

\[
\hat{w} = e^{S/k_B}.
\]

As mentioned above, in general the weight of a macrostate is not the expectation value of the weight operator in that state. Here can be added that neither is it the exponential of the expectation value of the entropy operator in that state. Further, although the weight of a microstate is the expectation value of the weight operator in that state, in general it is not the exponential of the expectation value of the entropy operator in that state. Because of this difference, one needs to explicitly distinguish the expectation value of the entropy operator,

\[
S_m^{<} = \langle \zeta_m \hat{S} | \zeta_m \rangle,
\]

from the entropy as the logarithm of the weight,

\[
S_m = k_B \ln w_m = k_B \ln \langle \zeta_m | \hat{w} | \zeta_m \rangle.
\]

When one speaks of the entropy of a state, one has to be clear whether one means \( S_m^{<} \) or \( S_m \).

The distinction between the two disappears for the case of entropy microstates, \( \hat{S}|\zeta_{ak}^S\rangle = S_{\alpha}^a|\zeta_{ak}^S\rangle \). In this case the expectation value of the exponential is equal to the exponential of the expectation value,

\[
w_{\alpha k}^{S} = \langle \zeta_{ak}^S | \hat{w} | \zeta_{ak}^S \rangle = \langle \zeta_{ak}^S | e^{S/k_B} | \zeta_{ak}^S \rangle
\]

\[
= \exp \left( \langle \zeta_{ak}^S | \hat{S} | \zeta_{ak}^S \rangle / k_B \right)
\]

\[
= e^{S_{\alpha}/k_B}.
\]
In this case the two definitions of the entropy are both equal to the entropy eigenvalue, $S_{\text{ent}}^{\alpha,k} = S_{\text{ent},\text{sup}}^{\alpha,k} = S_{\text{ent}}$.

The weight of the macrostate $\{\alpha,S\}$ is

$$w_{\alpha}^S = \sum_{k \in \alpha} w_{\alpha,k}^S$$
$$= N_{\alpha}^S e^{S_{\alpha}/k_B}$$
$$= N_{\alpha}^S \exp \left( \frac{\langle S | \hat{S} | S \rangle}{k_B} \right).$$

That is, the weight of an entropy macrostate is the number of degenerate states times the exponential of the expectation value of the entropy operator in that macrostate.

Obviously, the entropy operator can be related to the probability operator,

$$\hat{\rho} = \frac{1}{W} e^{S/k_B}.$$

The probability of a state of a complete operator (microstate) is

$$\varphi_{n}^A = \langle \zeta_{n}^A | \hat{\rho} | \zeta_{n}^A \rangle$$
$$= \frac{\langle \zeta_{n}^A | e^{S/k_B} | \zeta_{n}^A \rangle}{\sum_{n} \langle \zeta_{n}^A | e^{S/k_B} | \zeta_{n}^A \rangle}$$
$$\neq \frac{\exp \left\{ \langle \zeta_{n}^A | \hat{S} | \zeta_{n}^A \rangle / k_B \right\}}{\sum_{n} \exp \left\{ \langle \zeta_{n}^A | \hat{S} | \zeta_{n}^A \rangle / k_B \right\}} = \frac{e^{S_{\text{ent}}^{A} / k_B}}{\sum_{n} e^{S_{\text{ent}}^{A} / k_B}},$$

assuming a normalized basis, $\langle \zeta_{n}^A | \zeta_{n}^A \rangle = 1$. The probability of a principle state of an incomplete operator (macrostate) is

$$\varphi_{\alpha}^C = \sum_{k \in \alpha} \langle \zeta_{\alpha,k}^C | \hat{\rho} | \zeta_{\alpha,k}^C \rangle$$
$$= \frac{\sum_{k \in \alpha} \langle \zeta_{\alpha,k}^C | e^{S/k_B} | \zeta_{\alpha,k}^C \rangle}{\sum_{\alpha,k} \langle \zeta_{\alpha,k}^C | e^{S/k_B} | \zeta_{\alpha,k}^C \rangle}$$
$$\neq \frac{\sum_{k \in \alpha} \exp \left\{ \langle \zeta_{\alpha,k}^C | \hat{S} | \zeta_{\alpha,k}^C \rangle / k_B \right\}}{\sum_{\alpha,k} \exp \left\{ \langle \zeta_{\alpha,k}^C | \hat{S} | \zeta_{\alpha,k}^C \rangle / k_B \right\}} = \frac{1}{\sum_{\alpha,k} e^{S_{\text{ent}}^{C} / k_B}} \frac{\sum_{k \in \alpha} e^{S_{\text{ent}}^{C} / k_B}}{\sum_{\alpha,k} e^{S_{\text{ent}}^{C} / k_B}},$$

again assuming a normalized basis, $\langle \zeta_{\alpha,k}^C | \zeta_{\alpha,k}^C \rangle = 1$. The error arises in both cases because non-diagonal elements (superposition states) preclude the interchange of expectation and exponentiation.

Since entropy eigenfunctions are also probability eigenfunctions, $\varphi_{\alpha,k}^{S} = \varphi_{\alpha,k}^{S} = W^{-1} e^{S_{\alpha}/k_B} | \zeta_{\alpha,k}^S \rangle$, the probability operator matrix is diagonal in the entropy representation, $\varphi_{\alpha,k,\beta l} = \varphi_{\alpha,k}^{S} \delta_{\alpha,\beta} \delta_{l l}$. (The degeneracy subscript $k$ is redundant on the probability eigenvalue.) This means that

$$\varphi_{\alpha,k}^{S} = \frac{\langle \zeta_{\alpha,k}^S | \zeta_{\alpha,k}^S \rangle}{\sum_{\alpha,k} e^{S_{\alpha}/k_B} | \zeta_{\alpha,k}^S \rangle}$$

Further, the total entropy may be written

$$S = k_B \ln W$$
$$= k_B \sum_{\alpha,k} \varphi_{\alpha,k}^{S} \ln W$$
$$= -k_B \sum_{\alpha,k} \varphi_{\alpha,k}^{S} \ln \left[ \frac{k_B S_{\alpha}/k_B}{W} - S_{\alpha}/k_B \right]$$
$$= -k_B \sum_{\alpha,k} \langle \zeta_{\alpha,k} | \hat{\rho} | \zeta_{\alpha,k} \rangle \ln \left[ \frac{k_B \hat{S} - S_{\alpha}/k_B}{S_{\alpha}/k_B} \right]$$
$$= \text{Tr} \hat{\rho} \hat{S} - k_B \text{Tr} \hat{\rho} \ln \hat{\rho}.$$

The passage to the penultimate equality relied upon the fact that the probability operator and the entropy operator are diagonal in the entropy basis. Although the entropy basis was used for the derivation, the final expression is independent of any particular basis. This exact formal expression for the total entropy of the quantum system differs from what one finds in almost all other papers and text books. The difference is the first term on the right hand side of the final equality, whose physical interpretation is that of the internal entropy of the macrostates. This internal entropy of course contributes to the total entropy of the system, but unfortunately conventional treatments inadvertently neglect it.

### E. Averages

An arbitrary operator $\hat{O}$ has average value

$$\langle \hat{O} \rangle_{\text{stat}} = \text{Tr} \hat{\rho} \hat{O}$$
$$= \sum_{mn} \varphi_{mn}^{O} Q_{mn}^{O}$$
$$= \sum_{\beta l} \varphi_{\beta l,\beta l}^{O} O_{\beta l,\beta l}^{O}$$
$$= \sum_{\alpha,k} \varphi_{\alpha,k,\alpha,k}^{O} O_{\alpha,k,\alpha,k}^{O}. \quad (1.39)$$

The final two equalities hold in representations where one or other of the two operators is diagonal. In such cases $\varphi_{\beta l,\beta l}^{O}$ has the interpretation as the probability of the microstate $\{O,\beta l\}$, and $\varphi_{\alpha,k,\alpha,k}^{O}$ has the interpretation as the probability of the microstate $\{S,\alpha\}$. In these two case the trace may be directly interpreted as the weighted sum over microstates. This form for the average results from the collapse of the wave function.
II. TRANSITIONS

A. Transition Weight Operator

Now consider transitions between the quantum states. The transition \( n_1^A \rightarrow n_2^B \) has microstate transition weight \( w^{(2)BA}(\tau) = w^{(2)BA}(\tau) \). In essence, this answers the question: applying the operator \( \hat{A} \) at time \( t \), and the operator \( \hat{B} \) at time \( t + \tau \), what is the weight attached to measuring \( \hat{A} \) and \( \hat{B} \)?

One has to distinguish the present transition weight, say between macrostates, \( w^{(2)}(\beta^A, \alpha^C|\tau) \), from the weight of the joint commuting macrostates, \( w^{CD}_\alpha \), as used in Eq. (2.21) et seq. In the present case the operators do not necessarily commute, and some care has to be exercised in taking the \( \tau \to 0 \) limit.

For the case of transitions in time \( \tau \), one defines the transition (or two-time) weight operator \( \hat{w}^{(2)}(\tau) \), which can be represented as a double matrix with elements

\[
w^{(2)}_{AB; n_2 n_1}(\tau) = \langle \psi^{B}_{n_2} \psi^{A}_{n_1}| \hat{w}^{(2)}(\tau) | \psi^{A}_{n_1}, \psi^{B}_{n_2} \rangle, \tag{2.1}
\]

the basis functions being normalized. The meaning and use of such two-time operators will be clarified below.

The total transition weight is

\[
W^{(2)}(\tau) = \text{Tr}^{(2)} \hat{w}^{(2)}(\tau) = \sum_{n_2, n_1} w^{(2)BA}_{n_2 n_1}(\tau). \tag{2.2}
\]

The diagonal element that appears here, \( w^{(2)BA}_{n_2 n_1}(\tau) = w^{(2)BA}_{n_2 n_1}(\tau) \), is the weight attached to the transition between states \( n_1^A \rightarrow n_2^B \). Obviously this result for the total transitions weight is independent of the representation in terms of the states of the operators \( \hat{A} \) and \( \hat{B} \) in the second equality. It will be shown in Eq. (2.26) below that this total transition weight \( W^{(2)}(\tau) \) is equal to the total weight \( W \) (or more precisely \( W^{(1)} \), as given in Eq. (1.6)) for all \( \tau \).

The second (or transition, or two-time) entropy operator is simply defined as the logarithm of the transition weight operator,

\[
\hat{S}^{(2)}(\tau) = k_B \ln \hat{w}^{(2)}(\tau). \tag{2.3}
\]

The total transition entropy is of course \( S^{(2)}(\tau) = k_B \ln W^{(2)}(\tau) \). As in the case of the first entropy, one has to distinguish between the expectation value of the second entropy operator, \( S^{(2)}(|\tau) \), and the logarithm of the expectation value of the transition weight operator, \( S^{(2)}(\tau) = k_B \ln W^{(2)}(\tau) \).

The transition probability operator is

\[
\hat{\psi}^{(2)}(\tau) = \hat{w}^{(2)}(\tau) = e^{\hat{S}^{(2)}(\tau)/k_B} W^{(2)}(\tau). \tag{2.4}
\]

This is obviously normalized, \( \text{Tr}^{(2)} \hat{\psi}^{(2)}(\tau) = 1 \).

The state transition probability is

\[
\psi^{(2)}(n_2^B, n_1^A|\tau) = \psi^{(2)}_{B; n_2 n_1}^{A}(\tau) = \frac{w^{(2)BA}_{n_2 n_1}(\tau)}{W^{(2)}(\tau)}. \tag{2.5}
\]

This gives the unconditional probability of the transition \( n_1^A \rightarrow n_2^B \), and it may also be written \( \psi^{(2)BA}(\tau) \). Explicitly this is

\[
\psi^{(2)}(n_2^B, n_1^A|\tau) = \langle \psi^{B}_{n_2}, \psi^{A}_{n_1}| \hat{w}^{(2)}(\tau) | \psi^{A}_{n_1}, \psi^{B}_{n_2} \rangle. \tag{2.6}
\]

The transition between two states is evidently analogous to the joint probability of commuting macrostates, and as in Eq. (1.25), the conditional and unconditional state transition probability are related by Bayes’ theorem,

\[
\psi^{(2)}(n_2^B, n_1^A|\tau) = \psi^{(2)}(n_2^B|n_1^A, \tau) \psi^{(1)}(n_1^A), \tag{2.7}
\]

where \( \psi^{(1)}(n_1^A) = \psi^{A}_{n_1} \). The conditional state transition probability \( \psi^{(2)}(n_2^B|n_1^A, \tau) \) is the probability of the system being in the state \( n_2^B \) at time \( t_2 = t_1 + \tau \) given that it is in the state \( n_1^A \) at time \( t_1 \). The time interval \( \tau \) may be positive or negative; if positive, then this is the probability of the transition from the current state, and if negative, then this is the probability of the transition that led to the current state. Since \( \psi^{(2)}(n_2^B, n_1^A|\tau) = \psi^{(2)}(n_1^A, n_2^B|\tau) \) (time homogeneity combined with statistical symmetry), one must also have

\[
\psi^{(2)}(n_2^B, n_1^A|\tau) = \psi^{(2)}(n_1^A, n_2^B|\tau) \psi^{(1)}(n_2^B). \tag{2.8}
\]

The conditional transition probability is conditioned on pure quantum states, which is to say that it is not defined here for off-diagonal conditioning states.

The evolution of the present open equilibrium quantum system can also be characterized by a stochastic dissipative time propagator, \( \hat{U}(\tau) \),

\[
|\psi(t + \tau)\rangle = \hat{U}(\tau)|\psi(t)\rangle. \tag{2.9}
\]

This time propagator must obey certain statistical rules and symmetries that will be derived below. The conditional state transition probability can be expressed in terms of the propagator, namely

\[
\psi^{(2)}(n_2^B|n_1^A, \tau) = \langle \psi^{B}_{n_2} | \hat{U}^{BA}_{n_2 n_1}(\tau) \rangle_{\text{stoch}} \equiv \langle \langle \psi^{A}_{n_1} | \hat{U}(\tau) | \psi^{B}_{n_2} \rangle \psi^{A}_{n_1} \rangle_{\text{stoch}}. \tag{2.10}
\]

The angular brackets signify an average over the stochastic propagator. This propagator form for the conditional state transition probability is motivated by the analysis of the time correlation function in the section that follows.

The conditional transition probability operator is a two-time operator, and writing it as the composition of
The two one-time time propagators is a notational challenge that is perhaps best met by
\[ \tilde{\psi}^{(2), \text{cond}} (\tau) = \left\langle \left\{ \hat{\mathcal{U}}(\tau) \dagger, \hat{\mathcal{U}}(\tau) \right\} \right\rangle_{\text{stoch}}. \] (2.11)

The meaning of the notation can be best gauged from the representation,
\[ \tilde{\psi}^{(2), \text{cond}} (\tau) = \left\langle \mathcal{U}_{m_1 n_2} (\tau) \mathcal{U}_{m_2 n_1} (\tau) \right\rangle_{\text{stoch}}. \] (2.12)

The unconditional transition probability operator is the composition of the conditional transition probability operator and the singlet probability operator, which can be arranged in four ways,
\[ \tilde{\psi}^{(2)} (\tau) = \left\langle \left\{ \hat{\mathcal{U}}(\tau) \dagger, \hat{\mathcal{U}}(\tau) \tilde{\psi}^{(1)} \right\} \right\rangle_{\text{stoch}} \]
\[ = \left\langle \left\{ \tilde{\psi}^{(1)} \hat{\mathcal{U}}(\tau) \dagger, \hat{\mathcal{U}}(\tau) \right\} \right\rangle_{\text{stoch}} \]
\[ = \left\langle \left\{ \hat{\mathcal{U}}(\tau) \dagger, \tilde{\psi}^{(1)} \hat{\mathcal{U}}(\tau) \right\} \right\rangle_{\text{stoch}} \]
\[ = \left\langle \left\{ \hat{\mathcal{U}}(\tau) \dagger, \tilde{\psi}^{(1)} \hat{\mathcal{U}}(\tau) \right\} \right\rangle_{\text{stoch}}, \] (2.13)

recalling that \( \tilde{\psi}^{(1)} \dagger = \tilde{\psi}^{(1)} \). In these singlet probability is combined with a time propagator using the ordinary one-time composition of operators. Hence one has four representations of the unconditional transition probability,
\[ \tilde{\psi}^{(2)}_{m_1 n_2} (\tau) = \sum_{m_2, n_2} \left\langle \mathcal{U}_{m_1 n_2} (\tau) \mathcal{U}_{m_2 n_1} (\tau) \tilde{\psi}^{(1)}_{n_1} \right\rangle_{\text{stoch}}, \]
\[ = \sum_{m_2, n_2} \left\langle \tilde{\psi}^{(1)}_{m_1} \mathcal{U}_{m_1 n_2} (\tau) \mathcal{U}_{m_2 n_1} (\tau) \right\rangle_{\text{stoch}}, \]
\[ = \sum_{m_2, n_2} \left\langle \mathcal{U}_{m_1 n_2} (\tau) \tilde{\psi}^{(1)}_{m_2} \mathcal{U}_{m_2 n_1} (\tau) \right\rangle_{\text{stoch}}, \]
\[ = \sum_{m_2, n_2} \left\langle \mathcal{U}_{m_1 n_2} (\tau) \tilde{\psi}^{(1)}_{m_2} \mathcal{U}_{m_2 n_1} (\tau) \right\rangle_{\text{stoch}}, \] (2.14)

respectively. As usual, \( \mathcal{U}_{m_1 n_2} (\tau) \dagger = \mathcal{U}_{m_2 n_1} (\tau)^{\ast} \).

If the system is in the wave state \( \psi_1 \) at time \( t_1 \) and \( \psi_2 \) at time \( t_2 = t_1 + \tau \), then the expectation value of the transition probability is
\[ \tilde{\psi}^{(2)} (\psi_2, \psi_1 | \tau) = \left\langle \psi_2 | \psi_1 \right\rangle \tilde{\psi}^{(2)} (\psi_2, \psi_1 | \psi_2, \psi_1) \]
\[ = \frac{1}{N(\psi_2) N(\psi_1)} \sum_{m_2, n_2} \psi_{m_2}^* \psi_{n_2} \psi_{1, m_1} \psi_{1, n_1} \psi_{m_2, n_1} (\tau) \]
\[ = \frac{1}{N(\psi_2) N(\psi_1)} \sum_{m_2, n_2} \psi_{m_2}^* \psi_{n_2} \psi_{1, m_1} \psi_{1, n_1} \times \left\langle \mathcal{U}_{m_1 n_2} (\tau) \mathcal{U}_{m_2 n_1} (\tau) \right\rangle_{\text{stoch}} \psi_{1, n_1}^{(1)}. \] (2.15)

There are three other versions of the final equality that can be derived from the preceding equation. As will be shown next, in practice one deals with fully collapsed states, \( m_2 = n_2 \) and \( l_1 = m_1 = n_1 \).

**B. Time Correlation Function**

In order to understand the meaning of a two-time operator, one can look at the correlation of two operators, \( \mathcal{B} \) applied at time \( t_2 = t_1 + \tau \) and \( \mathcal{A} \) applied at time \( t_1 \). The time correlation function is
\[ C_{BA} (\tau) = \text{Tr}^{(2)} \left[ \tilde{\psi}^{(2)} (\tau) \{ \mathcal{B} (t_1 + \tau), \mathcal{A} (t_1) \} \right] \]
\[ = \sum_{m_2, n_2} \psi_{m_2 n_2} (\tau) B_{n_2 m_2} A_{n_1 m_1}. \] (2.16)

If one uses the basis \( \{ \psi_A \} \) at \( t_1 \) and \( \{ \psi_B \} \) at \( t_2 = t_1 + \tau \), then the operator matrices are diagonal and this becomes
\[ C_{BA} (\tau) = \sum_{n_1, n_2} \psi_{n_2} (\tau) B_{n_2} A_{n_1} \]
\[ = \sum_{n_1} \psi_{n_1} (\tau) \mathcal{B} \mathcal{A}_{n_1} \mathcal{A}_{n_1}. \] (2.17)

Since \( \tilde{\psi}_{n_1 n_2} (\tau) \) is the unconditional probability of the transition between states of the two operators, \( n_1 A \to n_2 B \), this second form emphasizes the collapse of the wave function into the pure quantum states of the two operators.

Using the propagator expression in the preceding section for the conditional transition probability, Eq. (2.13), and combining it with the notion of collapse into the pure quantum states, the time correlation function can also be written in terms of the propagator,
\[ C_{BA} (\tau) = \sum_{m_2, n_2} \left\langle \mathcal{U}_{m_1 n_2} (\tau) \mathcal{U}_{m_2 n_1} (\tau) \right\rangle_{\text{stoch}} \psi_{n_1}^{(1)} B_{n_2 m_2} A_{n_1 m_1} \]
\[ \Rightarrow \sum_{n_1, n_2} \left\langle \mathcal{U}_{n_1 n_2} (\tau) \right\rangle_{\text{stoch}} \psi_{n_1}^{(1)} B_{n_2} A_{n_1} \]
\[ = \sum_{n_1, n_2} \left\langle \mathcal{U}_{n_1 n_2} (\tau) \right\rangle_{\text{stoch}} \psi_{n_1}^{(1)} A_{n_1} \] (2.18)

The operator \( \mathcal{A} \) has collapsed the probability operator from superposition states into pure states, \( \psi_{n_1} \to \psi_{n_1} \equiv \psi_{n_1}^{A} \). This has a straightforward physical interpretation for the meaning of the time correlation function, which adds credibly to Eq. (2.10). In words, \( \psi_{n_1}^{A} \) is the probability of measuring \( A_{n_1} \), and, given the state \( n_2^A \), \( \mathcal{A}_{n_2} (\tau) \mathcal{A}_{n_1} \mathcal{A}_{n_1} \) is the probability of making the transition to the state \( n_2^B \) and then measuring \( B_{n_2} \). The expression for the conditional transition probability, Eq. (2.13), can only be applied to two-time averages in the context of such a collapse.
A second version of the time correlation function results upon replacing \( \varphi^A_{n_1} \) by \( \varphi^B_{n_2} \) in the final equality.

If one sets \( \hat{B} \equiv \hat{I} \), then the time correlation function is just the average value of the operator \( \hat{A} \),

\[
C_{1A}(\tau) = \langle \hat{A} \rangle_{\text{stat}} = \text{Tr} \, \hat{\varphi}^{(1)} = \sum_{mn} \varphi^{(1)}_{mn} A_{nm}. \tag{2.19}
\]

Prior to the collapse the time correlation function is explicitly

\[
C_{1A}(\tau) = \sum_{n_2} \sum_{m_1,n_1,l_1} \langle U_{m_1,n_2}(\tau) U_{n_2,l_1}(\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_1,n_1} A_{n_1,m_1} = \sum_{m_1,n_1} \left\{ \langle \hat{u}(\tau) \rangle_{\text{stoch}} \hat{\varphi}^{(1)} \right\}_{m_1,n_1} A_{n_1,m_1} \tag{2.20}
\]

Equating these two yields

\[
\hat{\varphi}^{(1)} = \langle \hat{u}(\tau) \rangle_{\text{stoch}} \hat{\varphi}^{(1)}, \tag{2.21}
\]

or

\[
\langle \hat{u}(\tau) \rangle_{\text{stoch}} = \hat{I}. \tag{2.22}
\]

(The probability operator can be taken in or out of the stochastic average as desired.) On the left hand side is the ordinary composition of one-time operators. This says that the time propagator must on average be unity.

It is an arguable point whether one should equate the two expressions for the time correlation function before or after the collapse. If it is done after the collapse, then one obtains the weaker result that says that the diagonal elements are unity, but is silent about the non-diagonal elements. The point will be rendered moot in the following section when the general result and its variants will be derived in a more rigorous fashion.

Using the relationship between the conditional probability and the propagators, this last result shows that the conditional state probability must sum to unity,

\[
\sum_{n_2} \varphi^{(2)}(n_2|n_1,\tau) = 1. \tag{2.23}
\]

As for the unconditional probability, inserting \( \hat{B} \equiv \hat{I} \) into Eq. (2.16) and comparing it to \( \langle \hat{A} \rangle_{\text{stat}} \), one obtains

\[
\sum_{n_2} \varphi^{(2)}_{n_2,n_1}(\tau) = \varphi^{(1)}_{n_1,n_1}. \tag{2.24}
\]

This and the preceding two results will now be obtained by an alternative method.

C. Reduction Condition

Since the microstates are complete, one must have the reduction conditions,

\[
\sum_{n_2} w^{(2)}_{n_2,n_1}(\tau) = w_{n_1}^{(2)}, \quad \text{and} \quad \sum_{n_1} w^{(2)}_{n_2,n_1}(\tau) = w_{n_2}^{(2)}. \tag{2.25}
\]

Recall the variant notations: \( w^{(2)}_{n_2,n_1}(\tau) \equiv w^{(2)}_{n_2,n_1,A}(\tau) \equiv w^{(2)}_{n_2,n_1^A}(\tau) \), and \( w_{n_1}^{(2)} \equiv w_{n_1}^{(2),A} \equiv w^{(1)}(n_1^A) \).

It follows that the total transition weight is equal to the total weight, \( W^{(1)} \equiv W \),

\[
W^{(2)}(\tau) = \sum_{n_2} w^{(2)}_{n_2,n_1}(\tau) = \sum_{n_1} w_{n_1}^{(2)} = W. \tag{2.26}
\]

These are a type of conservation law for weight, and the results only hold for the present equilibrium system. The reduction also occurs in macrostates,

\[
\sum_{n_2^B} w^{(2)}_{n_2^B,n_1}(\tau) = w_{n_1}^{(2),B} \quad \text{and} \quad \sum_{n_1^C} w^{(2)}_{n_2^B,n_1^C}(\tau) = w_{n_2^B,n_1^C} \tag{2.27}
\]

The reduction condition on microstate weights leads to a reduction condition on the weight operators,

\[
\text{Tr}^{(1)} \hat{w}^{(2)}(\tau) = \hat{w}^{(1)}. \tag{2.28}
\]

The notation signifies the partial trace over one of the two times of the operator; this could be made a little clearer by signifying explicitly which one of the two times were traced over. Explicitly, applying the trace to the second time this is

\[
\sum_{n_2} w^{(2)}_{B:n_2,n_1}(\tau) = \sum_{n_2} \langle \tau_B | \langle n_2 | w^{(2)}(\tau) | n_1 \rangle_B \rangle_{\text{stat}} = \langle \langle n_1 | w^{(1)}(\tau) | n_1 \rangle_B \rangle_{\text{stat}} = w^{(1)}(n_1^B) \tag{2.29}
\]

(The superscript ‘A’ rather than the more precise but not particularly useful ‘AA’ is used for the representation of one-time operators here and below.) Alternatively, applying the trace to the first time it is

\[
\sum_{n_1} w^{(2)}_{B:n_2,n_1}(\tau) = \sum_{n_1} \langle \langle n_2 | w^{(2)}(\tau) | n_1 \rangle_B \rangle_{\text{stat}} = \langle \langle n_2 | w^{(1)}(\tau) | n_2 \rangle_B \rangle_{\text{stat}} = w^{(1)}(n_2^B) \tag{2.30}
\]

These generalize the reduction condition for the transition weight to off-diagonal elements.

Because the total transition weight is also the total weight, \( W^{(2)}(\tau) = W \), the reduction condition for the weight operators carry over directly to the probability operators,

\[
\text{Tr}^{(1)} \hat{\varphi}^{(2)}(\tau) = \hat{\varphi}^{(1)}. \tag{2.31}
\]

The general (off-diagonal) results from this are

\[
\sum_{n_2} \varphi^{(2)}_{B:n_2,n_1}(\tau) = \varphi^{(1),A}_{n_1,n_1} \tag{2.32}
\]

and

\[
\sum_{n_1} \varphi^{(2)}_{B:n_2,n_1}(\tau) = \varphi^{(1),B}_{n_2,n_2} \tag{2.33}
\]
In terms of the transitions between the operator microstates these become,

$$\sum_{n_B^2} \phi^{(2)}_{n_B^2 n_1^A} (\tau) = \phi^{(1)}_{n_1^A}, \quad \text{and} \quad \sum_{n_B^1} \phi^{(2)}_{n_B^1 n_1^A} (\tau) = \phi^{(1)}_{n_B^1},$$

(2.34)

and similarly for macrostates.

For the conditional state transition probability, the reduction becomes

$$\sum_{n_B^2} \phi(n_B^2 | n_1^A, \tau) = 1, \quad \text{and} \quad \sum_{n_B^1} \phi(n_1^A | n_B^2, -\tau) = 1.$$  

(2.35)

This confirms Eq. (2.22). Explicitly, in terms of the propagator this is

$$1 = \sum_{n_B^2} \left\langle \langle \zeta_{n_1}^A | \hat{U}(\tau) | \zeta_{n_2}^B \rangle \langle \zeta_{n_2}^B | \hat{U}(\tau) | \zeta_{m_1}^A \rangle \right\rangle_{\text{stoch}}$$

$$= \sum_{n_B^2} \left\langle \langle U_{AB}^{n_B^2} (\tau) | \hat{U}_{n_B^2 n_1} (\tau) \langle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \zeta_{m_1}^A | \hat{U}(\tau) | \hat{U}(\tau) | \zeta_{m_1}^A \rangle \right\rangle_{\text{stoch}}.$$  

(2.36)

These are just the diagonal elements of Eq. (2.22).

Inserting the propagator expressions for the transition probability operator, Eq. (2.14), into the reduction condition, Eq. (2.31), and taking the trace over $t_2$ yields

$$\hat{\phi}^{(1)} = \left\langle \langle \hat{U}(\tau) \hat{U}(\tau) \hat{\phi}^{(1)} (\tau) \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{\phi}^{(1)} \hat{U}(\tau) \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{U}(\tau) \hat{\phi}^{(1)} \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{U}(\tau) \hat{U}(\tau) \hat{\phi}^{(1)} \rangle \right\rangle_{\text{stoch}}.$$  

(2.37)

In this case the trace over the second time has become the ordinary one-time composition of operators. Taking the trace over the first time yields

$$\hat{\phi}^{(1)} = \left\langle \langle \hat{U}(\tau) \hat{\phi}^{(1)} \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{\phi}^{(1)} \hat{U}(\tau) \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{U}(\tau) \hat{\phi}^{(1)} \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{U}(\tau) \hat{U}(\tau) \hat{\phi}^{(1)} \rangle \right\rangle_{\text{stoch}}.$$  

(2.38)

In this case the trace over $t_1$ has rearranged the order of the operators in order to express the result as the ordinary one-time composition of the operators.

From the first two equations of the first set, and from the last two equations of the second set, one sees that

$$\left\langle \langle \hat{U}(\tau) \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}} = \left\langle \langle \hat{U}(\tau) \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}} = \hat{1}.$$  

(2.39)

This says that on average the stochastic dissipative propagator is unitary, just as in the adiabatic case. This confirms Eq. (2.22).

Because the identity operator is transpose symmetric (the same result follows by invoking its reality), it follows from these that

$$\langle \langle \hat{U}(\tau)^{\dagger} \hat{U}(\tau) \rangle \rangle_{\text{stoch}} = \langle \langle \hat{U}(\tau)^{\dagger} \hat{U}(\tau) \rangle \rangle_{\text{stoch}}$$

$$= \langle \langle \hat{U}(\tau)^{\dagger} \hat{U}(\tau) \rangle \rangle_{\text{stoch}}.$$  

(2.40)

For the second equality to equal the left hand side, it is sufficient that the propagator be transpose symmetric. It is certainly a convenience for the propagator to be transpose symmetric, but the author has not been able to develop a mathematical proof or a physical argument that this is in fact a necessary condition.

The remaining equations of the reduction condition correspond to the stationarity of the probability operator under the action of the propagator,

$$\hat{\phi}^{(1)} = \left\langle \langle \hat{U}(\tau)^{\dagger} \hat{\phi}^{(1)} \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{\phi}^{(1)} \hat{U}(\tau) \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{U}(\tau) \hat{\phi}^{(1)} \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}.$$  

(2.41)

Since the singlet probability operator is transpose symmetric, (the same result follows by invoking its reality), one also has

$$\hat{\phi}^{(1)} = \left\langle \langle \hat{U}(\tau)^{\dagger} \hat{\phi}^{(1)} \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}$$

$$= \left\langle \langle \hat{\phi}^{(1)} \hat{U}(\tau) \hat{U}(\tau) \rangle \right\rangle_{\text{stoch}}.$$  

(2.42)

It is sufficient, but not necessary, for the propagator and the probability operator to commute in order for these stationarity results to follow directly from the unitary condition.

The reduction condition for the second entropy may be rewritten as

$$S_{n_1}^{A} = k_B \ln w^{A}_{n_1}$$

$$= k_B \ln \sum_{n_2} w^{BA}_{n_1 n_2} (\tau)$$

$$\approx k_B \ln \omega^{BA}_{n_1} (\tau)$$

$$= S_{n_1}^{(2), BA} (\tau).$$  

(2.43)

Here $\pi_2^{B} (\tau | n_1^A)$ denotes the most likely destination state of the operator $\hat{B}$ for the transition from the initial state $n_1^A$ in time $\tau$. This most likely state is the one that maximizes the second entropy,

$$\frac{\partial S_{n_2,n_1}^{(2), BA} (\tau)}{\partial n_2} \bigg|_{n_2 = \pi_2} = 0, \quad \pi_2^{B} (\tau | n_1^A).$$  

(2.44)

This is of course the same as maximizing the transition weight, or as maximizing the transition probability. The third equality above follows because the weight distribution may be expected to be sharply peaked, and consequently the logarithm of the sum is equal to the logarithm of the largest term in the sum.
D. Parity and Reversibility

1. Parity

In general the complex conjugate corresponds to velocity reversal. Every microstate \( n \) has a conjugate state \( n^\dagger \) that is the same state but with the velocities reversed.

A real operator, \( \hat{A}^* = \hat{A} \), is said to have even parity because its eigenvalues are insensitive to the sign of the velocity. This means that the eigenvalues of the conjugate operator, \( \hat{A}^*|\psi_n^A\rangle = A_n^\dagger |\psi_n^A\rangle \), and that of the original, \( \hat{A}|\psi_n^A\rangle = A_n|\psi_n^A\rangle \), are equal \( A_n^\dagger = A_n \). In general microstates are defined such that their eigenvalues are distinct (i.e. non-degenerate). In the case of an even parity operator, this means that the conjugate and the original state are the same state, \( \{ A, n^\dagger \} \equiv \{ A, n \} \).

An odd parity operator is imaginary, \( \hat{B}^* = -\hat{B} \), and \( \hat{B}^*|\psi_n^B\rangle = -B_n|\psi_n^B\rangle \). In this case the eigenvalues are different, \( B_n^\dagger = -B_n \), and the conjugate state is different to the original state, \( \{ B, n^\dagger \} \neq \{ B, n \} \). Taking the complex conjugate of the eigenvalue equation shows that \( \hat{B}|\psi_n^{B^*}\rangle = -B_n|\psi_n^{B^*}\rangle \), and hence \( |\psi_n^{B^*}\rangle = |\psi_n^B\rangle \), and that this is a distinct eigenfunction of the operator \( \hat{B} \).

Whether an operator is real or imaginary or complex, one always has the conjugate state \( n^\dagger \). It is only in the real case that this is the same as the original state. In general (i.e. for an even, odd, or complex operator), \( \langle \gamma_n | n^\dagger \rangle = \delta_{\gamma_n,n} \).

When one writes \( \sum_n \), both \( n \) and \( n^\dagger \) are included in the sum. For an even parity operator these are the same state and it is included once only, whereas for an odd parity operator they are distinct. Since \( n \) is a dummy summation index one can freely write \( \sum_n f_n = \sum_{n^\dagger} f_{n^\dagger} = \sum_n f_n^\dagger \). Obviously \( (n^\dagger)^\dagger = n \).

The set of eigenfunctions of a complete operator forms a complete basis, which means that there is the same number (possibly infinite) of microstates for all operators. For example, the sum over the microstates of an even parity operator might be written, \( \sum_n (A^\dagger) = \sum_{n=1}^{2N} \), whereas the sum over the microstates of an odd parity operator might be written, \( \sum_n (B^\dagger) = \sum_{n=-N}^{N-1} \), with the \( n = 0 \) term excluded, and \( n^\dagger = -n \). There is no reason why the microstates could not be relabeled so that they cover the same range in both cases, with some convenient code linking the index of a state and its conjugate in the odd parity case.

For an equilibrium system, the weight of a microstate is equal to that of its conjugate,

\[
w_n^A = w_n^A, \tag{2.45}
\]

whatever the parity of \( \hat{A} \). This is because an equilibrium system is insensitive to the direction of time, and hence it is insensitive to the sign of the molecular velocities. This means that the weight operator is real, \( \hat{w}^* = \hat{w} \), as also is the probability operator and the entropy operator.

2. Microstate Reversibility

For an open equilibrium quantum system (i.e. a subsystem and a reservoir in total isolated), the sub-system microstate transition \( \{ A, n_1 \} \to \{ B, n_2 \} \) has conjugate \( \{ B, n_2^\dagger \} \to \{ A, n_1^\dagger \} \). For the present open equilibrium quantum system, these have equal weight

\[
w_{BA}(n_2, n_1 | \tau) = w_{AB}(n_1^\dagger, n_2^\dagger | \tau). \tag{2.46}
\]

This is called microstate reversibility. A detailed justification for it will be given in the derivation of Eq. (2.59) in the following section.

The general expression for the macrostate transition weight is

\[
w_{\alpha_2 \beta_1}(\tau) = \sum_{k_2 l_1} w_{\alpha_2 k_2, \alpha_2 k_2^\dagger}(\tau). \tag{2.47}
\]

This could be written alternatively as

\[
w_{\alpha_2 C, \beta_1 D}(\tau) = \sum_{k_2 \in \alpha_2} \sum_{l_1 \in \beta_1} w_{\alpha_2 C k_2, \alpha_2 k_2^\dagger l_1}(\tau), \tag{2.48}
\]

or as

\[
w_{\alpha_2 C, \beta_1 D}(\tau) = \sum_{k_2 \in \alpha_2} \sum_{l_1 \in \beta_1} w_{\alpha_2 C k_2, \alpha_2 k_2^\dagger l_1^\dagger}(\tau). \tag{2.49}
\]

Recall that the eigenfunction equation for an incomplete operator \( \hat{C} \) is \( \hat{C}|\psi_n^{C}\rangle = C_{\alpha} n |\psi_n^{C}\rangle \), and similarly for the incomplete operator \( \hat{D} \). In this case macrostate reversibility is

\[
w_{CD}(\beta, \alpha | \tau) = \sum_{k_2 l_1 \in \beta} \sum_{l_2 ^\dagger \in \alpha} w_{CD}(\beta l_1, \alpha l_2 ^\dagger | \tau) = \sum_{k_2 l_1 \in \beta} \sum_{l_1 ^\dagger \in \alpha} w_{CD}(\alpha l_1, \beta l_1 ^\dagger | \tau) = w_{CD}(\alpha, \beta | \tau). \tag{2.50}
\]

In passing to the second equality, the fact that \( k^\dagger \) and \( l^\dagger \) are dummy summation variables has been used; for every \( k^\dagger \in \alpha^\dagger \) there is a \( k \in \alpha \), and for every \( l^\dagger \in \beta^\dagger \) there is an \( l \in \beta \). The third equality invokes microstate reversibility.

3. Transition Symmetries

The weight of a sub-system transition \( |\psi_1\rangle \to |\psi_2\rangle \) is the number of adiabatic total trajectories that project onto it. For each total trajectory, \( |\psi_{1s}\rangle \to |\psi_{2s}\rangle \) (‘s’ denotes the sub-system, ‘r’ denotes the reservoir, allowed wave functions are not entangled) there are several trajectories related by conjugation and time reversal,

\[
|\psi_{1s}\rangle \to |\psi_{2s}\rangle \quad |\psi_{2s}\rangle \to ^\dagger |\psi_{1s}\rangle
\]
The probability of a transition, $\langle \psi_1 \rangle \to | \psi_2 \rangle$, assuming normalized wave functions, is

$$
\langle \psi_2, \psi_1 | \tau \rangle = \langle \psi_2 | \psi_1 | \tau \rangle = \sum_{m_1, n_1} \psi_{m_1, n_1}^* \phi_{A, n_1, m_1}^2(\tau). 
$$

The reality of the expectation value means that the transition probability operator is Hermitian conjugate,

$$
\phi^{(2)}(\tau) = \phi^{(2)}(\tau)^*,
$$

or

$$
\phi_{B, n_2, m_2}(\tau) = \phi_{B, m_2, n_2}(\tau)^*.
$$

Hence one has three symmetry relations

$$
\phi_{n_2, m_2}(\tau) = \phi_{n_1, m_1}(\tau) = \phi_{m_1, n_2}(\tau) = \phi_{m_2, n_1}(\tau)^*.
$$

The operators used for the representation have not been shown. The first equality expresses microstate reversibility, and the second equality expresses time reversibility. Time reversibility is the combination of time homogeneity and statistical symmetry.

Note that the operators used for the representation, here $A$ and $B$, determine the relationship between the state $n$ and its conjugate, $n^\dagger$. However these symmetry rules depend upon the probability operator and not upon the particular operators used for the representation. Hence one can drop explicit signification of the operators, with the understanding that a single operator is used for $t_1$ and a single operator, either the same or different, is used for $t_2$.

Recall that this is the unconditional transition probability. For an equilibrium system time reversibility must hold: the unconditional probability of observing the forward transition must be equal to the probability of observing the backward transition, otherwise there would be a net flux between the states. This is distinct from the conditional transition probability, which the second law of thermodynamics would ensure was asymmetric in time, as is further discussed shortly.

For the state transitions the symmetries mean that

$$
\phi_{n_2, m_2}^{(2), AB}(\tau) = \phi_{n_1, m_1}^{(2), AB}(\tau) = \phi_{n_1, m_2}^{(2)}(-\tau) = \phi_{n_2, m_1}^{(2)}(\tau)^*,
$$

(2.59)

The first equality here is consistent with, and is the justification for, microstate reversibility given above in terms of weight, Eq. (2.10).

Again it is emphasized that these are unconditional transition probabilities, which are related to the conditional transition probability by Bayes’ theorem,

$$
\phi_{n_2, m_2}^{(2), n_1, A}(\tau) = \phi_{n_2, n_1, m_1}^{(2)}(\tau) \phi(n_1^A).$

As such the time reversibility result, $\phi_{n_2, m_1}^{(2), n_1, B}(\tau)$ implies that $\phi_{n_2, n_1, m_1}^{(2)}(\tau) \phi(n_1^A)$, or

$$
\frac{\phi_{n_2, m_1}^{(2), n_1, B}(\tau)}{\phi_{n_2, m_1}^{(2), n_1, B}(-\tau)} = \phi(n_1^B).
$$

(2.60)

That is, the ratio of the forward and reverse conditional transition probabilities is the inverse of the ratio of the probabilities of the respective starting states. This is what one would expect from the second law of thermodynamics: transitions to a more probable state are more likely than are transitions from a more probable state.

The transition weight has of course the same symmetries as the unconditional transition probability. It was shown above, Eq. (2.13), that the unconditional transition probability operator could be written in terms of the propagator, $\hat{\phi}^{(2)}(\tau) = \{\hat{U}(\tau), \hat{U}(\tau) \phi(1)\}$, and three other
permutations. This has representation
\[ \varphi^{(2)}_{m_1 n_1} (\tau) = \sum_{l_1} \langle U_{m_1 n_2} (\tau) U_{m_2 l_1} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_1 n_1}, \] (2.61)
with \( U_{m_1 n_2} (\tau) \rangle = U_{n_2 m_1} (\tau)^\dagger \). There is no need to explicitly denote the operators used for the representation. The symmetry rules applied to this yield
\[
\sum_{l_1} \langle U_{m_1 n_2} (\tau) U_{m_2 l_1} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_1 n_1}
= \sum_{l_2} \langle U_{n_2 m_1} (\tau) U_{n_1 l_2} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{n_1 l_2}
= \sum_{l_2} \langle U_{m_2 n_1} (\tau) U_{m_1 l_2} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_2 n_2}
= \sum_{l_1} \langle U_{m_2 n_1} (\tau) U_{l_1 n_2} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_1 n_1}. \] (2.62)
Of course \( \varphi^{(1)}_{l_1 m_1} = \varphi^{(1)}_{m_1 l_1} = \varphi^{(1)}_{m_1 l_2}, \) and \( \varphi^{(1)}_{n_2 l_2} = \varphi^{(1)}_{l_2 n_2}. \)

Setting in these \( m_2 = n_2 \) and summing over \( n_2 \) one obtains
\[
\sum_{n_2, l_1} \langle U_{m_1 n_2} (\tau) U_{n_2 l_1} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_1 n_1}
= \sum_{n_2, l_2} \langle U_{n_2 m_1} (\tau) U_{n_1 l_2} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_2 n_2}
= \sum_{n_2, l_2} \langle U_{n_2 m_1} (\tau) U_{n_1 l_2} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_2 n_2}
= \sum_{n_2, l_1} \langle U_{n_2 m_1} (\tau) U_{l_1 n_2} (\tau) \rangle_{\text{stoch}} \varphi^{(1)}_{l_1 n_1}. \] (2.63)
Now
\[ U_{m_1 n_1} (\tau) = \langle \zeta_n^\dagger | \hat{U} (\tau) | \zeta_n \rangle = \langle \zeta_n^\dagger | \hat{U} (\tau) | \zeta_n \rangle^* = \langle \hat{U} (\tau)^* \rangle_{m_1 n_1}^* \] (2.64)
Note that the propagator is neither Hermitian nor of pure parity. Hence
\[
U_{n_2 m_1} (\tau) U_{n_1 l_2} (\tau) \varphi^{(1)}_{n_2 l_2}
= U_{m_1 n_1} (\tau)^* \varphi^{(1)}_{l_2 n_2} U_{l_1 n_2} (\tau)^\dagger
= \{ \hat{U} (\tau)^* \}_{m_2 n_2} \{ \hat{U} (\tau)^* \}_{l_2 n_1} \] (2.65)
After summation over \( l_2 \) and \( n_2 \), this is equivalent to the \( \{ m_1, n_1 \} \) element of the representation of \( \hat{U} (\tau)^* \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \). Hence the symmetry relations may be written for the operators as
\[
\langle \hat{U} (\tau)^\dagger \hat{U} (\tau) \rangle_{\text{stoch}} \hat{\varphi}^{(1)} = \langle \hat{U} (\tau)^* \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau) \rangle_{\text{stoch}}. \] (2.66)
It has already been established that the propagator is on average unitary, Eq. (2.31). Hence these become
\[
\hat{\varphi}^{(1)} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau) \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^* \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}}\] (2.67)
the third and fourth equalities following upon taking the complex conjugate of the first two equalities and using the fact that the singlet probability operator is real. The second equality represents the backward evolution of the probability operator, (for positive \( \tau \)). Changing \( \tau \) to \( -\tau \) in the second equality provides an alternative derivation of the third equality, which represent the forward evolution of the probability operator. Equating each to the left hand side shows that the equilibrium probability operator is on average stationary under the evolution given by the stochastic dissipative time propagator. This result has previously been derived using the reduction condition, Eq. (2.41).

As has been mentioned, the unconditional transition probability operator can also be written in terms of the propagator as \( \hat{\varphi}^{(2)} (\tau) = \langle U_{m_1 n_2} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau) \rangle = \{ \hat{U} (\tau)^\dagger, \hat{\varphi}^{(1)} \hat{U} (\tau) \}. \) These have respective representations
\[
\varphi^{(2)}_{m_1 n_1} (\tau) = \sum_{l_2} \langle U_{m_1 n_2} (\tau)^\dagger \varphi^{(1)}_{l_2 n_2} U_{l_2 n_1} (\tau) \rangle_{\text{stoch}} = \sum_{l_2} \langle U_{m_1 n_2} (\tau)^\dagger \varphi^{(1)}_{l_2 n_2} U_{l_2 n_1} (\tau) \rangle_{\text{stoch}} \] (2.68)
Applying the symmetry conditions to this yields an alternative set of stationary conditions on the probability operator. It seems plausible that these should simply interchange the propagator and its Hermitian conjugate, yielding
\[
\hat{\varphi}^{(1)} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau) \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}} = \langle \hat{U} (\tau)^\dagger \hat{\varphi}^{(1)} \hat{U} (\tau)^\dagger \rangle_{\text{stoch}}\] (2.69)
One can, for example, take the transpose of the first equality in Eq. (2.67) and compare it to the first equality here,
\[
\hat{\varphi}^{(1)} = \langle \hat{U} (\tau) \hat{\varphi}^{(1)} \hat{U} (\tau) \rangle_{\text{stoch}} = \langle \hat{U} (\tau) \hat{\varphi}^{(1)} \hat{U} (\tau) \rangle_{\text{stoch}}\] (2.70)
One can see that it is sufficient for the propagator to be transpose symmetric, \( \hat{U} (\tau)^\dagger = \hat{U} (\tau) \), for this to be
satisfied. Similar identities hold for the transpose of each of the remaining three equalities in Eq. (2.67). This does not prove that it is necessary for the propagator to be transpose symmetric.

In terms of state transitions the uncondition state transition probability is

$$\varphi_{n_2,n_1}^{(2)}(\tau) = \langle U_{n_1,n_2}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}} \varphi_{n_1,n_1}^{(1)}. \quad (2.71)$$

Hence the symmetry rules yield

$$\langle U_{n_2,n_1}(\tau)^* U_{n_2,n_1}(\tau) \rangle_{\text{stoch}} \varphi_{n_1,n_1}^{(1)}$$

$$= \langle U_{n_1,n_2}(\tau) U_{n_1,n_2}(\tau) \rangle_{\text{stoch}} \varphi_{n_1,n_1}^{(1)}$$

$$= \langle U_{n_1,n_2}(\tau) U_{n_1,n_2}(\tau) \rangle_{\text{stoch}} \varphi_{n_1,n_1}^{(1)}$$

$$= \langle U_{n_2,n_1}(\tau) U_{n_2,n_1}(\tau)^* \rangle_{\text{stoch}} \varphi_{n_1,n_1}^{(1)}. \quad (2.72)$$

Of course $\varphi_{n_1,n_1}^{(1)} = \varphi_{n_2,n_2}^{(1)}$.

Assume that the operator $\tilde{A}$ has pure parity, $\varepsilon_A = \pm 1$, then $\tilde{A}^* = \varepsilon_A \tilde{A}$, and $A_{n_1} = \varepsilon_A A_{n_1}$, and similarly for the operator $B$. In this case the time correlation function has the symmetries

$$C_{BA}(\tau) = C_{AB}(-\tau) = C_{A \cdot B^*}(\tau) = \varepsilon_A \varepsilon_B C_{AB}(\tau). \quad (2.73)$$

In terms of the propagator these are

$$C_{BA}(\tau) = \sum_{n_1,n_2} \langle U_{n_1,n_2}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}} B_{n_2} A_{n_1} \varphi_{n_1,n_1}^{A},$$

$$= \sum_{n_1,n_2} \langle U_{n_1,n_2}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}} \times B_{n_1} A_{n_2} \varphi_{n_1,n_1}^{B}_r,$$

$$= \sum_{n_1,n_2} \langle U_{n_2,n_1}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}} B_{n_1} A_{n_2} \varphi_{n_1,n_1}^{B},$$

$$= \varepsilon_A \varepsilon_B \sum_{n_1,n_2} \langle U_{n_1,n_2}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}} \times B_{n_1} A_{n_2} \varphi_{n_1,n_1}^{B}. \quad (2.74)$$

Here $\varphi_{n_1,n_1}^{B} \equiv \varphi_{n_1,n_1}^{(1),BB}$ etc. Hence

$$\langle U_{n_2,n_1}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}}$$

$$= \varepsilon_A \varepsilon_B \langle U_{n_1,n_2}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}}$$

$$= \varepsilon_A \varepsilon_B \langle U_{n_1,n_2}(\tau) | U_{n_2,n_1}(\tau) \rangle_{\text{stoch}}. \quad (2.75)$$

The equality of the left hand side with the second right hand side here is equivalent to the equality of the second and third right hand sides in Eq. (2.72).

E. Symmetries of the Time Propagator

The goal of this section is to elucidate the symmetries or properties of the most likely time propagator that are a consequence of macroscopic reversibility (as opposed to the properties of the average of the product of the time propagators analyzed above).

The above results for the consequences of microstate reversibility for the transition probability yielded two main results for the time propagator: it was on average unitary, $\langle \bar{U}(\tau) \bar{U}(\tau) \rangle_{\text{stoch}} = \langle \bar{U}(\tau) \bar{U}(\tau) \rangle_{\text{stoch}} = \bar{I}$, and evolving under its action the probability distribution was on average stationary, $\bar{\varphi} = \langle \bar{U}(\tau) \bar{\varphi} \bar{U}(\tau) \rangle_{\text{stoch}} = \langle \bar{U}(\tau) \bar{\varphi} \bar{U}(\tau) \rangle_{\text{stoch}}$.

Both of these results invoke the average of the product of the time propagator. In terms of the time propagator itself, one can define the most likely value as

$$\bar{U}(\tau) = \langle \bar{U}(\tau) \rangle_{\text{stoch}}. \quad (2.76)$$

This assumes a Gaussian distribution for the stochastic propagator (means equal modes), which is reasonable on physical grounds.

It does not follow from the unitary condition that the Hermitian conjugate is the inverse, $\bar{U}(\tau)^* \neq \bar{U}(\tau)^{-1}$. The reason is that the unitary condition applies only to the average of the product, which is not equal to the product of the averages. In general terms, the inverse of an operator is only defined in conjunction with its product with the original operator, and so one cannot expect $\bar{U}(\tau)^{-1}$ to have any physical meaning. Instead, it is $\bar{U}(\tau)$ that plays the role of undoing the action of the original propagator, the meaning of which must be carefully understood. (In contrast, in the adiabatic case, $\bar{U}(\tau)^{-1} = \bar{U}(\tau)^{1/2} \bar{U}(\tau)^{-1/2}.$)

By definition, the most likely wave function at time $t_1 + \tau$ given that the system has wave function $\psi_1$ at time $t_1$ is

$$|\psi_2\rangle \equiv \langle \bar{\psi}(\tau | \psi_1) \rangle = \bar{U}(\tau) | \psi_1 \rangle. \quad (2.77)$$

In Eq. (2.81) above, eight statistically equivalent trajectories were given. Focussing on the left hand column projected onto the sub-system, (i.e. trajectories that originate from $\psi_{n_1}$ or its conjugate), the most likely trajectories are

$$|\psi_2\rangle = \bar{U}(\tau) | \psi_1 \rangle \quad \text{and} \quad |\psi_2\rangle = \bar{U}(\tau) | \psi_1 \rangle \quad (2.78)$$

(Although all eight trajectories in Eq. (2.51) have the same weight, due to thermodynamic irreversibility, the most likely trajectory obtained by maximizing over $\psi_2$ for fixed $\psi_1$ is not necessarily related to the most likely trajectory obtained by maximizing over $\psi_1$ for fixed $\psi_2$. This is why only the four trajectories starting at $\psi_1$ are compared here.) The second and third equations must be equivalent to the complex conjugate and to the Hermitian conjugate of the first equation respectively, and the fourth equation must be equivalent to applying both operations simultaneously to the first equation. These mean that

$$\bar{U}(\tau)^* = \bar{U}(\tau), \quad \text{and} \quad \bar{U}(\tau)^\dagger = \bar{U}(\tau)^T. \quad (2.79)$$
These are equivalent to each other. The fourth equation yields the identity \( \overrightarrow{U}(t)^T = \overleftarrow{U}(t) \). (From these, one cannot conclude anything about the transpose symmetry of the most likely propagator.)

The physical interpretation of this symmetry, \( \overrightarrow{U}(-\tau)^* = \overleftarrow{U}(\tau) \), and the reason why it is consistent with thermodynamic irreversibility, is as follows. In general if \( \psi_2 = \overline{\psi}(\tau|\psi_1) \), then \( \psi_2 \) has higher entropy then \( \psi_1 \). But it does not follow that it is also the most likely origin of \( \psi_1, \psi_2 \neq \overline{\psi}(-\tau|\psi_1) \), because the adiabatic contribution is odd in \( \tau \). (It is only the reservoir contribution that can be expected to be even). However, \( \psi_2^\ast \) also has higher entropy then \( \psi_1^\ast \). So in this case one can expect \( \psi_2^\ast \) to be the most likely origin of \( \psi_1^\ast \), which is to say that it is the most likely backward transition from \( \psi_1^\ast, \psi_2^\ast = \overline{\psi}(-\tau|\psi_1^\ast) \). This satisfies both the adiabatic part and the thermodynamic part.

Mathematically, for small time intervals one expects to be able to write the most likely propagator as the sum of an adiabatic part and a reservoir part, \( \overrightarrow{U}(\tau) = \hat{U}^0(\tau) + \overrightarrow{U}^r(\tau) \). This expectation is borne out by the results in Paper II. Hence the most likely propagator is

\[
\overrightarrow{U}(\tau) = \hat{1} + \frac{\tau}{\hbar} \hat{H} + |\tau| \hat{U}^r + O(\tau^2). \tag{2.80}
\]

The absolute value of the time interval arises because for the present equilibrium case, the reservoir should be insensitive to the direction of time. By inspection, the adiabatic part has the symmetry, \( \overrightarrow{U}^0(-\tau)^* = \overleftarrow{U}^0(\tau) \). \tag{2.81}

The most likely reservoir part by design has the symmetry \( \overrightarrow{U}^r(-\tau)^* = \overleftarrow{U}^r(\tau) \). Since the reservoir is insensitive to the sign of the velocities, the propagator arising from it must also be real,

\[
\overrightarrow{U}^r(\tau)^* = \overleftarrow{U}^r(\tau). \tag{2.82}
\]

Combining these, the most likely propagator must have the symmetry deduced above,

\[
\overrightarrow{U}(\tau)^* = \overleftarrow{U}(\tau). \tag{2.83}
\]

Although this third derivation has been obtained explicitly in the small time interval limit, it would not strain credibility to suppose that it holds in general. Indeed, the first two arguments were not restricted to any particular time regime.

III. FLUCTUATION FORM OF THE SECOND ENTROPY

A. Fluctuation Form of the First Entropy

The expectation value of the first entropy is

\[
S^{(1)}(\psi) = \overline{\psi | \hat{S}^{(1)}(\psi) | \psi} = \overline{S^{(1)}(\psi) + (\Delta \psi | \hat{S}''(\psi) | \Delta \psi)}. \tag{3.1}
\]

Here the departure from the most likely wave function is \( \Delta \psi = \psi - \overline{\psi} \). The most likely wave function is an eigenfunction of the entropy operator,

\[
\hat{S}^{(1)}(\overline{\psi}) = S_0 |\overline{\psi} = -\frac{E_0}{T} |\overline{\psi}, \tag{3.2}
\]

The final equality holding in the canonical equilibrium case, \( \hat{S}^{(1)} = -\hat{H}/T \). The entropy fluctuation operator is

\[
\hat{S}'' = \frac{1}{N(\psi)} [\hat{S}^{(1)} - S_0 \hat{1}]. \tag{3.3}
\]

Hence \( \hat{S}''(\overline{\psi}) = |0\rangle \). The most likely wave function may be taken to be normalized, \( N(\overline{\psi}) = 1 \).

In the canonical equilibrium case, the most likely wave function has adiabatic time dependence,

\[|\overline{\psi}(t)\rangle = e^{E_0 t/\hbar} |\overline{\psi}(0)\rangle. \tag{3.4}\]

It will be shown below that at least to linear order in the time step, and almost certainly in general, this adiabatic evolution is the complete evolution.

B. Second Entropy

The expectation value of the second entropy for the wave state transition \( \psi_1 \rightarrow \psi_2 \) is

\[
S^{(2)}<>(\psi_2, \psi_1 | \tau) = \frac{\langle \psi_2, \psi_1 | \overrightarrow{S}^{(2)}(\tau) | \psi_1, \psi_2 \rangle}{N(\psi_2) N(\psi_1)} \tag{3.5}
\]

With \( \overline{\psi} \) being the most equilibrium state, one can define

\[
\hat{a}(\tau) = \overline{\psi} | \frac{\partial^2 S^{(2)}<>(\psi_2, \psi_1 | \tau)}{\partial (\psi_2 | \partial (\psi_1)} | \overline{\psi}, \tag{3.6}
\]

\[
\hat{c}(\tau) = \overline{\psi} | \frac{\partial^2 S^{(2)}<>(\psi_2, \psi_1 | \tau)}{\partial (\psi_1 | \partial (\psi_2)} | \overline{\psi}, \tag{3.7}
\]

\[
\hat{b}(\tau) = \overline{\psi} | \frac{\partial^2 S^{(2)}<>(\psi_2, \psi_1 | \tau)}{\partial (\psi_2 | \partial (\psi_1)} | \overline{\psi}. \tag{3.8}
\]

These derivative are evaluated at \( \psi_1 = \overline{\psi} \), and \( \psi_2 = \overline{\psi}(\tau) \).

As mentioned above, the most likely wave state has an adiabatic evolution, \( \overline{\psi}(t) = e^{E_0 t/\hbar} |\overline{\psi}(0)\rangle \), and so the departures from the most likely equilibrium states are \( \Delta \psi_1 = \psi_1 - \overline{\psi} \) and \( \Delta \psi_2 = \psi_2 - \overline{\psi}(\tau) \). (It remains to show that the adiabatic evolution of the most likely wave function equals the most likely evolution. This explicit result for the time dependence of the most likely wave function is not required for most of what follows.) The
The expectation value of the second entropy may be expanded to quadratic order about the most likely values,

\[ S^{(2)<>}(\psi_2, \psi_1 | \tau) \approx S^{(1)} + \langle \Delta \psi_2 | \partial \psi_2 | \Delta \psi_2 \rangle + \langle \Delta \psi_1 | \partial \psi_1 | \Delta \psi_1 \rangle + \langle \Delta \psi_2 | \hat{b}(\tau) | \Delta \psi_1 \rangle + \langle \Delta \psi_1 | \hat{b}(\tau)^\dagger | \Delta \psi_2 \rangle. \]  
(3.9)

The constant term comes from the reduction condition.

The three symmetries are statistical symmetry combined with time homogeneity,

\[ S^{(2)}(\psi_2, \psi_1 | \tau) = S^{(2)}(\psi_1, \psi_2 | -\tau), \]  
(3.10)

microscopic reversibility,

\[ S^{(2)}(\psi_2, \psi_1 | \tau) = S^{(2)}(\psi_2^*, \psi_1^* | \tau), \]  
(3.11)

and reality,

\[ S^{(2)}(\psi_2, \psi_1 | \tau) = S^{(2)}(\psi_2, \psi_1 | \tau)^*. \]  
(3.12)

Statistical symmetry implies that

\[ \hat{a}(\tau) = \hat{c}(\tau), \]  
(3.15)

Reality implies that

\[ \hat{a}(\tau)^\dagger = \hat{a}(\tau), \]  
(3.16)

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

\[ \hat{a}(\tau)^* = \hat{c}(\tau), \]  
(3.17)

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

It ought to be emphasized that the fluctuation form for the expectation value of the second entropy is an approximation. Essentially, the exact second entropy operator is a four dimensional object, whereas the fluctuation form consists of the sum of four operators (reduced to three by symmetry) that are each two dimensional objects.

### C. Most Likely Terminus

The derivative of the fluctuation form for the second entropy with respect to the terminal arrival departure \( \langle \Delta \psi_2 \rangle \) is

\[ \frac{\partial S^{(2)<>}(\psi_2, \psi_1 | \tau)}{\partial \langle \Delta \psi_2 \rangle} = \hat{a}(\tau) | \Delta \psi_2 \rangle + \hat{b}(\tau) | \Delta \psi_1 \rangle. \]  
(3.18)

(The unusual phrase ‘terminal arrival departure’ means the terminus at the arrival end of the transition (i.e. the \( \psi_2 \)) expressed as the departure from the most likely value (i.e. \( \psi_2 - \bar{\psi}(t_2) \)). Setting this to zero, the most likely transition departure, \( \Delta \bar{\psi}_2 = \bar{\psi}(\tau)|\psi_1\rangle - \bar{\psi}(\tau) \), is

\[ |\Delta \bar{\psi}_2\rangle = -\hat{a}(\tau)^{-1} \hat{b}(\tau) |\Delta \psi_1\rangle. \]  
(3.19)

Since in quantum mechanics one is dealing with operator equations that are linear homogeneous functions of the wave function, this implies that the most likely destination itself is

\[ |\bar{\psi}(\tau)|\psi_1\rangle = -\hat{a}(\tau)^{-1} \hat{b}(\tau) |\psi\rangle. \]  
(3.20)

Consequently, the most likely wave function trajectory must satisfy

\[ |\bar{\psi}(\tau)\rangle = -\hat{a}(\tau)^{-1} \hat{b}(\tau) |\bar{\psi}\rangle. \]  
(3.21)

The meaning of this latter result, and its consistency with the assertion made above that the evolution of the most likely wave function is adiabatic, will be discussed below. (See also the appendix.)

### D. Reduction Condition

The second entropy may be re-written in terms of the departure from the most likely terminus, \( \psi_2 - \bar{\psi}_2 \),

\[ S^{(2)<>}(\psi_2, \psi_1 | \tau) = \]  
(3.22)

\[ S^{(1)} + \langle \Delta \psi_2 - \Delta \bar{\psi}_2 | \hat{a}(\tau) | \Delta \psi_2 - \Delta \bar{\psi}_2 \rangle + \langle \Delta \psi_1 | \{ \hat{c}(\tau) - \hat{b}(\tau)^\dagger \hat{a}(\tau)^{-1} \hat{b}(\tau) \} | \Delta \psi_1 \rangle. \]

The reduction condition is that in the most likely state, the second entropy reduces to the first entropy, \( S^{(2)<>}(\psi_2, \psi_1 | \tau) = S^{(1)<>}(\psi_1 | \tau) \) (see also Eq. 3.14). In view of the fluctuation expression for the first entropy, Eq. 3.1, this implies that

\[ \hat{c}(\tau) - \hat{b}(\tau)^\dagger \hat{a}(\tau)^{-1} \hat{b}(\tau) = \hat{S}'' \]  
(3.23)

This result must hold for each value of the time step \( \tau \).

### E. Small Time Expansion

Almost all of §IIIA4 of Paper II goes through unchanged, giving the small time expansions as

\[ \hat{a}(\tau) = \frac{-1}{|\tau|} \hat{a}_0 + \hat{a}_0' + \mathcal{O}(\tau), \]  
(3.24)

\[ \hat{b}(\tau) = \frac{1}{|\tau|} \hat{b}_0 + \hat{b}_0' + \mathcal{O}(\tau), \]  
(3.25)
and
\[
\hat{c}(\tau) = \frac{-1}{|\tau|} \lambda^{-1} + \hat{a}_0 - \tau \hat{a}_0' + O(\tau). \tag{3.26}
\]
The operator $\lambda$ is real, symmetric (and hence it is Hermitian), and positive definite.

From the symmetries given above, $\hat{a}(\tau) = \hat{a}(\tau)^\dagger = \hat{a}(-\tau)^*$, and $\hat{c}(\tau) = \hat{c}(\tau)^*$, 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 $\hat{b}(\tau) = \hat{b}(\tau)^* = \hat{b}(-\tau)^*$, the unprimed $\hat{b}$ are real and self-adjoint, and the primed $\hat{b}$ are imaginary and anti-self-adjoint.

The reduction condition yields
\[
\hat{a}_0 + \hat{b}_0 = \frac{1}{2} \hat{S}''. \tag{3.27}
\]
The is the same as in Paper II. This result is the analogue of the result for classical fluctuations in macrostates or microstates given in Ref. 26.

Using this, the expansion for the most likely terminal wave function becomes
\[
|\psi_2\rangle = -\hat{a}(\tau)^{-1} \hat{b}(\tau)|\psi_1\rangle
= \left[ I + |\tau|\lambda \hat{a}_0 + 2|\tau|\lambda \hat{a}_0' \right]
\times \left[ I + |\tau|\lambda \hat{b}_0 + 2|\tau|\lambda \hat{b}_0' \right]|\psi_1\rangle
= |\psi_1\rangle + \lambda \left[ \hat{a}_0' + \hat{b}_0' \right]|\psi_1\rangle
+ \frac{|\tau|}{2} \lambda \hat{S}''|\psi_1\rangle + O(\tau^2). \tag{3.28}
\]

The adiabatic evolution must be contained in the reversible term, which is the one that is proportional to $\tau$, $|\psi_2\rangle = (1/\sqrt|i\hbar|)|\hat{H}|\psi_1\rangle$. There may be reversible reservoir contributions, but since the reservoir is nothing but a perturbation to the adiabatic evolution, they can be neglected compared to the reversible adiabatic term. One cannot neglect the irreversible reservoir term because there is not an adiabatic irreversible term with which to compare it. Since it is the only irreversible term, and since irreversibility is an essential ingredient in the evolution that follows directly from the second law of thermodynamics, one must retain the irreversible reservoir term.

Hence equating the reversible term here with the adiabatic evolution of the wave function, one must have
\[
\lambda \left[ \hat{a}_0' + \hat{b}_0' \right] = \frac{1}{2i\hbar} \hat{H}. \tag{3.29}
\]
Both sides are imaginary. Since the right hand side is anti-Hermitian, one must have
\[
\lambda \left[ \hat{a}_0' + \hat{b}_0' \right] = - \left[ \hat{a}_0'' + \hat{b}_0'' \right] \lambda = - \left[ \hat{a}_0' - \hat{b}_0' \right] \lambda. \tag{3.30}
\]
Contrary to what was asserted following Eq. (3.32) of Paper II, this does not imply that $\hat{b}_0 = 0$. Fortunately, that erroneous assertion does not affect anything in that paper beyond the assertion itself.

Inserting this adiabatic result, the formula for the most likely transition terminal is
\[
|\psi(\tau|\psi_1)\rangle = |\psi_1\rangle + \frac{\tau}{i\hbar} \hat{H}|\psi_1\rangle + \frac{|\tau|}{2} \lambda \hat{S}''|\psi_1\rangle. \tag{3.31}
\]

As mentioned above, in order for this linear homogeneous form to result from the formula for the most likely departure of the transition terminal, the most likely wave state has to cancel both sides. The validity of doing this can be seen by inserting into this result the most likely wave function as the initial wave function, which gives
\[
|\psi(\tau|\psi)\rangle = |\psi\rangle + \frac{\tau}{i\hbar} \hat{H}|\psi\rangle + \frac{|\tau|}{2} \lambda \hat{S}''|\psi\rangle
= \left[ 1 + \frac{\tau E_0}{i\hbar} \right]|\psi\rangle. \tag{3.32}
\]
This is just the adiabatic development of the most likely wave function to linear order in the time step, as foreshadowed above. That to leading the reservoir does not contribute to this evolution is to be expected because by definition there is no entropy gradient at this most likely wave state and so there is no driving force from the reservoir.

Several points follow from this. The final argument regarding the vanishing of the entropy gradient holds for all equilibrium systems, not just the canonical one. It is therefore plausible that in the general equilibrium case evolution of the most likely wave function should be reversible and adiabatic. This appears to hold beyond the leading order in the time step. This is reasonable and it says that there is a unique most likely trajectory, $\psi(t)$.

From the above result for the most likely terminal wave function of a transition, one can identify the most likely propagator as
\[
\hat{U}(\tau) = \hat{I} + \frac{\tau}{i\hbar} \hat{H} + \frac{|\tau|}{2} \lambda \hat{S}'' + O(\tau^2). \tag{3.33}
\]
It consists of an adiabatic part, the first two terms, and a dissipative part, the final term, which is proportional to the gradient of the reservoir entropy. The fluctuation operator $\lambda$ may also be called the drag or friction operator.

The most likely propagator must satisfy the reversibility condition obtained above, Eq. (2.79),
\[
\hat{U}(\tau) = \hat{U}(-\tau)^*, \quad \text{and} \quad \hat{U}(\tau)^T = \hat{U}(-\tau)^T. \tag{3.34}
\]
Since both $\lambda$ and $\hat{S}''$ are real, one sees that this is indeed satisfied.

F. Stochastic, Dissipative Propagator

To the most likely propagator may be added a stochastic operator to give the stochastic dissipative time prop-
agator
\[ \hat{U}(\tau) = \hat{U}(\tau) + \hat{R}. \] (3.35)

The probability distribution of the stochastic operator must obey certain properties that are derived from the symmetry conditions on the transition probability (equivalently transition entropy) and the other conditions that were established above for the propagator.

It was established above that the propagator is on average unitary, Eq. (2.30). From this it follows that the variance of the stochastic part of the propagator must be
\[ \left\langle \hat{R}^\dagger \hat{R} \right\rangle_{\text{stoch}} = \frac{1}{2} \left[ \hat{S}'' + \hat{S}'' + \hat{\lambda} \right]. \] (3.36)

The symmetry relations showed that the equilibrium probability distribution was stationary under the action of the stochastic propagator, Eq. (2.67),
\[ \hat{\phi}^{(1)} = \left\langle \hat{U}(\tau) \hat{\phi}^{(1)} \right\rangle_{\text{stoch}}. \] (3.37)

For the case of a canonical equilibrium system, the Maxwell-Boltzmann probability operator is readily shown to be stationary under the adiabatic evolution,
\[ \hat{\phi}^{(1)}_{\text{MB}} = \left\langle \hat{U}^0(\tau) \hat{\phi}^{(1)}_{\text{MB}} \hat{U}^0(\tau) \right\rangle_{\text{stoch}}. \] (3.38)

(Hint: The Hamiltonian operator is proportional to the entropy operator and so commutes with it.) Assuming that in general the equilibrium probability distribution is stationary under the adiabatic evolution, then the stationary condition becomes
\[ \left\langle \hat{R}^\dagger \hat{\phi}^{(1)} \hat{R} \right\rangle_{\text{stoch}} = \frac{1}{2} \left[ \hat{\lambda} \hat{S}'' + \hat{\lambda} \hat{S}'' \right]. \] (3.39)

This may be called the quantum fluctuation dissipation theorem.

If the probability operator and the time propagator commute, then the quantum fluctuation dissipation theorem is identical to the unitary condition.

If the entropy operator $\hat{S}^{(1)}$ or $\hat{S}''$ and the fluctuation operator $\hat{\lambda}$ commute, and if the entropy operator and the stochastic operator $\hat{R}$ commute, then the quantum fluctuation dissipation theorem is identical to the unitary condition.

G. Ansatz for the Drag and Stochastic Operators

The drag and stochastic operators represent the contribution of the reservoir to the evolution of the sub-system wave function. The concept of a reservoir is a key element in statistical mechanics that allows detailed analysis and calculation to be focussed on that part of the system that is of immediate interest while treating the interactions with the neighboring and far regions in a averaged, integrated fashion. The reservoir contributions represent a perturbation on the adiabatic motion of the sub-system that has to obey certain statistical and symmetry rules (the unitary and stationarity conditions deduced above) but are otherwise arbitrary.

Perhaps the simplest ansatz for the drag and stochastic operators is to construct them from the entropy eigenfunctions such that they are diagonal in the entropy representation. The drag operator can be taken to be of the form
\[ \hat{\lambda} = \sum_{\alpha, g} \lambda_{\alpha} \langle \zeta_\alpha^S | \zeta_\alpha^S \rangle. \] (3.40)

The coefficients can be chosen as desired, although since $\hat{\lambda}$ must be Hermitian and positive semi-definite, $\lambda_{\alpha} \geq 0$. (If the drag coefficient vanishes, then the corresponding stochastic coefficient vanishes — see below.) The stochastic operator may similarly be taken to be
\[ \hat{R} = \sum_{\alpha, g} r_{\alpha} \langle \zeta_\alpha^S | \zeta_\alpha^S \rangle. \] (3.41)

Inserting these into the unitary condition, Eq. (3.36), one obtains
\[ \langle r_{\alpha}^* r_{\beta} \rangle_{\text{stoch}} = -\delta_{\alpha, \beta} \langle |S_{\alpha} - S_{\beta}| \rangle \lambda_{\alpha}. \] (3.42)

This says that the coefficients of the stochastic operator of different entropy states are uncorrelated.

With this ansatz, there is no stochastic contribution to the evolution of the ground state, $r_0 = 0$. The ground state drag coefficient may be non-zero, $\lambda_0 > 0$, but the dissipative contribution to the ground state evolution is zero, $(S_n - S_0)\lambda_n = 0$ if $n = 0$. With this ansatz, the evolution of the ground state is purely adiabatic.

Since this ansatz for the drag operator is diagonal in the entropy representation, it commutes with the entropy operator, $\hat{\lambda} \hat{S} = \hat{S} \hat{\lambda}$, and with the entropy fluctuation operator, $\hat{\lambda} \hat{S}'' = \hat{S}'' \hat{\lambda}$. (Incidently, this means that with this ansatz the propagator is transpose symmetric, $\hat{U}(\tau)^T = \hat{U}(\tau)$.) For the same reason the stochastic operator commutes with the entropy operator, $\hat{R} \hat{S} = \hat{S} \hat{R}$. Since the probability operator is the exponential the entropy operator, it commutes with the drag operator, the stochastic operator, and the the entropy fluctuation operator. Hence it commutes with the stochastic dissipative propagator, $\hat{U}(\tau) \hat{\phi} = \hat{\phi} \hat{U}(\tau)$. Hence with this ansatz, the stationarity condition is automatically satisfied if the unitary condition is satisfied,
\[ \left\langle \hat{U}(\tau)^\dagger \hat{\phi} \hat{U}(\tau) \right\rangle_{\text{stoch}} = \left\langle \hat{U}(\tau)^\dagger \hat{U}(\tau) \right\rangle_{\text{stoch}} \hat{\phi} = \hat{\phi}. \] (3.43)

IV. NATURE OF NON-EQUILIBRIUM PROBABILITY

Non-equilibrium systems are defined by the increase in total entropy with time. Hence in setting out the nature of non-equilibrium probability, the functions given
in \( W \) become time dependent. For example the weight operator is \( \hat{w}(t) \).

The relationships between weight, probability, and entropy are unchanged functionally. The microstate weight is

\[
 w_n^A(t) = \langle \zeta_n^A | \hat{w}(t) | \zeta_n^A \rangle, \tag{4.1}
\]

the macrostate weight is

\[
 w_n^C(t) = \sum_k \langle \zeta_{nk}^C | \hat{w}(t) | \zeta_{nk}^C \rangle, \tag{4.2}
\]

and the total weight is

\[
 W(t) = \sum_{\alpha} \langle C \rangle w_\alpha^C(t) = \sum_{\alpha,k} \langle C \rangle w_{\alpha k}^C(t). \tag{4.3}
\]

Similarly the non-equilibrium probability operator is \( \hat{\psi}(t) = \hat{w}(t)/W(t) \), and the non-equilibrium entropy operator is \( \hat{S}(t) = k_B \ln \hat{w}(t) \). The distinction between the expectation value of the entropy, \( S_{\text{stoch}} \equiv \langle \zeta_m | \hat{S}(t) | \zeta_n \rangle \) and the entropy of states \( S_{\text{stoch}} \equiv k_B \ln \langle \zeta_m | \hat{w}(t) | \zeta_n \rangle \) remains, with \( \hat{\psi}^\dagger(t) = \hat{w}^\dagger(t) / W(t) \).

In the case of transitions (c.f. \( \Box \)), some changes are required. Consider the transition from the state \( n_1^A \) at \( t_1 \) to \( n_2^B \) at \( t_2 = t_1 + \tau \), and define the mid-time as \( t \equiv [t_2 + t_1]/2 \). The weight of this transition may be denoted \( w^{(2)}(n_1^A, t_1; n_2^B, t_2) \equiv w^{(2)}(n_1^A, n_2^B | \tau, t) \). Unlike the equilibrium case, one cannot assume time homogeneity, and so both time arguments have to appear in the transition operator, \( \hat{w}(\tau, t) \). Practically all of the analysis of \( \Box \) goes through with the change \( \tau \Rightarrow \tau, t \).

One significant change in the non-equilibrium case is the reduction condition. This now takes the form

\[
 \sum_{n_2^B} w^{(2)}(n_1^A, t_1; n_2^B, t_2) = w_{n_1^A}(t_1) \sqrt{W(t_2)/W(t_1)}, \tag{4.4}
\]

and

\[
 \sum_{n_1^A} w^{(2)}(n_1^A, t_1; n_2^B, t_2) = w_{n_2^B}(t_2) \sqrt{W(t_1)/W(t_2)}. \tag{4.5}
\]

The scale factor is new compared to the equilibrium case and is necessary for the correct symmetry for the total transition weight, as is now shown (see also §8.3.1 of Ref. [26]). The total transition weight, \( W^{(2)}(t_2, t_1) \equiv W^{(2)}(\tau, t) \), is

\[
 W^{(2)}(t_2, t_1) = \sum_{n_2^B, n_1^A} w^{(2)}(n_1^A, t_1; n_2^B, t_2)
 = \sum_{n_1^A} w_{n_1^A}(t_1) \sqrt{W(t_2)/W(t_1)}
 = \sqrt{W(t_2)W(t_1)}. \tag{4.6}
\]

The same result follows if the order of the summations is changed. Because of this scaling, the reduction condition on the weight operators is

\[
 \text{Tr}^{(1)}_1 \hat{w}^{(2)}(t_2, t_1) = \frac{W(t_1)}{W(t_2)} \hat{w}(t_2), \tag{4.7}
\]

and

\[
 \text{Tr}^{(1)}_2 \hat{w}^{(2)}(t_2, t_1) = \frac{W(t_2)}{W(t_1)} \hat{w}(t_1), \tag{4.8}
\]

where the subscript on the trace indicates which time is traced over. In terms of the transition probability operator, \( \hat{\psi}^{(2)}(t_2, t_1) = \hat{w}^{(2)}(t_2, t_1)/W^{(2)}(t_2, t_1) \), the reduction condition is

\[
 \text{Tr}^{(1)}_1 \hat{\psi}^{(2)}(t_2, t_1) = \frac{1}{\sqrt{W(t_2)W(t_1)}} \text{Tr}^{(1)}_1 \hat{w}^{(2)}(t_2, t_1)
 = \frac{1}{\sqrt{W(t_2)W(t_1)}} \sqrt{W(t_1)/W(t_2)} \hat{w}(t_2)
 = \hat{\psi}(t_2), \tag{4.9}
\]

and, analogously, \( \text{Tr}^{(1)}_2 \hat{\psi}^{(2)}(t_2, t_1) = \hat{\psi}(t_1) \).

The propagator gives the evolution of the wave function in the non-equilibrium system,

\[
 |\psi(t_2)\rangle = \hat{U}(t_2, t_1) |\psi(t_1)\rangle. \tag{4.10}
\]

It may also be written \( \hat{U}(\tau, t) \). The conditional transition probability operator is a two-time operator that can be written as the composition of the two one-time propagators,

\[
 \hat{\psi}_{\text{cond}}^{(2)}(t_2, t_1) = \langle \{ \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \} \rangle_{\text{stoch}}. \tag{4.11}
\]

Accordingly the unconditional transition probability operator is the composition of the conditional transition probability operator and the singlet probability operator that can be arranged in four ways,

\[
 \hat{\psi}^{(2)}(t_2, t_1) = \langle \{ \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \hat{\psi}^{(1)}(t_1) \} \rangle_{\text{stoch}}
 = \langle \{ \hat{\psi}^{(1)}(t_1), \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \} \rangle_{\text{stoch}}
 = \langle \{ \hat{U}(t_2, t_1)^\dagger, \hat{\psi}^{(1)}(t_2), \hat{U}(t_2, t_1) \} \rangle_{\text{stoch}}
 = \langle \{ \hat{U}(t_2, t_1)^\dagger, \hat{U}(t_2, t_1) \hat{\psi}^{(1)}(t_2) \} \rangle_{\text{stoch}}. \tag{4.12}
\]

Taking the traces of this and using the reduction condition, one obtains the stationarity condition and the unitary condition for the propagator.
In applications of quantum statistical mechanics, the total entropy to avoid any ambiguity.

Appendix A: Fluctuations Revisited

1. Most Likely Sub-Space

In the text, particularly \[\text{(III)}\], the fluctuation forms of the first and second entropy were analyzed. This analysis was based upon the departure from the most likely wave function \(\Delta \psi(t) \equiv \psi - \bar{\psi}(t)\). In this appendix, a clearer, more rigorous, and more general analysis of fluctuations is given, as well as some discussion of the consequences of the analysis.

Denote the eigenstates of maximum entropy by the principle quantum number \(g\). Taking into account degeneracy, the corresponding eigenfunctions are \(\zeta_{S_{0g}}^g\). The total entropy operator and the reservoir entropy operator are equivalent and are both denoted here by \(\hat{S}\). For the present equilibrium system, the sub-space is constant in time. One can ignore the time dependence of the phase angle of the eigenfunctions. The sub-space that these span may be called the most likely sub-space. It can also be called the entropy ground state, since it is the space with the largest eigenvalue that is smallest in magnitude, (equivalently, since the eigenvalues are negative, the largest signed eigenvalue). The projection operator for this most likely sub-space is

\[
\hat{P}_0 \equiv \sum_g \langle \zeta_{S_{0g}}^g | \zeta_{S_{0g}}^g \rangle.
\] (A.1)

The projector for the orthogonal sub-space, the excited sub-space, is \(\hat{P}_\perp \equiv \hat{I} - \hat{P}_0\).

In general an operator can be decomposed into its projections onto the two sub-spaces,

\[
\hat{O} = [\hat{P}_0 + \hat{P}_\perp] \hat{O} [\hat{P}_0 + \hat{P}_\perp]
\]

\[
= \hat{P}_0 \hat{O} \hat{P}_0 + \hat{P}_\perp \hat{O} \hat{P}_\perp + \hat{P}_0 \hat{O} \hat{P}_\perp + \hat{P}_\perp \hat{O} \hat{P}_0
\]

\[
\equiv \hat{O}_{00} + \hat{O}_{0\perp} + \hat{O}_{\perp 0} + \hat{O}_{\perp \perp}.
\] (A.2)

The projection of the wave function \(\psi(t)\) onto the ground state sub-space is

\[
|\psi_0(t)\rangle \equiv \hat{P}_0 |\psi(t)\rangle = \sum_g \langle \zeta_{S_{0g}}^g | \psi(t) \rangle |\zeta_{S_{0g}}^g\rangle.
\] (A.3)

One could also write \(\bar{\psi}(t) \equiv \psi_0(t)\). The fluctuation of a wave state is the part orthogonal to the most likely sub-space,

\[
|\Delta \psi(t)\rangle \equiv \hat{P}_\perp |\psi(t)\rangle.
\] (A.4)

With \(\psi_0 \equiv \bar{\psi}\) and \(\psi_\perp \equiv \Delta \psi\) , the first entropy in fluctuation form is

\[
S^{<>}(\psi) = \frac{\langle \psi | \hat{S} | \psi \rangle}{\langle \psi | \bar{\psi} \rangle}
\]
Because the entropy operator is block diagonal, one can write

$$
\hat{S}'' = \sum_{p=0} N(\psi) + N(\Delta \psi)
$$

and the continuation of this to the full Hilbert space is

$$
\hat{S}'' = \hat{S}_{\perp\perp} + \hat{S}_{0\perp}.
$$

One has an analogous result for \( \hat{S}'' \).

For future reference, in the canonical equilibrium case, the energy operator is proportional to the entropy operator, \( \hat{H} = -T \hat{S} \), and so it is similarly block diagonal, \( \hat{H} = \hat{H}_{00} + \hat{H}_{0\perp} \).

Accordingly, all of the terms on the right hand side of the propagator on the orthogonal sub-space are of the form of orthogonal projections of operators on the full Hermitian space. Hence it does not strain credulity to write for the most likely part of the propagator on the full Hermitian space

$$
\hat{\mathcal{P}}(\tau) = \hat{I} + \frac{\tau}{\tau} \hat{H} + \frac{|\tau|}{2} \lambda \left[ \hat{S} - S_0 \hat{I} \right].
$$

Adding a stochastic operator, the full stochastic dissipative propagator is

$$
\hat{\mathcal{U}}(\tau) = \hat{I} + \frac{\tau}{\tau} \hat{H} + \frac{|\tau|}{2} \lambda \left[ \hat{S} - S_0 \hat{I} \right] + \hat{\mathcal{R}}.
$$

The unitary condition to linear order in the time step is

$$
\hat{I} = \left\langle \hat{\mathcal{U}}(\tau) | \hat{\mathcal{U}}(\tau) \right\rangle_{\text{stoch}}
$$

$$
= \sum_{\alpha,\beta,\gamma=0,\perp} \left\langle \hat{\mathcal{U}}_{\alpha\beta}(\tau) | \hat{\mathcal{U}}_{\beta\gamma}(\tau) \right\rangle_{\text{stoch}}
$$

$$
= \hat{I} + \frac{|\tau|}{2} \left[ \lambda_{0\perp} + \lambda_{\perp\perp} \right] \left[ S_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \right]
$$

$$
+ \frac{|\tau|}{2} \left[ \hat{S}_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \right] \left[ \lambda_{\perp\perp} + \lambda_{\perp\perp} \right]
$$

$$
+ \sum_{\alpha,\beta,\gamma=0,\perp} \left\langle \hat{\mathcal{R}}_{\alpha\beta} \hat{\mathcal{R}}_{\beta\gamma} \right\rangle_{\text{stoch}}.
$$

The third equality uses the fact that \( \hat{S} - S_0 \hat{I} = \hat{S}_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \), since \( S_{00} = S_{0\perp} \). By definition the average of the stochastic operator vanishes, \( \langle \hat{\mathcal{R}} \rangle_{\text{stoch}} = 0 \).

Explicitly this gives for the 00 component

$$
0 = \langle \hat{\mathcal{R}}_{00} \hat{\mathcal{R}}_{00} \rangle_{\text{stoch}} + \langle \hat{\mathcal{R}}_{00} \rangle_{\text{stoch}}.
$$

For the 0 component it gives

$$
-\frac{|\tau|}{2} \lambda_{0\perp} \left[ \hat{S}_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \right]
$$

$$
= \langle \hat{\mathcal{R}}_{0\perp} \hat{\mathcal{R}}_{\perp\perp} \rangle_{\text{stoch}} + \langle \hat{\mathcal{R}}_{0\perp} \rangle_{\text{stoch}}.
$$

For the \( \perp \) component it gives

$$
-\frac{|\tau|}{2} \left[ \hat{S}_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \right] \lambda_{\perp\perp}
$$

$$
= \langle \hat{\mathcal{R}}_{\perp0} \hat{\mathcal{R}}_{00} \rangle_{\text{stoch}} + \langle \hat{\mathcal{R}}_{\perp0} \rangle_{\text{stoch}}.
$$

For the \( \perp \perp \) component it gives

$$
-\frac{|\tau|}{2} \left[ \lambda_{\perp\perp} \left( \hat{S}_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \right) + \left( \hat{S}_{\perp\perp} - S_0 \hat{I}_{\perp\perp} \right) \lambda_{\perp\perp} \right]
$$

$$
= \langle \hat{\mathcal{R}}_{\perp\perp0} \hat{\mathcal{R}}_{00} \rangle_{\text{stoch}} + \langle \hat{\mathcal{R}}_{\perp\perp0} \rangle_{\text{stoch}}.
$$
From the 00 component one concludes that \( \hat{R}_{00} = \hat{R}_{\perp 0} = 0 \). (One would also get \( \hat{R}_{0\perp} = 0 \) from the unitary condition in the form \( \{\hat{U}(\tau)\hat{U}(\tau)^\dagger\}_{\text{stoch}} = \hat{I} \).) Combining this result with the \( 0\perp \) and the \( \perp 0 \) components implies that \( \lambda_{0\perp} = \lambda_{\perp 0} = 0 \). Hence only the orthogonal components of the stochastic and dissipative operators are non-zero, and these are related by

\[
\langle \hat{R}^\dagger_{\perp \perp} \hat{R}_{\perp \perp} \rangle_{\text{stoch}} = \frac{-|\tau|}{2} \left[ \hat{S}_{\perp \perp} + \hat{S}_{\perp \perp} \hat{S}_{\perp \perp} - 2 \hat{S}_{\perp \perp} \hat{S}_{\perp \perp} \right] \quad (A.19)
\]

One concludes that for the above propagator, there is no stochastic or dissipative coupling between the ground state and the excited states, and there is no stochastic or dissipative term in the ground state.

This conclusion is reason to argue that the above form for the propagator is not completely satisfactory. In essence the problem arises because the dissipative driving force acts only on the orthogonal sub-space

\[
\hat{S} - \hat{S}_0 = \hat{S}_{\perp \perp} - \hat{S}_{\perp \perp}, \quad (A.20)
\]

since \( \hat{S}_0 = S_0 \hat{I}_{00} \). The consequence of this is that the ground state is decoupled from the excited states. For example, the norm of the fluctuation does not decay but is on average constant, \( \langle N(\Delta \psi(t))\rangle_{\text{stoch}} = \langle N(\Delta \psi(0))\rangle_{\text{stoch}} \), which is counter-intuitive.

The present derivation only gives explicitly the evolution on the orthogonal sub-space. It does not preclude additional terms in the full propagator of the form \( \hat{A}_{0g}(\tau), \hat{A}_{0h}(\tau) \), and \( \hat{A}_{l0}(\tau) \), which would circumvent the decoupling.

2. Cross-Coupling Ansatz

In view of the last comment, one possibility is

\[
\hat{U}(\tau) = \hat{I} + \frac{\tau}{\hbar} \hat{H} + \frac{|\tau|}{2} \lambda \left[ \hat{S} - \hat{S}_0 \hat{P}_\perp \right] + \hat{R}. \quad (A.21)
\]

The projection of this on the orthogonal sub-space is unchanged from above, and it therefore in this case follows from the derivation. But it is emphasized that there is nothing in the present derivation that justifies this form for the propagator for the ground state. And it is also worth pointing out that in the classical case the dissipative force vanishes on the most likely trajectory\cite{1} just as it would vanish in the present quantum case except for this alternative formulation.

Inserting this into the unitary condition in the form \( \langle \hat{U}(\tau)\hat{U}(\tau)^\dagger\rangle_{\text{stoch}} = \hat{I} \) leads to

\[
\frac{-|\tau|}{2} \left[ \hat{S} \lambda + \hat{S} \hat{\lambda} - S_0 \hat{\lambda} \hat{P}_\perp - S_0 \hat{\lambda} \hat{P}_\perp \hat{\lambda} \right] = \langle \hat{R}^\dagger \hat{R} \rangle_{\text{stoch}}. \quad (A.22)
\]

The 00 component of this is

\[
-\frac{|\tau|}{2} \left[ \lambda_{00} \hat{S}_{00} + \hat{S}_{00} \lambda_{00} \right]
\]

\[
= -|\tau| S_0 \lambda_{00}
\]

\[
= \langle \hat{R}^\dagger_{0\perp} \hat{R}_{\perp 0} \rangle_{\text{stoch}} + \langle \hat{R}^\dagger_{00} \hat{R}_{00} \rangle_{\text{stoch}}. \quad (A.23)
\]

The 0 \perp component is

\[
-\frac{|\tau|}{2} \left[ \lambda_{0\perp} \left( \hat{S}_{\perp \perp} - S_0 \hat{I}_{\perp \perp} \right) + \hat{S}_{00} \lambda_{0\perp} \right]
\]

\[
= -\frac{|\tau|}{2} \left( \hat{S}_{\perp \perp} \hat{\lambda}_{0\perp} + \hat{S}_{00} \lambda_{0\perp} \right)
\]

\[
= \langle \hat{R}^\dagger_{0\perp} \hat{R}_{\perp 0} \rangle_{\text{stoch}} + \langle \hat{R}^\dagger_{00} \hat{R}_{00} \rangle_{\text{stoch}}. \quad (A.24)
\]

The \( \perp 0 \) component is

\[
-\frac{|\tau|}{2} \left[ \lambda_{\perp 0} \left( \hat{S}_{\perp \perp} - S_0 \hat{I}_{\perp \perp} \right) + \hat{S}_{00} \lambda_{\perp 0} \right]
\]

\[
= \langle \hat{R}^\dagger_{\perp 0} \hat{R}_{0\perp} \rangle_{\text{stoch}} + \langle \hat{R}^\dagger_{\perp \perp} \hat{R}_{\perp \perp} \rangle_{\text{stoch}}. \quad (A.25)
\]

For the \( \perp \perp \) component it gives

\[
-\frac{|\tau|}{2} \left[ \lambda_{\perp \perp} \left( \hat{S}_{\perp \perp} - S_0 \hat{I}_{\perp \perp} \right) + \hat{S}_{00} \lambda_{\perp \perp} \right]
\]

\[
= \langle \hat{R}^\dagger_{\perp \perp} \hat{R}_{\perp \perp} \rangle_{\text{stoch}} + \langle \hat{R}^\dagger_{\perp \perp} \hat{R}_{\perp \perp} \rangle_{\text{stoch}}. \quad (A.26)
\]

One obtains variants on these from the unitary condition in the form \( \{\hat{U}(\tau)\hat{U}(\tau)^\dagger\}_{\text{stoch}} = \hat{I} \). It is possible to satisfy these with consistent expressions for the drag and stochastic operators that couple the ground and excited states.

The feasibility of such a coupling can be explored more explicitly with a specific ansatz for the drag and stochastic operators. The drag operator can be taken to be of the form

\[
\hat{\lambda} = \sum_{n,g,h} \lambda_n |S_n^g\rangle\langle S_n^g| \hat{\lambda}.
\]

Since \( \hat{\lambda} \) must be Hermitian and positive semi-definite, \( \lambda_n = \lambda_n^* \geq 0 \). (The drag coefficient vanishes if and only if the corresponding stochastic coefficient vanishes.) The stochastic operator may be taken to be of the form

\[
\hat{R} = \sum_{n,g,h} r_n |S_n^g\rangle\langle S_n^g| \hat{R}.
\]

The results that follow can be simplified somewhat by taking \( g = h \) in these expressions for \( \hat{\lambda} \) and \( \hat{R} \). In this case the number of degenerate entropy states, \( N_n \), is replaced by unity in the following formulae.

The left hand side of the unitary condition is

\[
-\frac{|\tau|}{2} \left[ \lambda \hat{S} + \hat{S} \lambda - S_0 \lambda \hat{P}_\perp - S_0 \lambda \hat{P}_\perp \lambda \right]
\]
where \( \delta_{n0}^\dagger = 1 - \delta_{n0} \).

The right hand side of the unitary condition is

\[
(\hat{R}^\dagger \hat{R})_{\text{stoch}} = \sum_{n,g,h} \sum_{l,m,f,k} \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S)
\]

\[+ \sum_{n > g, h} \sum_{m > f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[+ \sum_{m > g, h} \sum_{n > f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[= \sum_{n, g, h} \sum_{m, f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[+ \sum_{m > g, h} \sum_{n > f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[= \sum_{n, g, h} \sum_{m, f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[+ \sum_{m > g, h} \sum_{n > f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[= \sum_{n, g, h} \sum_{m, f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[+ \sum_{m > g, h} \sum_{n > f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[= \sum_{n, g, h} \sum_{m, f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

\[+ \sum_{m > g, h} \sum_{n > f, k} \left\{ \langle r_n^* r_m \rangle_{\text{stoch}} |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* (\zeta_{mf}^S)^* (\zeta_{mk}^S) \right\} \]

Equating the coefficients of \( |\zeta_{nh}^S \rangle (\zeta_{ng}^S)^* \) yields

\[-\tau [S_n - \delta_{n0}^\dagger S_0] \lambda_n \] (A.31)