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The Essential Nonlinearity of *N*-Level Quantum Thermodynamics

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This paper explores the possibility that linear *dynamical maps might be used to describe the energy-conserving, entropy-increasing motions which occur in closed thermodynamic systems as they approach canonical thermal equilibrium. For* N*-level quantum systems with* $\mathrm{N} > 2$, *we prove that no such maps exist which are independent of the initial state.*

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1. INTRODUCTION

In the canonical version of quantum statistical thermodynamics, thermal equilibrium states are represented by density operators having the familiar form

$$\hat{\rho} = \frac{\exp(-\beta H)}{\operatorname{Tr} \exp(-\beta H)} \tag{1}$$

where H is the Hamiltonian. For any quantum state ρ, the statistical analog for internal energy U is given by

$$U = \operatorname{Tr}(\rho H) \tag{2}$$

and the entropy is expressed as

$$S(\rho) = -k \operatorname{Tr}(\rho \ln \rho) \tag{3}$$

When S is maximized subject to constraint (2), the unique result is the canonical state (1), with inverse temperature β uniquely determined by (2).

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According to the usual understanding of the first and second laws of thermodynamics, a system left to itself will eventually evolve, or "relax," without change in its internal energy, to a unique state of stable thermal equilibrium characterized as having the maximum entropy compatible with the constraint of fixed energy. Unfortunately such a process is inconceivable within the conventional framework of quantum dynamics, since (3) is a constant of the motion. The reason for this invariance is that the value of $S(\rho)$ depends only on the eigenvalues of ρ, which are invariant under unitary transformation.

Some authors have circumvented this problem by reinterpreting ρ in the entropy functional by coarse graining.[3] Others have applied the von Neumann projection postulate in varying degrees to obtain an increase in entropy.[4] Still others,(3) using methods of quantum field theory, obtain an increase in the in the entropy after taking the thermodynamic limit N, $V \to \infty$, $N/V =$ const, where N is the particle number and V the volume.

We will not criticize these methods. The literature abounds with arguments for and against each of them. Particularly significant, however, is an exhaustive study of the foundations of thermodynamics and its relationship to quantum mechanics by Hatsopoulos and Gyftopoulos,(4–7) who demonstrated quite conclusively that some as yet unknown, nonunitary principle of quantal motion must be devised in order to achieve a satisfactory unification of those two fundamental theories into one uncontradictory science of quantum thermodynamics. A general essay on quantum thermodynamics by the present authors appears in the Yourgrau memorial volume.(8)

Motivated either by the foregoing dilemma or by the desire to obtain phenomenological descriptions of the evolution of subsystems, various authors have considered generalizations of quantum dynamics in which the laws of motion do not conserve S. These efforts have generally been based upon dynamical maps which, though nonunitary, are nevertheless linear, thus assuring the applicability of a substantial body of standard mathematical structures. This approach has yielded several interesting contributions(9–14) to the quantum dynamics of subsystems; in these cases entropy may rise or fall, but energy need not be conserved. Moreover, Band and Park(15–17) found that for two-level quantum systems there exist linear maps—independent of the initial density operator—which describe energy-conserving, entropy-increasing processes. The latter would be an essential feature of a unified theory of quantum thermodynamics.

The present paper outlines the mathematical framework of proposed linear generalizations of quantum dynamics, investigates the possibility that

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[3] The idea of coarse graining originated with Gibbs and is discussed in many textbooks on statistical mechanics, e.g., Ref. 1.

[4] The projection postulate is used in this manner by many authors, e.g., Landé.(2)

linear dynamical maps might be used in quantum thermodynamics, and proves that, for N-level systems with $N > 2$, there are no linear maps describing energy-conserving, entropy-increasing motion.

2. LINEAR GENERALIZATIONS OF QUANTUM DYNAMICS

Only one modification of the underlying axiomatic structure of quantum theory is contemplated in the search for a new dynamics. The nondynamical postulates are retained in the standard form and may be expressed as follows^(18):

With every quantum system there is associated a complex, separable, complete inner product space, a Hilbert space $\mathscr{H}$. If $\mathscr{H}_A$, $\mathscr{H}_B$ are Hilbert spaces associated with distinguishable systems A, B, then the direct product space $\mathscr{H}_A \otimes \mathscr{H}_B$ is associated with the composite system of A and B together.

To every reproducible preparation of state for a quantum system there corresponds a density operator ρ, which is a positive-semidefinite, self-adjoint, unit-trace linear operator on $\mathscr{H}$. All the density operators are elements of $\mathscr{T}(\mathscr{H})$, the real normed linear space of all linear self-adjoint trace class operators on $\mathscr{H}$. Within the space $\mathscr{T}(\mathscr{H})$ is a set called the positive cone $\mathscr{V}^+(\mathscr{H})$, which contains the positive-semidefinite operators on $\mathscr{H}$, and within the set $\mathscr{V}^+(\mathscr{H})$ is a convex subset $\mathscr{V}_1^+(\mathscr{H})$ containing the elements of $\mathscr{V}^+(\mathscr{H})$ with unit trace. $\mathscr{V}_1^+(\mathscr{H})$ is therefore the set of density operators, the mathematical representatives of quantum states.

Some elements $\{A, B, \ldots, H, \ldots\}$ of the real Banach space $\mathscr{B}(\mathscr{H})$ of all continuous, linear, self-adjoint operators on $\mathscr{H}$ correspond to observables of the system. The arithmetic mean value $\langle A \rangle$ of the results of measurements of observable A collected on an ensemble of systems prepared in the state associated with density operator ρ is given by the continuous linear functional $\langle A \rangle = \mathrm{Tr}(\rho A)$.

Any proposed dynamical law must involve only mappings of the convex set $\mathscr{V}_1^+(\mathscr{H})$ into itself, and the formulation of such laws is complicated by the fact neither $\mathscr{V}^+(\mathscr{H})$ nor $\mathscr{V}_1^+(\mathscr{H})$ is a subspace of $\mathscr{T}(\mathscr{H})$. The dynamical postulate of conventional quantum theory describes the motions of a system by a one-parameter (time) unitary group $\{\Lambda_t\}$ of linear transformations of $\mathscr{T}(\mathscr{H})$ into $\mathscr{T}(\mathscr{H})$, the unitarity guaranteeing that no density operator will be transformed out of $\mathscr{V}_1^+(\mathscr{H})$.

A natural generalization of the dynamical postulate is obtained by letting $\{\Lambda_t\}$ be a one-parameter semigroup of linear transformations of $\mathscr{T}(\mathscr{H})$ into $\mathscr{T}(\mathscr{H})$ which need not be unitary. In this way irreversible motions are included among the dynamical possibilities since there may now be maps Λ_t which have no inverse and under which S is not invariant. Since Λ_t

is a linear transformation, the Hille–Yoshida theorem[(19)] can be used to obtain an equation of motion for $\rho(t)$ in terms of the infinitesimal generator L of the semigroup:

$$\frac{d\rho(t)}{dt} = \frac{d}{dt}\Lambda_t\rho(0) = L\Lambda_t\rho(0) = L\rho(t) \tag{4}$$

[Equation (4) is commonly referred to as the "Liouville equation" due to its similarity with the Liouville equation of classical mechanics. Since $\rho(t)$ is an operator on $\mathscr{H}$, and L is a linear operator on $\mathscr{T}(\mathscr{H})$, L is sometimes called a "superoperator." When applied to relaxation processes the Liouville equation is often called a "master equation."]

Although there is some agreement that unitary evolution must be abandoned, not all authors view this as a requirement for a new postulate of dynamics, but prefer simply to reinterpret unitary evolution. For example, Gorini *et al.*[(9)] and Lindblad[(10)] are concerned with the evolution of quantum subsystems (open systems). Consider two systems A and B with Hilbert spaces $\mathscr{H}_A$ and $\mathscr{H}_B$. If there is an interaction between the two systems, then the density operator for the composite system is an operator defined on the tensor product space $\mathscr{H}_A \otimes \mathscr{H}_B$ and in general

$$\rho_{AB} \neq \rho_A \otimes \rho_B \tag{5}$$

where $\rho_A \in \mathscr{V}_1^+(\mathscr{H}_A)$ and $\rho_B \in \mathscr{V}_1^+(\mathscr{H}_B)$.

If for some reason we restrict our interest to system A only but also assume an interaction between A and B, then A is called an open system. The semigroup time evolution is then applied to the open system A. The equation of motion for the state of A is then taken to be the Liouville equation,

$$d\rho_A(t)/dt = L\rho_A(t) \tag{6}$$

When two systems are interacting there is one state for the composite system and there is no state ρ_A for system A alone unless by ρ_A we mean the partial trace over $\mathscr{H}_B$ of ρ_{AB}, the so-called reduced density operator,

$$\rho_A = \mathrm{Tr}_B(\rho_{AB}) \tag{7}$$

Taking the partial trace destroys all correlations between A and B. Under these conditions one can find an L satisfying the conditions imposed by self-adjointness, positivity, and preservation of trace which leads to the final state $\rho_A(\infty)$, which may be a canonical state. It is therefore claimed that the evolution successfully leads to the relaxation to equilibrium of system A. Since the dynamics of system B is completely ignored, it is impossible to prove that energy is conserved. To avoid this problem, it is assumed that whatever energy is lost or gained by A is gained or lost by B but in such a way that these changes in B do not affect the time evolution of A. Then B becomes a thermodynamic heat bath, i.e., a large system which is at all times in a canonical state at a fixed temperature and capable of absorbing or emitting any amount of energy to system A without the temperature of B changing. The importance of the concept of a heat bath in thermodynamics is well known and appreciated, but it is also well known that systems not in contact with a heat bath do reach equilibrium. To allow for this and still describe the evolution of a system as an open system, Ingarden and Kossakowski(11) claim that no system is ever completely isolated, i.e., that no closed systems exist in nature. Every system, no matter how well it is isolated, is affected by its environment, i.e., the rest of the universe. The effect of the infinite environment on the "closed" system of interest is that it introduces a randomizing mechanism in the dynamics of the system. The increase in entropy of a "closed" system is, therefore, a result of the random effect of the environment. This idea was also published by Blatt(20) as an explanation for the increase in entropy of a system subject to incessant, completely random impacts of the molecules of the atmosphere on the boundaries of the system of interest. Although the interpretation of the semigroup evolution appears now to be different from the idea of the evolution being the subdynamics of an open subsystem in contact with a heat bath, the predictions are the same. Indeed, after declaring the infinite environment to be a *randomizing* mechanism, Ingarden and Kossakowski (Ref. 11, p. 478) find that it is capable of either increasing or decreasing the entropy of the system of interest. These authors admit at the end of an example that the infinite environment does not simply provide a randomizing mechanism, but the environment is actually a heat bath. Their interpretation of the semigroup evolution is, therefore, still that the evolution is the subdynamics of an open subsystem in contact with a heat bath.

With the same philosophical position, that the semigroup evolution applies only to open subsystems, a number of authors(9,10) have postulated that the semigroup mapping should be completely positive, a stronger restriction than positivity. Undoubtedly Λ_t must be a positive map in order to guarantee that $\rho(t)$ is a positive operator for all times. Complete positivity requires that the map $\Lambda_t \otimes I_n$ be positive for all $n \in \{0, 1, 2, \ldots\}$. In this mapping, I_n denotes the identity map I_n: $M(n) \to M(n)$ in the C^* algebra of complex $n \times n$ matrices. Gorini *et al.*(9) argue that if the evolution of the isolated system A plus B is given by a unitary group, then the subdynamics of system A must be described by a completely positive semigroup. Here no new fundamental dynamical postulate is being proposed; rather, the effort is directed toward describing the dynamics of a subsystem within the framework of global unitary evolution of the entire isolated system. The total entropy of the isolated system is of course constant under the assumed unitary evolution. A more detailed analysis of the efficacy of the complete positivity assumption has been given elsewhere.(21)

3. INADEQUACY OF LINEAR $\{\Lambda_t\}$ FOR N-LEVEL QUANTUM THERMODYNAMICS

The fundamental problem of quantum thermodynamics is not to describe only the evolution of a subsystem or the evolution of a system in contact with a heat bath, but to account for the increase in entropy of a closed system. If the dynamics of a closed system is unitary, there is no hope of predicting a change in the entropy. Therefore it is necessary to abandon the unitary evolution in favor of a generalized evolution.

The evolution as given by a one-parameter semigroup of *linear transformations* on $\mathscr{T}(\mathscr{H})$, as we have seen, has been applied mainly to subsystems. Is this particular generalization suitable for the description of a closed system ? The work of Band and Park(15–17) on two-level systems suggests an affirmative answer; but we shall now prove that for systems with Hilbert spaces of dimension $N > 2$ the answer is no. There does not exist a linear transformation Λ: $\mathscr{V}_1^+(\mathscr{H}) \to \mathscr{V}_1^+(\mathscr{H})$ that is capable of mapping all initial states ρ^0 with $\mathrm{Tr}(\rho^0 H) = U$ into the canonical state $\hat{\rho}$ with $\mathrm{Tr}(\hat{\rho} H) = U$.

To prove this, we first introduce an equivalence relation in $\mathscr{V}_1^+(\mathscr{H})$ with the equivalence class denoted by $[\rho U]$: $\rho_1^0, \rho_2^0 \in [\rho U]$ if and only if $\mathrm{Tr}(\rho_1^0 H) = \mathrm{Tr}(\rho_2^0 H) = U$. The equivalence class can be parametrized by the real number α, $\rho^0(\alpha) \in [\rho U]$.

It is assumed that the Hilbert space $\mathscr{H}_N$ associated with the system is N-dimensional and, for notational convenience, that the spectrum of the Hamiltonian H is nondegenerate. The real Banach space $\mathscr{T}(\mathscr{H}_N)$ can be identified with the C^* algebra of the complex $N \times N$ matrices. Any element $\sigma \in \mathscr{T}(\mathscr{H}_N)$ can be represented as an N^2-component column vector. We will work exclusively with the energy basis, the representation in which H is diagonal. To simplify the notation, the elements of the column vector representing $\sigma \in \mathscr{T}(\mathscr{H}_N)$ will be labeled by an index j,

$$\{j\}_{j=1}^{N^2} \leftrightarrow \{k, l\}_{k,l=1}^{N} \tag{8}$$

with the understanding that the $j \in \{1, 2,..., N\}$ are identified with m, $m \in \{k, l\}_{k,l=1}^{N}$; i.e., the first N elements of the column vector are the diagonal elements of the matrix, in the energy representation, associated with $\sigma \in \mathscr{T}(\mathscr{H}_N)$.

The linear transformations $\Lambda: \mathscr{V}_1^+(\mathscr{H}_N) \rightarrow \mathscr{V}_1^+(\mathscr{H}_N)$ can now be represented by $N^2 \times N^2$ matrices, the elements of which are constants. The mapping Λ must be positive and trace-preserving, but these restrictions are not necessary for the proof.

A general linear transformation Λ from $\rho^0(\alpha) \in [\rho U]$ to $\rho^f \in [\rho U]$ is written in vector notation as

$$\rho_i^f = \sum_{j=1}^{N^2} \Lambda_{ij} \rho_j^0(\alpha) \tag{9}$$

The canonical density operator is a function of H and therefore must be diagonal in the energy representation. Consequently, we can restrict our attention to the diagonal elements of ρ^f only, i.e., $i \in \{1, 2,..., N\}$ in the above equation. Among the density operators $\rho^0 \in [\rho U]$ is a set which is diagonal in the energy representation. Since Λ must map all $\rho^0 \in [\rho U]$ into $\hat{\rho}$, it is sufficient to show that no Λ exists which maps the subset of diagonal density operators $\rho^0(\alpha) \in [\rho U]$ into the canonical state $\hat{\rho}$. We therefore focus our attention on the diagonal density operators $\rho^0(\alpha)$ which are mapped by Λ into diagonal density operators ρ^f. Accordingly, we have

$$\rho_i^f = \sum_{j=1}^{N} \Lambda_{ij} \rho_j^0(\alpha), \qquad i = \{1, 2,..., N\} \tag{10}$$

There are N^2 constants, the elements of Λ_{ij}, which could be chosen to make ρ^f the canonical state $\hat{\rho}$. To determine whether a density operator ρ^f given in terms of the components ρ_i^f is canonical, we use the following test:

Lemma. The density operator ρ^f is the canonical state $\hat{\rho}$ if and only if ρ^f is a diagonal matrix in the basis in which H is diagonal and the diagonal elements ρ_i^f satisfy the $\frac{1}{2}N(N-1)$ conditions

$$\beta = \frac{1}{E_j - E_i} \ln \frac{\rho_i^f}{\rho_j^f} \tag{11}$$

where $i, j = \{1, 2,..., N\}$, $i \neq j$, $\beta = \text{const}$, and E_i is the ith eigenvalue of H.

Proof (Necessity). The canonical state is a function of the Hamiltonian and is therefore diagonal in the energy basis. Furthermore, the canonical state $\hat{\rho}$ satisfies Eq. (11) identically.

(Sufficiency). Using $N - 1$ of the equations given by (11), $N - 1$ diagonal elements of ρ^f can be expressed in terms of any one diagonal element of ρ^f, say ρ_j^f. The normalization condition Tr $\rho^f = 1$ can then be used to determine ρ_j^f as having the form

$$\rho_j^f = \frac{\exp(-\beta E_j)}{\sum_{i=1}^N \exp(-\beta E_i)} \tag{12}$$

which is obviously the j, j element of the canonical density operator $\hat{\rho}$. QED

It is now easy to demonstrate the inadequacy of linear dynamical maps for quantum thermodynamics. Combining (10) and (11), we obtain

$$\beta = \frac{1}{E_j - E_i} \ln \frac{\sum_{k=1}^N \Lambda_{ik} \rho_k{}^0(\alpha)}{\sum_{l=1}^N \Lambda_{jl} \rho_l{}^0(\alpha)} \tag{13}$$

For each value of α there are $K = \frac{1}{2}N(N-1)$ conditions to be satisfied by choosing N^2 constants.

Consider m values of α such that

$$mK > N^2 \Rightarrow m > 2N/(N-1) \tag{14}$$

The number of equations mK now exceeds the number of adjustable parameters, so we must restrict the values of $\rho_i{}^0(\alpha)$ to satisfy all conditions. In general the parameter α is continuous. Therefore we have an unlimited number of conditions to be satisfied, and there is no choice of the N^2 numbers Λ_{ij} which will satisfy the conditions for all $\rho^0 \in [\rho U]$.

We conclude that there exists no linear transformation Λ capable of mapping all $\rho^0 \in [\rho U]$ into the canonical state $\hat{\rho}$. *Hence a generalized equation of motion for ρ in the form $d\rho/dt = L\rho$ with L linear and independent of ρ cannot describe the approach to thermodynamic equilibrium of a closed N-level system.*

The only exception occurs when $N = 2$, in which case the set of diagonal density operators is a singleton set. There is then only one diagonal density operator in $[\rho U]$ because the matrix representation of ρ^0 has only two diagonal elements and these are uniquely determined by the conditions $\mathrm{Tr}(\rho^0) = 1$ and $\mathrm{Tr}(\rho^0 H) = U$. In this case a linear transformation does exist which conserves energy and leads to the canonical state. In fact, the transformation must have $\Lambda_{11} = \Lambda_{22} = 1$ and $\Lambda_{12} = \Lambda_{21} = 0$. A linear transformation of this type was found by Park and Band,(17) which led them to conjecture that generalized evolution might be given by a set of linear transformations.

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