

A Characterization of the Entropy–Gibbs Transformations

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ABSTRACT. Let H be a finite dimensional complex Hilbert space, $B(H)_+$ be the set of all positive semi-definite operators on H and φ is a (not necessarily linear) unital map of $B(H)_+$, preserving the Entropy-Gibbs transformation. Then there exists either a unitary or an anti-unitary operator U on H such that $\varphi(A) = UAU^*$ for any $A \in B(H)_+$.

Keywords: Preserver transformations, entropy, rank one operator, Gibbs free energy.

1. INTRODUCTION

Thermodynamics, a branch of physics that is concerned with the study of heat (thermo) and power (dynamics), might at first seem more important for engineers trying to invent a new engine than for biochemists trying to understand the mechanisms of life. However, since chemical reactions involve atoms and molecules that are bound by the laws of physics, studying thermodynamics should be a priority for every aspiring biochemist.

There are two laws of thermodynamics that are important to the study of biochemistry. These two laws have to do with energy and order both essential for life as we know it. It is easy to understand that our bodies need energy to function from the visible muscle movement that gets us where we want to go, to the microscopic cellular processes that keep our brains thinking and our organs functioning. Order is also important. Our bodies represent a high degree of order: atoms and molecules are meticulously organized into a complex system ranging in scale from the microscopic to the macroscopic. Atoms are organized into molecules, which are organized into cells, which are in turn organized into the organs, bones, muscles, and skin that make up the human body.

The Second Law of Thermodynamics is the Law of Increasing Entropy. This law states that the universe is always moving toward a greater state of disorder, or entropy. Anything that happens spontaneously, that is, without an input of energy, will result in molecules being more disorganized, more random, more mixed together, and

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more spread out. In other words, processes always tend naturally toward the state with the least potential energy. An easy way to visualize this is to think of running water. Liquid water will always find the lowest spot, and collect there.

This second law of thermodynamics explains why the molecules of gas that leak out of a broken pipe will disperse evenly, filling a room with the smell of gas, rather than staying together in a localized compact cloud. Similarly, you can smell the chlorine in the air at an indoor pool because some of the chlorine molecules escape from the water into the air. The law of increasing entropy also explains why houses do not spontaneously assemble from a pile of wood on the lawn, spills do not mop themselves up, and dust does not gather itself into a neat pile, ready to be swept up. Such processes that result in an increase of organization (that is, a decrease in entropy) require energy input and are not spontaneous.

We need to appreciate the principles of thermodynamics to understand how biochemical reactions occur. Already explained how the first two laws of thermodynamics dictate the flow of energy through our universe. But how can we understand bio chemical reactions in terms of these laws of energy flow? In the 1800s, a scientist named J. Willard Gibbs described a new value, free energy, to help us to do exactly that. Gibbs Free Energy, denoted by G , describes the energy available to do work within a system, in this case a chemical reaction. Free Energy can be used to make things occur that wouldn't happen without a source of energy. Examples of work being done include the progress of a chemical reaction to create a new product, an engine running to turn the wheels of a car, and falling water moving the turbines of a hydroelectric power plant. Keep in mind that Free Energy, which is useful because it can be harnessed to do work, is different from the heat energy that is always lost in any process. This heat energy is generated as the cost of doing work, and is therefore often called nature heat tax. The Gibbs Free Energy Change, or ΔG , is the difference between the G of the reactants and the G of the products.

Let's look at how ΔH (enthalpy change or heat of reaction) and ΔS (entropy change of a reaction) fit together with ΔG to explain the behavior of a chemical reaction. Consider the thermodynamic equation:

$$\Delta G = \Delta H - T\Delta S.$$

It is clear that the value of ΔG (positive or negative) depends on the values of ΔH and ΔS as well as the temperature of the reaction. Another way to think about it is that the ΔG , or maximum potential usable energy of the reaction, is distributed between the two terms, ΔH and $T\Delta S$. The ΔH (enthalpy) term represents energy that can be measured as the evolution or absorption of heat during the course of the reaction. The $T\Delta S$ (entropy) term indicates energy associated with the change of entropy, or disorder, of the system during the course of the reaction. This is the energy that increases the random motion or orientation of molecules involved in the reaction and is thus lost to the system, because it cannot be utilized productively.

2. PRELIMINARIES

In the Hilbert space formulation of quantum mechanics, which is mainly due to von Neumann, several mathematical objects appear whose physical meaning is connected with the probabilistic aspects of the theory. The corresponding objects in which we are interested in the present work are the following. Let H be a finite dimensional complex Hilbert space. Let $B(H)$ denote the algebra of all bounded linear operators (matrices) on a finite dimensional Hilbert space H equipped with Hilbert-Schmidt inner product. As usual, an operator $A \in B(H)$ is called positive semi-definite if $\langle Ax, x \rangle \geq 0$. The set of all positive semi-definite operators on H is denoted by $B(H)_+$. If x and y are in H , then $x \otimes y$ stands for the rank one operator defined by

$$(x \otimes y)(z) = \langle z, y \rangle x = y^*(z)x. \quad (1)$$

The support of an operator A is standing for the orthogonal complement of the kernel of A and denoted by $\text{supp } A$. The state of a quantum mechanical system is represented by a nonnegative trace operator B with $\text{tr } B = 1$, the state operator. Let $S(H)$ be the set of all state operators on H . In the quantum observables are modeled by self adjoint operators and we suppose that the energy operator H is a positive semi-definite operator. In 2004, Bebbiano, Lemos and Providencia [1] proved that if H is a self adjoint matrix, then $\log \text{tr}(e^H) = \max \{ \text{tr}(AH) - \text{tr}(A \log A) : A \in S(H) \}$. Therefore, the important thermodynamic inequality $\log \text{tr}(e^H) \geq \text{tr}(AH) - \text{tr}(A \log A)$ implies from it. For the energy operator H , the statistical mean value of the state described by the statistical operator A is $E = \text{tr}(AH)$ and the free energy of the state is $\text{tr}(AH) + q \text{tr}(A \log A)$; where $q = kT$, k is the Boltzman constant and T is the absolute temperature. For convenience we take $q = -1$, which is meaningful in finite dimensional vector spaces. We denote by \log^* the extension of \log to the domain $[0, \infty)$; defined to be 0 at 0; we also set $0 \cdot \infty = 0$ and now, for positive semi-definite operators A, B and the energy operator H , we define Entropy–Gibbs transformation by $G(A, B, C) = \text{tr}(AH) - \text{tr}(A(\log^* A - \log^* B))$.

Following some ideas of [5] and [6], let H be the energy operator and H be a finite dimensional complex Hilbert space and $B(H)_+$ be the set of all positive semi-definite operators on H . We prove that if $\varphi: B(H)_+ \rightarrow B(H)_+$ be a unital (not necessarily linear) map such that

$$G(A, B, C) = G(\varphi(A), \varphi(B), \varphi(H)). \quad (2)$$

Then there exists either a unitary or an anti-unitary operator U on H such that $\varphi(A) = UAU^*$ for any $A \in B(H)_+$.

Moreover, a bijective map φ on the set of all rank one projections on H is called a symmetry transformation if it preserves the quantity $\text{tr}PQ$ called transition probability between pure states, i.e., if φ has the property that $\text{tr}PQ = \text{tr}\varphi(P)\varphi(Q)$ holds for all rank one projections $P; Q$ on H . It is clear that every transformation φ of the form $\varphi(P) = UPU^*$ with some unitary or antiunitary operator U on H is a symmetry transformation. Wigner's theorem says that the converse statement is also true: every symmetry transformation can be obtained in this way. As non-bijective versions classical theorems like Wigner's theorem or the fundamental theorem of projective geometry are notable and more applicable compared to the original bijective versions, see [2].

The aim of this paper is to prove the following theorem:

Theorem: If $\varphi : B(H)_+ \rightarrow B(H)_+$ is a unital map such that

$$G(A, B, C) = G(\varphi(A), \varphi(B), \varphi(H))$$

then there exists either a unitary or an anti-unitary operator U on H such that $\varphi(A) = UAU^*$ for any $A \in B(H)_+$.

3. PROOF OF THE MAIN THEOREM

The proof is divided into several steps.

Step 1. Due to φ preserves the Entropy-Gibbs transformation, implicitly it said that $G(A; B; H) < \infty$ if and only if $G(\varphi(A); \varphi(B); \varphi(H)) < \infty$. Therefore by Example 2.7 of [4], $\text{supp } A \subseteq \text{supp } B$ if and only if $\text{supp } \varphi(A) \subseteq \text{supp } \varphi(B)$. From this we can deduce that $\text{supp } A = \text{supp } B$ if and only if $\text{supp } \varphi(A) = \text{supp } \varphi(B)$. By what we have learnt we conclude $\text{supp } A \subset \text{supp } B$ if and only if $\text{supp } \varphi(A) \subset \text{supp } \varphi(B)$. for every $A; B \in B(H)_+$. So that for any operator $A \in B(H)_+$, the rank of $\varphi(A)$ equals the rank of A and vis versa. Indeed, let $\dim(H) = n$ and suppose that $\text{rank } A = k$.

Then there is a chain $\text{supp } A_1 \subseteq \text{supp } A_2 \subseteq \dots \subseteq \text{supp } A_n$ of supports of elements of $B(H)_+$ such that $\text{supp } A$ stands at k -th place. From it, the chain $\text{supp } \varphi(A_1) \subseteq \text{supp } \varphi(A_2) \subseteq \dots \subseteq \text{supp } \varphi(A_{n-1}) \subseteq \text{supp } \varphi(A_n)$, where $\text{supp } \varphi(A_k)$ stands also at the k th place, is existed. By our arguments we obtain the rank of $\varphi(A)$ equal k . This shows that φ preserves the rank of the elements of $B(H)_+$. Particularly, φ preserves the rank-one operators.

Step 2. In this step we prove that φ preserves the nonzero transition probability between rank-one projections.

First we prove that φ is \log^* - trace preserving map on full rank operators of $B(H)_+$. Assume that $A=B \in B(H)_+$ then $G(A; B; H) = \text{tr}AH$. Since φ preserves the Entropy-Gibbs transformation we obtain

$$\text{tr}AH = \text{tr} \varphi(A)\varphi(H). \tag{3}$$

Moreover φ is unital, therefore from the last equality we have

$$\text{tr}H = \text{tr} \varphi(H). \tag{4}$$

Suppose that $\dim H = 2$. If $B \in B(H)_+$ is a full rank operator, then $G(I, B, H) = \text{tr}(H) + \text{tr}(\log^* B)$. Since φ is unital, by the similar way we have $G(I, \varphi(B), \varphi(H)) = \text{tr}(\log^* \varphi(B))$. Because φ preserves the Entropy-Gibbs transformation and by 4, we conclude $\text{tr} \log^* B = \text{tr} \log^* \varphi(B)$,

$$\text{tr}AH = \text{tr} \log^* \varphi(B) \tag{5}$$

for any full rank operator $B \in B(H)_+$.

Pick mutually orthogonal rank-one projections $P; Q$ and set $B = aP + bQ$, where $a; b$ are arbitrary positive real numbers with $a + b = 1$ and $a > \frac{\lambda}{2} > b$. By Step 1, φ preserves rank of operators, then there exists positive real numbers a', b' such that $a' + b' = 1$ and $a' > \frac{\lambda}{2} > b'$ and mutually orthogonal rank-one projections on H such that $\varphi(B) = a'P' + b'Q'$. By 5, φ is a \log^* -trace preserving, so that $\log^* a + \log^* b = \log^* a' + \log^* b'$. Hence $a(\lambda - a) = a'(\lambda - a')$. Thus $(a - a')(a + a') = \lambda(a - a')$. So that $a = a'$ and $b = b'$. This means

$$\text{sp}(B) = \text{sp}(\varphi(B)).$$

Now let $A = x \otimes y$ be a rank-one projection with $\|x\| = 1$ and pick mutually orthogonal rank-one projections $P; Q$ and set $B = aP + bQ$, where $a; b$ are arbitrary positive real numbers with $a > b$. Then the quantity $G(A; B; H)$ is obtained in this via:

$$\begin{aligned} G(A, B, H) &= \text{tr}AH - \text{tr}[A(\log^* A - \log^* B)] \\ &= (x, Hx) + (x, \log^* Bx) \\ &= (x, Hx) + [\log^* a (x, Px) - \log^* b (x, Qx)]. \end{aligned}$$

So that when A runs through the set of all rank-one projections, the quantity $G(A; B; H)$ runs through the closed interval $[(x, Hx) + \log^* b; (x, Hx) + \log^* a]$ for arbitrary $x \in H$. Thus, $G(A; B; H) \in [m + \log^* b; M + \log^* a]$, where $m = \inf (x, Hx)$ and $M = \sup (x, Hx)$. Recall that $\text{sp} H \subseteq [m; M]$ and also $[m, M] \in \text{sp} H$. By Step 1, φ preserves rank of operators, then there exists positive real numbers $a'; b'$ with $a' > b'$ and mutually orthogonal rank-one projections on H such that $\varphi(B) = a'P' + b'Q'$: Since $\text{Sp}(B) = \text{Sp}(\varphi(B))$ we can imply that φ preserve lower and upper bounds of the Entropy-Gibbs transformation. We know there exists a sequence such as x_n with $\|x_n\| = 1$ such that $\lim_{n \rightarrow \infty} (x_n, Hx_n) = m$. Now, if we suppose that $A_n = x_n \otimes x_n$, then

$\lim_{n \rightarrow \infty} G(A_n; B; H) = m + \log^* b$ if and only if there exist natural number such as N which for $n \geq N$, we have $x_n \in \text{Rang}(Q)$. Assume that $\text{Rang}(Q)$ spanned by $x \in H$: So that for every $n \geq N$ there is scalar number a_n such that $x_n = a_n x$. Since for every $n \in N$ we have $\|x_n\| = 1$, so that $|a_n| = 1$ and $\|x\| = 1$. Therefore, for $n \geq N$ we have $A_n = x_n \otimes x_n = a_n x \otimes a_n x = |a_n|^2 x \otimes x = x \otimes x$. Now, by modifying the sequence x_n only for $n \geq N$ and redefine $A_n = x_n \otimes x_n$ and let $A = x \otimes x$, we can conclude that $\lim_{n \rightarrow \infty} G(A_n; B; H) = m + \log^* b$ if and only if $A = Q$. Therefore,

$$\begin{aligned} A = Q &\Leftrightarrow G(A, B, H) = m + \log^* b \Leftrightarrow G(\varphi(A), \varphi(B), H) = m + \log^* b \\ &\Leftrightarrow G(\varphi(A), a'P' + b'Q', H) = m + \log^* b \Leftrightarrow \varphi(A) = Q' \end{aligned}$$

Therefore, $\varphi(Q) = Q'$ and $\varphi(P) = P'$ which shows that φ preserves the orthogonality between rank-one projections. Moreover, we can conclude that $\varphi(B) = \varphi(aP + bQ) = a\varphi(P) + b\varphi(Q)$.

Now we prove that φ preserves the nonzero transition probability between rank-one projections. Let A and P be different rank-one projections which are not orthogonal to each other, and choose a rank one projection Q which is orthogonal to P . Choose positive real numbers a, b then we have $G(A; aP + bQ; H) = \text{tr}AH - [\log^* a \text{tr}aP + \log^* b \text{tr}bQ]$. Also, in similar way we get

$$\begin{aligned} G(\varphi(A), a\varphi(P) + b\varphi(Q), \varphi(H)) &= \text{tr} \varphi(A)\varphi(H) - \left[\log^* a \text{tr}\varphi(A)\varphi(P) \right. \\ &\quad \left. + \log^* b \text{tr}\varphi(A)\varphi(Q) \right] \end{aligned}$$

Since $G(A, aP + bQ, H) = G(\varphi(A), a\varphi(P) + b\varphi(Q), \varphi(H))$, by comparing we infer $\text{tr}\varphi(A)\varphi(P) = \text{tr}AP$.

In the follows process, we can reduce the general case to the previous case, where $\dim H = 2$. Let P and Q be arbitrary two rank one projections of $B(H)_+$. Then there exists a rank two element $A_2 \in B(H)_+$ such that $\text{supp } P$ and $\text{supp } Q$ are subspaces of $\text{supp } A_2$: Now let $\text{supp } A_2 = H_2$, obviously $\dim H_2 = 2$. Set $\text{supp } \varphi(A_2) = H_2'$.

Since φ preserves the rank of operators we have $\dim H_2' = 2$. Because φ maps any element of $B(H)_+$ whose support is included in H_2 to an element of $B(H)_+$ whose support is included in H_2' .

Therefore, in that way φ gives rise to a map $\psi : B(H_2)_+ \rightarrow B(H_2')_+$ which preserves the Entropy-Gibbs transformation. Considering that the unitary operator $U : H_2' \rightarrow H_2$ the map $U\psi(\cdot)U^* : B(H_2)_+ \rightarrow B(H_2')_+$ is well defined and preserves the Entropy-

Gibbs transformation. Moreover, if $A \in B(H)_+$, since φ preserves positivity then $U\varphi(A)U^*$ is positive semi-definite. Furthermore, $\text{tr}(U\varphi(A)U^*) = \text{tr}(\varphi(A)) = \text{tr}(A)$. By the above argument we can conclude that the map $U\varphi(\cdot)U^*$ preserves the nonzero transition probability between rank-one projections.

Step 3.

According to Step 2 and non-bijective version of Wigner's theorem, we imply that there is a unitary or an antiunitary operator U on H such that $\varphi(P) = UPU^*$ for any rank one projection $P \in B(H)_+$. Assume the map $\phi: B(H)_+ \rightarrow B(H)_+$ defined by $\phi(P) = U^*\varphi(P)U$. By Step 2, ϕ is well defined and preserves the Entropy-Gibbs transformation and has additional property that acts as the identity on rank one projections. By Step 1, for any rank one projection P on H we have

$$\text{supp } P \subset \text{supp } B \Leftrightarrow \text{supp } P = \text{supp } \phi(P) \subset \text{supp } \phi(B)$$

from which we obtain $\text{supp } B = \text{supp } \phi(B)$: Now we have

$$G(P, B, H) = \text{tr}(PH) - \text{tr}[P(\log^* P - \log^* B)]$$

and

$$G(P, \phi(B), \phi(H)) = \text{tr}(P\phi(H)) - \text{tr}[P(\log^* P - \log^* \phi(B))]$$

By comparing the right-hand sides, we can conclude that $[P(\log^* P - B \log^* \phi(B))] = 0$, for any rank one projection P . So that $\log^* B = \log^* \phi(B)$. From this we obtain $B = \phi(B) = U^*\varphi(B)U$, for any $B \in B(H)_+$. Therefore, $\varphi(B) = UBU^*$ for any $B \in B(H)_+$.

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