

A Unified Quantum Theory of Mechanics and Thermodynamics. Part IIa. Available Energy¹

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Received June 2, 1975

Part II of this three-part paper presents some of the most important theorems that can be deduced from the four postulates of the unified theory discussed in Part I. In Part IIa, it is shown that the maximum energy that can be extracted adiabatically from any system in any state is solely a function of the density operator $\hat{\rho}$ associated with the state. Moreover, it is shown that for any state of a system, nonequilibrium, equilibrium or stable equilibrium, a unique property S exists which is proportional to the total energy of the system minus the maximum energy that can be extracted adiabatically from the system in combination with a reservoir. For statistically independent systems, property S is extensive, it is invariant during all reversible processes, and it increases during all irreversible processes.

3. THEOREMS RELATED TO THE STABLE-EQUILIBRIUM POSTULATE

This part of the paper presents some of the most important theorems related to the stable-equilibrium postulate. For some theorems complete proofs are given either in the text or in appendices; for some others only outlines of the proofs are discussed. For the remainder proofs are available in the literature.

3.1. Energy Changes in Reversible Separable Processes

An isolated system is by definition separable and its parameters are fixed. Its unitary processes are described by Eqs. (4) and (5), Part I; they are

¹ Part I of this paper appeared in *Found. Phys.* 6(1) (1976). The numbering of the sections, equations, and references in this part of the paper continues from those in Part I.

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reversible and, by virtue of the time invariance of $\text{Tr}(\hat{\rho}\hat{H})$, they do not affect the value E of the energy. We will assume that the energy $\text{Tr}(\hat{\rho}\hat{H})$ is conserved for all processes in an isolated system.

In general, the energy of a system can be altered during a unitary process by means of changes in parameters, namely by means of changes in \hat{H} as a function of time. One such process that is described by Eqs. (4) and (6), Part I, alters the eigenvectors of $\hat{\rho}$ and the eigenvalues and eigenvectors of \hat{H} without affecting the eigenvalues of $\hat{\rho}$.

Another involves cyclic changes in parameters, namely the initial and final values of the parameters are the same and, therefore, the initial and final Hamiltonians of the system are identical.

A process involving Cyclic Changes in Parameters, whether unitary or nonunitary, will be denoted as a *CCP process*. In general, a CCP process results in a noncyclic variation of the eigenvectors of $\hat{\rho}$ and, therefore, noncyclic changes of both the state and the energy of the system. CCP processes, whether unitary or nonunitary, play an important role in the subsequent development of our theory.

3.2. Theorem

In any class of states of a separable system that are interconnected by unitary CCP processes, the state of least energy is the stationary state for which the eigenvalues x_k of $\hat{\rho}$ are numbered in order opposite to that of the energy eigenvalues ϵ_k , namely

$$x_1 > x_2 > \cdots > x_k > \cdots \quad \text{for } \epsilon_1 < \epsilon_2 < \cdots < \epsilon_k < \cdots \quad (9)$$

The proof of this theorem is given in Appendix B.

3.3. Theorem

For a separable system for which the set $\{\epsilon_k\}$ of the energy eigenvalues has no upper bound, any stable equilibrium state has the least energy of all the states that are interconnected with it by unitary CCP processes.

The proof of this theorem is given in Appendix D.

The restriction of this theorem to systems for which the set $\{\epsilon_k\}$ has no upper bound suggests a theorem of different form for other systems, such as, for example, pure nuclear spin systems. For simplicity and brevity we shall omit the set of theorems that apply to systems with bounded sets $\{\epsilon_k\}$. In the context of Theorem 3.3, we simply assert that some of the stable equilibrium states of such systems are states of largest energy, and that they are associated with negative Kelvin temperatures (Section 3.16, Part IIb).

In all that follows only systems with sets $\{\epsilon_k\}$ that have no upper bound will be considered.

It follows from Theorems 3.2 and 3.3 that for a stable equilibrium state $\hat{\rho}_0$ the eigenvectors of $\hat{\rho}_0$ are the energy eigenvectors, and the eigenvalues x_k^0 are numbered in order opposite to that of the eigenvalues ϵ_k , namely

$$x_1^0 > x_2^0 > \cdots > x_k^0 > \cdots \quad \text{for } \epsilon_1 < \epsilon_2 < \cdots < \epsilon_k < \cdots \quad (10)$$

3.4. Adiabatic and Nonadiabatic Processes

We shall call a process *adiabatic* if and only if its effects on each of the systems taking part in the process could have been brought about by means of interactions with systems undergoing unitary processes. If this criterion cannot be satisfied, we shall call the process *nonadiabatic*.

It follows from Section 2.15, Part I, that any unitary process is adiabatic, although it will be shown (Section 3.28, Part IIb) that some adiabatic processes are nonunitary.

3.5. Work Interactions

In an adiabatic process, interactions that alter the energy of a system will be called *work*. The measure of work will be the change in energy of the system during the adiabatic process.

If during a work interaction the energy E of a system decreases, the work is assigned a positive value and it is said that *work is done by the system*. Conversely, if during a work interaction the energy of a system increases, the work is assigned a negative value and it is said that *work is received by the system*.

A separable system can do or receive work by means of changes in its parameters. These changes may be either noncyclic or cyclic.

A separable system A can always do net work by means of net changes in its parameters. If the changes in parameters are cyclic, however, the system may or may not be capable of doing work. For example, by virtue of Theorem 3.2, system A can do work reversibly starting from a nonequilibrium state and ending in a stationary state by means of a unitary CCP process. On the other hand, by virtue of Theorem 3.6 below, a system in a stable equilibrium state cannot do work by means of an adiabatic CCP process.

3.6. Theorem

Starting from a stable equilibrium state, a separable system cannot do work in any adiabatic CCP process.

In effect this theorem denies the existence of a perpetual motion machine of the second kind (PMM2), namely a device acting as a “Maxwellian demon.” The proof is given in Appendix E.

3.7. Theorem

From any state of a system the maximum energy that can be extracted adiabatically in a CCP process is the work done in a reversible adiabatic process that ends in a stable equilibrium state. Moreover, the energy change of a system starting from a given state and ending at a stable equilibrium state is the same for all reversible adiabatic CCP processes.

Proof: Let $(W_{12})^a$ be the work done in an adiabatic CCP process α_{12} , reversible or irreversible, of a system starting from a given state A_1 and ending in a state A_2 . Let $(W_{10})_{\text{rev}}^a$ be the work done in a reversible adiabatic CCP process α_{10} of the system starting from the same state A_1 and ending in a stable equilibrium state A_0 . We shall prove that $(W_{12})^a$ cannot exceed $(W_{10})_{\text{rev}}^a$.

Starting with stable equilibrium state A_0 , we shall subject the system to reversible adiabatic CCP process α_{01} , the inverse of α_{10} , and then to adiabatic CCP process α_{12} . The net work done by the system during the combined adiabatic CCP process $\alpha_{01} + \alpha_{12}$ will be $(W_{01})_{\text{rev}}^a + (W_{12})^a$. By virtue of Theorem 3.6 this work must be nonpositive, namely

$$(W_{01})_{\text{rev}}^a + (W_{12})^a \leq 0 \quad (11)$$

But since α_{10} is a reversible process, $(W_{01})_{\text{rev}}^a = -(W_{10})_{\text{rev}}^a$ and, therefore, relation (11) becomes

$$(W_{12})^a \leq (W_{10})_{\text{rev}}^a \quad (12)$$

Moreover, if α_{12} was reversible and the end state A_2 was a stable equilibrium state A_s , then the work $(W_{1s})_{\text{rev}}^a$ would have to satisfy the relations

$$(W_{1s})_{\text{rev}}^a = -(W_{s1})_{\text{rev}}^a \quad \text{and} \quad (W_{s1})_{\text{rev}}^a + (W_{10})_{\text{rev}}^a \leq 0 \quad (13)$$

and, therefore, by virtue of relation (12) and the stable-equilibrium postulate,

$$(W_{1s})_{\text{rev}}^a = (W_{10})_{\text{rev}}^a \quad (14)$$

and state A_s must be identical with state A_0 . Equations (12) and (14) are formal statements of Theorem 3.7.

This theorem implies that the quantity $(W_{10})_{\text{rev}}^a$ is a function of the initial state A_1 only and, therefore, that it is a property (a state function) of the system. We shall call this property the *adiabatic availability* Ψ . Since

it is an energy, the value of Ψ is given by an arithmetic mean of measurement results. Clearly it cannot exceed the energy of the system, and for a stable equilibrium state it is equal to zero (Theorem 3.6).

3.8. Theorem

The adiabatic availability of any pure state is equal to its energy with respect to the ground state.

The proof of this theorem is the same as that of Theorem 2.18, Part I.

From Theorem 3.8 it follows that a pure state other than the ground state cannot be a stable equilibrium state because the adiabatic availability of any stable equilibrium state is equal to zero (Theorem 3.6).

The definitions given in Section 3.9 and 3.10 are necessary for the discussion of the property “available energy” that is disclosed by Theorem 3.11.

3.9. Mutual Stable Equilibrium

Two independent separable systems A and B are said to be in mutual stable equilibrium if the combined system AB is in a stable equilibrium state.

It is evident that if two systems are in mutual stable equilibrium, each must be in a stable equilibrium state; but two systems each in a stable equilibrium state need not be in mutual stable equilibrium.

3.10. Reservoir

A reservoir is a special kind of a system that provides useful reference states for the definition of properties to be introduced later. It satisfies the following conditions: (1) It is an independent separable grand system with a set of energy eigenvalues $\{\epsilon_k\}$ that have no upper bound; (2) its parameters are time invariant; (3) initially, it is in a stable equilibrium state; and (4) it consists of a large number of identical systems.

3.11. Theorem

The statement of Theorem 3.11 requires the following terminology. In process α_{12} involving system A , reservoir R , and other systems designated by X , the state of A changes from A_1 to A_2 without net changes in the parameters of A , the state of R from R_1 to R_2 , and each system X undergoes a unitary process which may or may not be cyclic. Because X undergoes a unitary

process, α_{12} is adiabatic for the combined system AR (Section 3.4), although it need not be adiabatic for A and R considered individually.

The work done by AR in process α_{12} , namely the energy decrease of AR , will be denoted by W_{12}^R in general, and by $(W_{12}^R)_{\text{rev}}$ if the process is reversible. In terms of this terminology, the theorem is as follows:

The work $(W_{10}^R)_{\text{rev}}$ done in any reversible adiabatic process of AR in which A starts from A_1 and ends in a state A_0 in mutual stable equilibrium with the reservoir is : (1) The same for all such reversible processes; (2) greater than any W_{12}^R for which either state A_2 is not in mutual stable equilibrium with the reservoir, or the process α_{12} is not reversible, or both; (3) for a finite range of values of energy, independent of the initial energy of the reservoir; and (4) the same for all reservoirs in mutual stable equilibrium.

The proofs of parts 1 and 2 of the theorem follow directly from Theorem 3.7 applied to the combined system AR . The proofs of parts 3 and 4 follow directly from the lemma presented in Appendix F.

The theorem implies that $(W_{10}^R)_{\text{rev}}$ is a property of system A and reservoir R . We shall call this property the *available energy* with respect to a fixed reservoir and denote it by Ω . Thus, Ω_1 of state A_1 is given by the relation

$$\Omega_1 = (W_{10}^R)_{\text{rev}} \quad (15)$$

Because it is an energy, the value of Ω is given by an arithmetic mean of measurement results.

In general, the available energy Ω_1 of state A_1 differs from the adiabatic availability Ψ_1 . For example, if state A_1 is a stable equilibrium state, Ψ_1 is equal to zero, whereas, in general, Ω_1 is different from zero. Moreover, whereas Ψ is always smaller than or equal to the energy of the system with respect to the ground state, Ω may in some cases be greater than the energy of the system. For example, it is shown in Section 3.25, Part IIb, that for a pure state the available energy is always greater than the energy. Of course, Ω can never exceed the sum of the energies of system and reservoir.

3.12. Theorem

In any process of system A starting from state A_1 and ending in state A_2 , the work W_{12}^R done by A in combination with reservoir R cannot exceed the negative of the change of the available energy of the system, namely

$$W_{12}^R \leq \Omega_1 - \Omega_2 \quad (16)$$

The proof of this theorem follows directly from Theorem 3.11 and the definition of available energy.

3.13. Theorem

In an adiabatic process of system A starting from state A_1 and ending in state A_2 , the energy change $(E_1 - E_2)^a$ cannot exceed the change $\Omega_1 - \Omega_2$ of the available energy.

Proof: This process is a special case of that described in Theorem 3.12. Consequently, the work $(W_{12})^a$ done in the process must satisfy the relation

$$(W_{12})^a \leq \Omega_1 - \Omega_2 \quad (17)$$

Since, on the other hand, in an adiabatic process $(W_{12})^a$ satisfies also the relation

$$(W_{12})^a = (E_1 - E_2)^a \quad (18)$$

it follows that

$$(E_1 - E_2)^a \leq \Omega_1 - \Omega_2 \quad (19)$$

It can be readily shown that the inequality sign in Eq. (19) applies only to irreversible processes.

The available energy Ω is an experimentally observable property of any system with few or many degrees of freedom in any state $\hat{\rho}$, which may be nonequilibrium, equilibrium, or stable equilibrium. An explicit expression for Ω in terms of other, more familiar quantities is given in Section 3.25, Part IIb.

3.14. Theorem

With respect to a reservoir R , if A and B are two independent separable systems in states with available energies Ω_A and Ω_B , respectively, the available energy Ω_{AB} of the combined system AB is equal to the sum of Ω_A and Ω_B , namely

$$\Omega_{AB} = \Omega_A + \Omega_B \quad (20)$$

In other words, for independent separable systems available energy is an additive (extensive) property.

Proof: We shall assume, contrary to the theorem, that the available energy of the combined system AB differs from the sum of the available energies of A and B . Since available energy is the work done during a reversible process, a cycle may be devised in which given changes of state of the two systems are carried out in one direction while the systems are separated and in the other direction while they are combined. The direction of the cycle which restores the states of A and B may be selected so that net

positive work is done by the reservoir R , which is in a stable equilibrium state. Because this conclusion violates Theorem 3.6, Theorem 3.14 is justified by the absurdity of our assumption.

The proof of the theorem is not valid if A and B are not independent separable systems. To show this, we suppose that changes of state from A_1 and B_1 to A_2 and B_2 are carried out while A and B are combined, and from A_2 and B_2 back to A_1 and B_1 while A and B are separated. If states A_1 and B_1 are correlated while A and B are combined, no assurance exists that the correlations would be completely reestablished by the two independent processes that restore state A_2 to A_1 and state B_2 to B_1 , respectively. Hence, the mere fact that each system has been restored to its corresponding initial state does not imply that the combined system has also been restored to its initial state unless A and B are independent separable systems.

3.15. Theorem

For any system in any state, a property S exists that remains invariant in any reversible adiabatic process, that increases in any irreversible adiabatic process, and that is additive for independent separable systems.

Proof: The energies of two independent separable systems are additive because for separable systems the Hamiltonian operators are additive and for independent systems the density operator of the combined system is given by the direct product of the density operators of the two systems (Theorem 2.12, Part I). Since available energies are also additive for independent separable systems (Theorem 3.14), so is the difference between energy E and available energy Ω . In any process that does not alter the degrees of freedom of the system, it follows that an additive property S can be defined such that its infinitesimal or finite change DS between any two states is given by the relation

$$DS = c_R D(E - \Omega) \quad (21)$$

where c_R is an arbitrary positive constant whose value will be selected once and for all,

$$E = \text{Tr}(\hat{\rho}\hat{H})$$

and Ω is defined with respect to a standard reservoir which, along with the value of c_R , fixes the units for measuring S . Since both E and Ω are expectation values, S is also an expectation value.

For a reversible adiabatic process the conservation of E and Theorem 3.13 require that the work done be equal to both the change ($-DE$)

in energy and the change $(-DQ)$ in available energy. Hence, by virtue of Eq. (21) the corresponding change $(DS)_{\text{rev}}^a$ satisfies the relation

$$(DS)_{\text{rev}}^a = 0 \quad (22)$$

On the other hand, for an adiabatic process that is not reversible the work done is again equal to the change $(-DE)$ in energy but smaller than the change $(-DQ)$ in available energy. Hence, by virtue of Eq. (21) it follows that in such a process S increases, namely

$$(DS)_{\text{irr}}^a > 0 \quad (23)$$

The derivation of Eqs. (21)–(23) constitutes the proof of Theorem 3.15. We shall now show that DS must be of the form

$$DS = cD \operatorname{Tr}(\hat{\rho} \ln \hat{\rho}) \quad (24)$$

Contrary to this proposition, let DS be of a form different than that of Eq. (24). Then by virtue of Theorem 2.16, Part I, either DS is not invariant in some unitary processes (for both fixed and time-dependent parameters), or it is not additive for independent separable systems, or both. But all unitary processes are reversible adiabatic and, by virtue of Eq. (22), involve no change in DS . Moreover, by virtue of Eq. (21), S is additive for independent separable systems. It follows that DS could not be of a form other than that given by Eq. (24).

Because the processes considered in the definition of DS [Eq. (21)] do not alter the degrees of freedom of the system and S is an additive property, the value of S can be at most the sum of $c \operatorname{Tr}(\hat{\rho} \ln \hat{\rho})$ plus a linear form of the numbers of particles of constituent species of the system. The constant coefficients of the linear form can be determined as follows. If no reversible adiabatic process exists which interconnects any two states of the system with differing numbers of degrees of freedom, then we are at liberty to assign to each coefficient any value, including zero. On the other hand, if reversible adiabatic processes (unitary or nonunitary) exist which interconnect any two states of the system with differing numbers of degrees of freedom, then each coefficient should be determined experimentally. But by virtue of the third law³ of classical thermodynamics it can be readily verified that each coefficient must be equal to zero.

As a result of these considerations we conclude that S must be of the form

$$S = c \operatorname{Tr}(\hat{\rho} \ln \hat{\rho}) \quad (25)$$

³ For brevity the third law will not be discussed in this paper.

The fixed constant c can be determined experimentally from measurements of available energy. Its value proves to be $-k$, the negative of the Boltzmann constant (Section 3.26, Part IIb).

It can be shown that the property S is equal to zero for any pure state and is greater than zero for any state that is not pure, namely for any mixed state. No state has a negative value of S .

3.16. Theorem

For any process experienced by an independent separable system having fixed values of energy, numbers of particles, and parameters (namely a process of an isolated system) the quantity S must either increase or remain invariant.

Proof: Equations (22) and (23) apply to all adiabatic processes, including those for which the change in energy and, therefore, the work are equal to zero. It follows that they apply to spontaneous changes in state of an isolated system. In terms of symbols we may write

$$(DS)_{\text{isol}} \geq 0 \quad (26)$$

Relation (26) represents the *principle of nondecrease of S* .

Additional theorems related to the stable-equilibrium postulate with special emphasis on stable equilibrium states are presented in Part IIb.

APPENDIX B: PROOF OF THEOREM 3.2

Given a petit separable system A in state A_1' , let the complete sets of eigenvalues and orthonormal eigenvectors of the density operator $\hat{\rho}$ be $\{y_k\}$ and $\{v_k\}$, respectively, and the energy

$$E_1' = \text{Tr}(\hat{\rho}\hat{H}) = \sum_k y_k H'_{kk} \quad (B.1)$$

where

$$H'_{kk} = \langle v_k, \hat{H} v_k \rangle \quad \text{and} \quad y_1 > y_2 > \dots > y_k > \dots \quad (B.2)$$

State A_1' can be connected by means of a unitary CCP process to state A_1 in which the diagonal elements H_{kk} of the Hamiltonian matrix $[H]$ have the same values as the elements H'_{kk} of the initial matrix $[H']$ but are numbered in order opposite to that of the y_k 's, namely

$$H_{11} < H_{22} < \dots < H_{kk} < \dots \quad (B.3)$$

Such a process changes the set of eigenvectors $\{v_k\}$ to the set $\{w_k\}$ but does not alter the set of eigenvalues $\{y_k\}$. The matrix of the unitary operator that relates $\{w_k\}$ and $\{v_k\}$ is given by the identity matrix with its columns rearranged in the same manner as the rearrangements that must be performed in the sequence $H'_{11}, H'_{22}, \dots, H'_{kk}, \dots$ in order to achieve the ordering given by relations (B.3).

As a result of the process just described, the energy E_1 in state A_1 will be given by the relations

$$E_1 = \sum_k y_k H_{kk} \leq E'_1 \quad (B.4)$$

The proof of the inequality between E_1 and E'_1 is given by Hardy *et al.*⁽⁹⁾

State A_1 can be connected by means of a unitary CCP process to stationary state A_e in which the energy eigenvalues ϵ_k are numbered in ascending order, namely

$$\epsilon_1 < \epsilon_2 < \dots < \epsilon_k < \dots \quad (B.5)$$

Such a process changes the set of eigenvectors $\{w_k\}$ to the set of energy eigenvectors $\{u_k\}$ but does not alter the set of eigenvalues $\{y_k\}$. Hence, upon denoting the eigenvalues of the density operator for stationary state A_e by $x_1, x_2, \dots, x_k, \dots$, it follows that

$$x_1 = y_1, \quad x_2 = y_2, \dots, \quad x_k = y_k, \dots \quad (B.6)$$

and

$$x_1 > x_2 > \dots > x_k > \dots \quad (B.7)$$

The matrix elements U_{mn} of the unitary transformation that relates $\{w_k\}$ and $\{u_k\}$ are given by the relations

$$U_{mn} = \langle w_m, u_n \rangle \quad \text{for all } m \text{ and } n \quad (B.8)$$

They satisfy the expressions

$$\sum_n U_{nl}^* U_{nk} = \delta_{lk} \quad \text{and} \quad \sum_k U_{nk}^* U_{mk} = \delta_{nm} \quad (B.9)$$

As a result of the unitary CCP process from A_1 to A_e , the energy E_e in stationary state A_e will be given by the relation

$$E_e = \sum_k x_k \epsilon_k \quad (B.10)$$

Moreover, the diagonal elements H_{kk} and the energy E_1 in state A_1 can be expressed in the forms

$$H_{kk} = \sum_l \epsilon_l |U_{lk}|^2 \quad (\text{B.11})$$

$$\sum_k H_{kk} = \sum_k \epsilon_k \quad (\text{B.12})$$

$$E_1 = \sum_k x_k \sum_l \epsilon_l |U_{lk}|^2 \quad (\text{B.13})$$

where use has been made of relations (B.6).

Karamata⁽¹⁰⁾ has shown that relations (B.7), (B.9), and (B.11) are the necessary and sufficient conditions for the quantities E_e and E_1 [Eqs. (B.10) and (B.13)] to satisfy the inequality

$$E_e \leq E_1 \quad (\text{B.14})$$

For a grand system, the preceding sequence of unitary processes and conclusions can be repeated, except that now the rearrangements will be performed within each Hilbert space α of the overall sum Hilbert space.

These results prove that in any class of states of a separable system that are interconnected by unitary CCP processes, the state of least energy is that stationary state for which the eigenvalues x_k of $\hat{\rho}$ are numbered in order opposite to that of the energy eigenvalues ϵ_k [conditions (B.5) and (B.7)], namely that Theorem 3.2 is valid.

APPENDIX C: WORK ELEMENT

The concept of a weight in a gravity field, which was introduced by Gibbs, plays an important role in the definition of work interactions of classical thermodynamics.⁽¹¹⁾ Its essential feature is that it is a system for which level in the gravity field is the only independent property.

It plays an important role in the present theory as well, but here it must be expressed in quantum mechanical language. To this end, we shall define a *work element* as a system that satisfies the following conditions: (1) It is an independent, separable, petit system having one (external) parameter only; (2) at any instant it is in a stationary state (Section 2.17, Part I); (3) it has a set of energy eigenvalues $\{\epsilon_m\}$ without upper bound; and (4) each ϵ_m is proportional to a single-valued function $f(\beta)$ of the parameter β , which function is common for all ϵ_m 's, namely

$$\epsilon_m = a_m f(\beta) \quad \text{for all } m \quad (\text{C.1})$$

where a_m is a constant. Examples are a perfect gas in a stationary state (stable or nonstable) in a container with volume as the only parameter, and an electron in a stationary state (stable or nonstable) in a one-parameter potential well. Given the set $\{x_m\}$ of the eigenvalues of its state, the energy E of a work element becomes a sole function of the value of the parameter because

$$E = \sum_m x_m \epsilon_m = \left(\sum_m x_m a_m \right) f(\beta) \quad (\text{C.2})$$

Given the eigenvalues of the initial state C_1 and a unitary process between states C_1 and C_2 brought about by a gradual change in the parameter from β_1 to β_2 , the final state C_2 of a work element is determined solely by the value β_2 for the following reasons: (1) By virtue of Eqs. (4) and (6) it can be shown⁽¹²⁾ that the final density operator has the same eigenvalues as the initial density operator, and has eigenvectors that are the energy eigenvectors corresponding to the value β_2 ; (2) the energy eigenvectors are determined solely by β_2 ; and (3) by virtue of Eq. (C.1) the energy eigenvalues are determined solely by β_2 . Conversely, under the same conditions and by virtue of Eq. (C.2) the state of a work element is a sole function of the value of the parameter β . Finally, it is evident that as a result of cyclic gradual changes of its parameter, a work element is restored to its initial state, namely it undergoes a cycle.

Work elements are used in the proofs of Theorems 3.3 and 3.6 that are given below.

APPENDIX D: PROOF OF THEOREM 3.3

Given a separable system A in a stable equilibrium state A_0 , let the complete sets of eigenvalues and orthonormal eigenvectors of the density operator $\hat{\rho}_0$ be $\{x_k^0\}$ and $\{u_k\}$, respectively, and let the energy be E_0 .

Suppose that E_0 is not the smallest of the energies of all the states that are interconnected with A_0 by unitary CCP processes. By virtue of Theorem 3.2 [Eqs. (B.5)–(B.14)] a unitary CCP process α_{0e} can connect A_0 to a stationary state A_e for which $x_1^0, x_2^0, \dots, x_k^0, \dots$, the eigenvalues of the density operator $\hat{\rho}_0$ in the energy representation, are numbered in order opposite to that of the energy eigenvalues $\epsilon_1, \epsilon_2, \dots, \epsilon_k, \dots$, and for which the energy E_e is less than E_0 [Eq. (B.15)]. The energy $E_e - E_0$ can be transferred to work element C (Appendix C), which undergoes a gradual unitary process γ_{12} and changes its state from C_1 to C_2 .

Subsequently, the energy $E_e - E_0$ can be transferred back from C to A by means of a gradual unitary process γ_{21} , the inverse of γ_{12} , for the work element C and a unitary process α_{ef} for system A that connects A_e to another state A_f . By virtue of Eqs. (B.8), (B.9), and (B.13) a large number of states

exist that have energy E_0 and that are connected to state A_e by unitary CCP processes. It follows that α_{ef} can be selected so that $A_f \neq A_0$.

As a result of the combined processes $\alpha_{0e} + \alpha_{ef}$ for A and $\gamma_{12} + \gamma_{21}$ for C , stable equilibrium state A_0 has been altered to state A_f while the work element has undergone a cycle. This result, since it contradicts the definition of a stable equilibrium state, is absurd. Therefore, any stable equilibrium state has the least energy of all the states that are interconnected with it by unitary CCP processes.

APPENDIX E: PROOF OF THEOREM 3.6

Given a separable system A in a stable equilibrium state A_0 having energy E_0 , let an adiabatic CCP process α_{0a} for A exist in which the system changes to state A_a as it does work $E_0 - E_a$. The work is received by a work element C (Appendix C), which undergoes a gradual unitary process γ_{12} and changes its state from C_1 to C_2 . Since by virtue of Theorem 3.3 process α_{0a} cannot be unitary, it alters the eigenvalues of the density operator for A_0 . On the other hand, the energy $E_0 - E_a$ can be used in a unitary CCP process α_{ab} for A to change that state from A_a to A_b while the work element C undergoes a gradual unitary process γ_{21} , the inverse of γ_{12} . The eigenvalues of the density operator for A_b are the same as those for A_a and, therefore, different than those for A_0 .

As a result of the combined processes $\alpha_{0a} + \alpha_{ab}$ for A and $\gamma_{12} + \gamma_{21}$ for C , stable equilibrium state A_0 has been altered to state A_b while the work element has undergone a cycle. Since this result contradicts the definition of a stable equilibrium state, it is absurd.

We conclude that starting from a stable equilibrium state, a separable system cannot do work in any adiabatic CCP process.

APPENDIX F: LEMMA ABOUT ADIABATIC AVAILABILITY OF RESERVOIRS

Given two reservoirs R and R' in states R_1 and R'_1 in mutual stable equilibrium and having energies E_R and $E_{R'}$, respectively, the minimum amount of work required to change states R_1 and R'_1 to stable equilibrium states R_2 and R'_2 having energies $E_R + \Delta E_R$ and $E_{R'} - \Delta E_R$, respectively, is equal to zero.

Proof. Consider systems X and Y in states X_1 and Y_1 in mutual stable equilibrium and having energies E_X and E_Y , respectively. By virtue of the stable-equilibrium postulate and Theorem 3.7, a change of states from X_1 and Y_1 , without net changes in both parameters and degrees of freedom of both X and Y , to stable equilibrium states X_2 and Y_2 having energies $E_X + \Delta E$

and $E_Y - \Delta E$, respectively, results in a change $\Delta\Psi_{XY}$ of adiabatic availability given by the relation

$$\Delta\Psi_{XY} = (\partial\Psi_{XY}/\partial E) \Delta E + O[(\Delta E)^2] \quad (\text{F.1})$$

where $O[(\Delta E)^2]$ is of order $(\Delta E)^2$.

Let reservoirs R and R' consist of N systems X and Y , respectively, and the states of R and R' be altered in a manner analogous to that of X and Y above so that the energy transfer ΔE_R from R' to R is given by the relation

$$\Delta E_R = N \Delta E \quad (\text{F.2})$$

Then, the change $\Delta\Psi_{RR'}$ of adiabatic availability, and, therefore, the minimum amount of work required for this change of states, is given by the relation

$$\Delta\Psi_{RR'} = N \Delta\Psi_{XY} = (\partial\Psi_{XY}/\partial E) \Delta E_R + O[(\Delta E_R)^2/N] \quad (\text{F.3})$$

or, since for a reservoir N is very large (Section 3.10),

$$\Delta\Psi_{RR'} \simeq (\partial\Psi_{XY}/\partial E) \Delta E_R \quad (\text{F.4})$$

On the other hand, by virtue of Theorem 3.7, $\Delta\Psi_{RR'} > 0$ for both $\Delta E_R > 0$ and $\Delta E_R < 0$ and, therefore, Eq. (F.4) requires that

$$\partial\Psi_{XY}/\partial E = 0 \quad \text{and} \quad \Delta\Psi_{RR'} = 0 \quad (\text{F.5})$$

Equation (F.5) is the formal proof of the lemma.

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