IL NUOVO CIMENTO VOL. 82 B, N. 2 11 Agosto 1984

Quantum Thermodynamics. A New Equation of Motion for a Single Constituent of Matter (*).

G. P. BERETTA (**) and E. P. GYFTOPOULOS
Massachusetts Institute of Technology - Cambridge, MA 02139

J. L. PARK
Washington State University - Pullman, WA 99164

G. N. HATSOPOULOS
Thermo Electron Corporation - Waltham, MA 02254

(ricevuto l'1 Febbraio 1984; manoscritto revisionato ricevuto il 3 Maggio 1984)

Summary. — A novel nonlinear equation of motion is proposed for quantum systems consisting of a single elementary constituent of matter. It is satisfied by pure states and by a special class of mixed states evolving unitarily. But, in general, it generates a nonunitary evolution of the state operator. It keeps the energy invariant and causes the entropy to increase with time until the system reaches a state of equilibrium or a limit cycle.

PACS. 03.65. – Quantum theory; quantum mechanics.

1. – Introduction.

The purpose of this paper is to present a novel nonlinear equation of motion for an isolated quantum system, including the irreversible motion from any initial state to a unique stable equilibrium or thermodynamic equilibrium state.

(*) This work is based on part of a doctoral dissertation submitted by the first author to the Massachusetts Institute of Technology.

(**) Address: G. P. Beretta, M.I.T., Room 3-339, Cambridge, MA 02139.

Ever since the enunciation of the first and second laws of thermodynamics, the relation between mechanics and thermodynamics has been the subject of intensive scientific inquiry and controversy. Invariably, the two theories are reconciled by regarding thermodynamics as a statistical, macroscopic, or phenomenological theory (1).

In particular, as stated in a recent review by WEHRL (2), « Entropy relates macroscopic and microscopic aspects of nature and determines the behavior of macroscopic systems, *i.e.* real matter, in equilibrium (or close to equilibrium). Why this is true unfortunately is not yet understood in full detail, in spite of a century's efforts of thousands and thousands of physicists. There are many opinions and proposals for a solution to this problem; however, none of them seems to be completely satisfactory. »

Because of concerns similar to those of Wehrl, HATSOPOULOS and GYFTOPOULOS (3) concluded that thermodynamics should not be regarded as a statistical, macroscopic theory. Instead, they proposed a unified quantum theory which within a single structure encompasses both mechanics and thermodynamics and in which the laws of thermodynamics are a necessary complement to those of quantum physics. In this theory, which applies to all systems, including a single constituent of matter, and to all states, including states of thermodynamic equilibrium, mixed states represent probabilities inherent only to the system, in the same sense that pure states represent probabilities inherent only to the system.

Among other results, the theory proves the following.

a) For any system in any state, the only extensive property that remains invariant in all reversible adiabatic processes and does not decrease in all adiabatic processes, in general, is given by the state functional

$$s(\varrho) = -k \operatorname{Tr}(\varrho \ln \varrho)\,, \tag{1}$$

where k denotes the Boltzmann constant. Because these two features are characteristic of the entropy of equilibrium states of classical thermodynamics, $s(\varrho)$ is called the entropy of the system in the state ϱ, irrespective of whether the state is thermodynamic equilibrium or not.

---

(1) See, *e.g.*, J. VON NEUMANN: *Mathematical Foundations of Quantum Mechanics*, English translation (Princeton University Press, Princeton, N.J., 1955); E. C. KEMBLE *Phys. Rev.*, **56**, 1013, 1146 (1939); U. FANO: *Rev. Mod. Phys.*, **29**, 74 (1957); E. T. JAYNES: *Phys. Rev.*, **106**, 620 (1957); **108**, 171 (1957); W. BAND: *Am. J. Phys.*, **26**, 440, 540 (1958); E. C. G. SUDARSHAN, P. M. MATHEWS and J. RAN: *Phys. Rev.*, **121**, 920 (1961); R. JANCEL: *Foundations of Classical and Quantum Statistical Mechanics*, (Pergamon Press, Oxford, 1969); J. MEHRA and E. C. G. SUDARSHAN: *Nuovo Cimento B*, **11**, 215 (1972).

(2) A. WEHRL: *Rev. Mod. Phys.*, **50**, 221 (1978).

(3) G. N. HATSOPOULOS and E. P. GYFTOPOULOS: *Found. Phys.*, **6**, 15, 127, 439, 561, (1976).

b) For a system with Hamiltonian operator H, the von Neumann equation of motion

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = -\frac{i}{\hbar}[H, \varrho] \tag{2}$$

is valid for unitary processes. But it is incomplete because it describes neither nonunitary reversible processes nor irreversible processes in which a system approaches thermodynamic equilibrium.

HATSOPOULOS and GYFTOPOULOS concluded that the complete equation of motion remained to be discovered and that *a*) it must describe nonunitary processes in general and, in the limit of unitary processes, reduce to eq. (2); *b*) for all processes of an isolated system, it must imply the invariance of the energy given by the expression $\mathrm{Tr}\,(H\varrho)$, and *c*), for an irreversible process of an isolated system, it must result in an increase of the entropy given by the expression $-k\,\mathrm{Tr}\,(\varrho \ln \varrho)$.

For a number of reasons, statistical, thermodynamic, or quantum-mechanical, many efforts have been made to modify or complete the von Neumann equation of motion ([2,4]). The starting point of most of these efforts has been the search for a superoperator $\hat{L}(\varrho)$ which is linear in ϱ and such that

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = \hat{L}(\varrho)\,. \tag{3}$$

However, SIMMONS and PARK ([5]) concluded that, in general, no linear superoperator is capable of describing the approach to a stable equilibrium state starting from an arbitrary initial state, as would be required in a unified theory of mechanics and thermodynamics.

A novel nonlinear quantum equation of motion which satisfies the requirements of quantum thermodynamics has been conceived by the first author. In this paper, we present the form of the equation for an isolated system consisting of a single constituent of matter (a particle, an assembly of indistinguishable particles, or a field). The form of the equation for a composite system of many distinguishable constituents will be discussed in a following communication.

We have adopted the new equation of motion because it has the following features: *a*) it is satisfied by pure states evolving according to the Schrödinger

---

([4]) A recent review of these attempts is given by J. L. PARK and R. F. SIMMONS, jr: *The knots of thermodynamics*, in *Old and New Questions in Physics, Cosmology, Philosophy and Theoretical Biology: Essays in Honor of Wolfgang Jourgrau*, edited by A. VAN DER MERWE (Plenum Press, New York, N.Y., 1983). See also J. L. PARK and W. BAND: *Found. Phys.*, **7**, 813 (1977).

([5]) R. F. SIMMONS, jr. and J. L. PARK: *Found. Phys.*, **11**, 297 (1981).

equation of motion and by a special class of mixed states evolving according to the von Neumann equation; *b*) it keeps the energy functional $e(\varrho) = \mathrm{Tr}\,(H\varrho)$ invariant and causes the state functional $s(\varrho) = -k\,\mathrm{Tr}\,(\varrho \ln \varrho)$ to increase until the system reaches a state of equilibrium or a limit cycle, and *c*) it implies that state functional $s(\varrho)$ satisfies all the requirements of entropy of thermodynamics.

The paper is organized as follows. Statements of the nondynamical postulates of quantum theory and the proposed equation of motion for a single constituent of matter are given in sect. **2**, some important theorems in sect. **3** and conclusions in sect. **4**.

2. – Postulates.

To establish a mathematical framework in which to present the proposed equation of motion, we begin by stating four nondynamical postulates of quantum theory (6).

2·1. *Postulate* 1: *Systems*. – To every physical system there corresponds a complex, separable, complete, inner product space, a Hilbert space $\mathscr{H}$. The Hilbert space of a composite system of two distinguishable subsystems 1 and 2, with associated Hilbert spaces $\mathscr{H}^1$ and $\mathscr{H}^2$, respectively, is the direct product space $\mathscr{H}^1 \otimes \mathscr{H}^2$.

2·2. *Postulate* 2: *Correspondence principle*. – Some linear, self-adjoint operators A, B, ... on Hilbert space $\mathscr{H}$ correspond to physical observables of the system. If operator P corresponds to the observable $\overline{P}$, then the operator $f(P)$, where f is a function, corresponds to the observable $f(\overline{P})$.

2·3. *Postulate* 3: *State preparations*. – To every reproducible unambiguous preparation (7) scheme Π for a physical system there corresponds a linear, self-adjoint, nonnegative-definite, unit-trace operator ϱ on $\mathscr{H}$ which contains all physical predictions regarding data gathered immediately subsequent to that preparation. The trace class operator ϱ thus represents the state of the system prepared in the unambiguous manner Π and, subject to some additional mathematical conditions discussed later, will be called the state operator.

2·4. *Postulate* 4: *Observables, measurements, data and ensembles*. – The arithmetic mean value of data yielded by measurements of the observable corres-

(6) The nondynamical postulates are equivalent to those used in ref. (3).
(7) The concept of unambiguous preparation has been defined in ref. (3).

ponding to operator A on an ensemble of identical systems, all prepared in the unambiguous manner Π with associated state operator ϱ, is given by the value of the continuous linear functional

$$a(\varrho) = \mathrm{Tr}\,(A\varrho)\,. \tag{4}$$

For example, the value $e(\varrho)$ of the energy of a system in state ϱ is given by the value of the functional

$$e(\varrho) = \mathrm{Tr}\,(H\varrho)\,. \tag{5}$$

Again, the value $n(\varrho)$ of the number of particles of a field (8) in state ϱ is given by the value of the functional

$$n(\varrho) = \mathrm{Tr}\,(N\varrho)\,, \tag{6}$$

where N is the particle-number operator.

Postulates 1 to 4, or some equivalent statements, represent the nondynamical foundations of quantum theory for any system in any state. To complete the theory, we must augment them by a causal principle. We emphasize that neither the four nondynamical postulates nor the causal principle discussed below can be derived from other axioms. If they could, the postulates would have been theorems and not the foundation of our theory.

As already stated, the von Neumann equation (eq. (2)) is valid but incomplete because it describes neither nonunitary reversible processes nor irreversible processes. Such processes must be included in order to achieve a satisfactory unification of quantum mechanics and thermodynamics.

We will postulate that the dynamical evolution of an isolated quantum system is described by an equation of motion proposed by BERETTA (9). Our motivation for adopting this postulate will become evident from the results that we obtain in sect. **3**.

2'5. *Postulate* 5: *Equation of motion for a single constituent of matter.* – For a system consisting of a single elementary constituent of matter, *i.e.* a single particle, a single assembly of indistinguishable particles or a single field, the state operator ϱ evolves according to the equation

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = -\frac{i}{\hbar}[H, \varrho] - \frac{1}{\tau} D\,, \tag{7}$$

where $[H, \varrho] = H\varrho - \varrho H$, τ is a positive time constant and D a linear, self-

(8) Here $\mathscr{H}$ is a Fock space.
(9) G. P. BERETTA: Thesis, Sc. D. M.I.T. (1981), unpublished.

adjoint operator on the Hilbert space of the system, defined as a nonlinear function of ϱ by

$$D = \tfrac{1}{2}\left(\sqrt{\varrho}\tilde{D} + (\sqrt{\varrho}\tilde{D})^\dagger\right), \tag{8}$$

$$\tilde{D} = \frac{\begin{vmatrix} \sqrt{\varrho}\ln\varrho & \sqrt{\varrho}R_0 & \sqrt{\varrho}R_1 & \dots & \sqrt{\varrho}R_z \\ (R_0, \ln\varrho) & (R_0, R_0) & (R_0, R_1) & \dots & (R_0, R_z) \\ (R_1, \ln\varrho) & (R_1, R_0) & (R_1, R_1) & \dots & (R_1, R_z) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (R_z, \ln\varrho) & (R_z, R_0) & (R_z, R_1) & \dots & (R_z, R_z) \end{vmatrix}}{\Gamma(\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, \dots, \sqrt{\varrho}R_z)}, \tag{9}$$

$$\Gamma(\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, \dots, \sqrt{\varrho}R_z) = \begin{vmatrix} (R_0, R_0) & (R_0, R_1) & \dots & (R_0, R_z) \\ (R_1, R_0) & (R_1, R_1) & \dots & (R_1, R_z) \\ \vdots & \vdots & \ddots & \vdots \\ (R_z, R_0) & (R_z, R_1) & \dots & (R_z, R_z) \end{vmatrix}, \tag{10}$$

$$(F, G) = (G, F) \equiv \tfrac{1}{2}\operatorname{Tr}\left(|\varrho|\{F, G\}\right) = (\sqrt{\varrho}F|\sqrt{\varrho}G) = (\sqrt{\varrho}G|\sqrt{\varrho}F), \tag{11a}$$

$$(A|B) = (B|A) \equiv \tfrac{1}{2}\operatorname{Tr}(A^\dagger B + B^\dagger A), \tag{11b}$$

$\{F, G\} = FG + GF$, F, G are self-adjoint operators, $|\varrho| = \sqrt{\varrho^\dagger\varrho}$ [10], $\Gamma(A, \dots, B)$ is the Gram determinant [11] of operators $A, \dots, B$ (in general non-self-adjoint) with respect to the real scalar product $(\cdot|\cdot)$ defined by relation (11b) on the set of linear operators on $\mathscr{H}$ [12], and operators R_i are determined as follows.

For each elementary constituent, we define a set of linearly independent self-adjoint operators $\{I, H, N_1, \dots, N_n\}$, where I is the identity, H the Hamiltonian and each N_i, for $i = 1, \dots, n$, commutes with the Hamiltonian. The operators in this set, which always includes the identity and the Hamiltonian,

---

(10) For a self-adjoint, unit trace but not necessarily definite operator ϱ, we can always write $\varrho = \sum p_k|\varphi_k\rangle\langle\varphi_k| + \int dk p_k|\varphi_k\rangle\langle\varphi_k|$, where $\{\varphi_k\}$ and $\{p_k\}$ are complete sets of orthonormal eigenvectors and real eigenvalues of ϱ. We then write $p_k = |p_k| \cdot \exp[i\pi\theta_k]$, where $\theta_k = 0$ for $p_k \geqslant 0$ and $\theta_k = 1$ for $p_k < 0$, and define operators $\sqrt{\varrho}$ and $\sqrt{\varrho}\ln\varrho$ as having the same eigenvectors as ϱ, and eigenvalues $\sqrt{p_k} \equiv \sqrt{|p_k|}\exp[i\pi\theta_k/2]$ and $\sqrt{p_k}\ln p_k \equiv \sqrt{p_k}(\ln|p_k| + i\pi\theta_k)$, respectively. With these definitions, eq. (7) is defined by postulate 5 for self-adjoint, unit-trace operators ϱ that are not necessarily nonnegative definite.

(11) See, *e.g.*, E. F. BECKENBACH and R. BELLMAN, *Inequalities* (Springer-Verlag, New York, N.Y., 1965), p. 59-60; see also G. P. BERETTA: in *Frontiers of Nonequilibrium Statistical Physics*, edited by G. T. MOORE and M. O. SCULLY (Plenum Press, New York, N.Y., in press).

(12) For a, b real scalars, A, B linear operators and $A^\dagger$, $B^\dagger$ their adjoints, we have $(A_1 + A_2|B) = (A_1|B) + (A_2|B)$, $(A|B_1 + B_2) = (A|B_1) + (A|B_2)$, $(aA|B) = a(A|B)$, $(A|bB) = b(A|B)$, and $(A|A) = \operatorname{Tr}(A^\dagger A) > 0$ for $A \neq 0$.

are called the generators of the motion of the elementary constituent. Any linear combination with real coefficients of the linearly independent generators of the motion is also a well-defined self-adjoint operator on $\mathscr{H}$ [13]. For each ϱ, if the operators $\{\sqrt{\varrho}I, \sqrt{\varrho}H, \sqrt{\varrho}N_1, \ldots, \sqrt{\varrho}N_n\}$ are linearly independent, then $z = n + 1$ and operators R_i are defined as $\{R_0 = I, R_1 = H, R_2 = N_1, \ldots, R_z = N_n\}$, otherwise $z < n + 1$ and the set $\{R_i\}$ is any smaller subset of generators of the motion such that operators $\{\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, \ldots, \sqrt{\varrho}R_z\}$ are linearly independent and span the set $(\sqrt{\varrho}I, \sqrt{\varrho}H, \sqrt{\varrho}N_1, \ldots, \sqrt{\varrho}N_n\}$. By using well-known properties of determinants, it can be readily verified that operator $\tilde{D}$ is invariant under transformation from one set $\{R_i\}$ to any other set $\{R_i'\}$ with the same defining properties. Moreover, it follows from the definition of operators R_i that the Gram determinant $\Gamma(\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, \ldots, \sqrt{\varrho}R_z)$ (eq. (10)) is always strictly positive.

We will show that the generators are among the constants of the motion of the system (theorem 4). This result would have been obtained even if the von Neumann equation (eq. (2)) were used, since each non-Hamiltonian generator N_i commutes with the Hamiltonian operator. We will see, however, that, according to eq. (7), not all operators that commute with the Hamiltonian are constants of the motion (theorem 5) as the system proceeds from an initial state to a state of higher entropy.

Some elementary constituents of matter, such as a structureless particle, would require only the identity and the Hamiltonian as generators of the motion. Others, such as a field, however, would require the identity, the Hamiltonian and the particle number operators as generators of the motion. Thus both the nature and the number of the generators of the motion other than I and H depend on the single constituent in question.

Because qualitatively none of the results to be derived below depends on the value of the time constant τ, on the specific nature of the physical observables represented by $N_1, N_2, \ldots, N_n$ or on whether their number is greater than or equal to zero, we will proceed without specifying explicitly these three characteristics of the single constituent.

If $\mathscr{H}$ is infinite-dimensional and some generators of the motion are unbounded, the self-adjoint operator $\mathrm{d}\varrho/\mathrm{d}t$ (eq. (7)) will be well defined only for a subset $\tilde{Q}$ of the linear, self-adjoint, unit-trace operators ϱ on $\mathscr{H}$.

---

[13] This requirement is generally nontrivial because one expects that some generators of the motion (in particular H) may be unbounded. For the definition of a well-defined (densely defined) operator and that of commutativity for unbounded operators see, *e.g.*, M. Reed and B. Simon: *Methods of Modern Mathematical Physics*, Vol. **1**: *Functional Analysis* (Academic Press, New York, N.Y., 1972), Chapt. I and VIII. For the extension of the definition of $\mathrm{Tr}(\varrho A)$ to unbounded operators A, see, *e.g.*, A. Jamiolkowski: *Rep. Math. Phys.*, **10**, 267 (1976); H. Araki and E. H. Lieb: *Commun. Math. Phys.*, **18**, 160 (1970). For the additional technical conditions that must be imposed on the generators of the motion in order for theorem 10 to hold, see W. Ochs and W. Bayer: *Z. Naturforsch.*, **28a**, 1571 (1973).

We have not been able to solve the technical mathematical problem to find necessary and sufficient conditions that define the set $\tilde{Q}$. These conditions will be in terms of the domains of definition of the unbounded generators of the motion. Similar conditions are required also by the von Neumann equation (eq. (2)) [14].

An operator-valued function $\varrho(t)$ defined for $t \geqslant 0$ will be called a solution if and only if $\varrho(0)$ is in $\tilde{Q}$, and $\varrho(t)$ satisfies eq. (7) for every $t \geqslant 0$. We will see that solutions remain in $\tilde{Q}$ for every $t \geqslant 0$ because $\varrho(t)$ remains self-adjoint and unit trace (theorems 1 and 2).

A solution $\varrho(t)$ will be called physical if and only if $\varrho(t)$ is also nonnegative definite, *i.e.* $|\varrho(t)| = \varrho(t)$ for every $t \geqslant 0$. We will denote by Q the subset of operators ϱ in $\tilde{Q}$ through which there passes a physical solution. Thus, by definition, every physical solution lies entirely in Q. Only the operators ϱ in Q will qualify as state operators.

Ideally, we would like to demonstrate that, for every nonnegative-definite $\varrho(0)$ in $\tilde{Q}$, the equation of motion admits a unique physical solution. The reason is that, in our attempts to unify quantum mechanics and thermodynamics, an underlying hypothesis has been that the basic causal structure of mechanics should be retained; specifically, future states of closed systems should deterministically unfold from initial states along smooth unique paths in state space. We recognize that this posture is subject to dispute. Other scholars may prefer, for example, to seek explanations of physical processes in such constructs as bifurcations born of singularities in the mathematical representation. For us, however, causality captures the quintessence of being « physical ».

Unfortunately, we are at present unable to demonstrate rigorously this desirable result. Instead, we will proceed by assuming only that physical solutions exist in addition to the trivial unitary solutions discussed in theorems 3 and 8. In support of this assumption, we derive a particular class of nontrivial, nonunitary, approximate solutions in appendix B. This derivation is very important because it proves that the set of physical solutions is nonempty.

Regarding the broader issue of existence and uniqueness of physical solutions, presently we can offer only some heuristic and circumstantial evidence. Specifically, we give rudiments of an approach to the proof of an existence and uniqueness theorem in appendix C and of a nonnegativity conservation theorem in appendix D.

We will see that the new equation of motion implies two alternative classifications of states; the first is into dissipative and nondissipative states (theorem 7), the second is into nonequilibrium, unstable equilibrium and stable

(14) See, *e.g.*, E. B. DAVIES: *Quantum Theory of Open Systems* (Academic Press, New York, N.Y., 1976), p. 82-83.

equilibrium states (theorems 9 to 11). Each class of states has physically interesting and nontrivial dynamical characteristics.

3. – Theorems.

By virtue of the nontrivial physical solutions discussed in appendix B, the set of physical solutions is nonempty. Thus some important consequences of the theory represented by postulates 1 to 5 are as follows.

Theorem 1. Any solution $\varrho(t)$ of eq. (7) it self-adjoint.

Proof. Because $\varrho(t)$ is a solution, $\varrho(0)$ is self-adjoint and $\dot{\varrho}(t) = \mathrm{d}\varrho/\mathrm{d}t$ is well defined. Because $\mathrm{d}\varrho/\mathrm{d}t$ (eq. (7)) is self-adjoint, $\varrho(t) = \varrho(0) + \int_0^t \dot{\varrho}(t')\,\mathrm{d}t'$ is self-adjoint for every $t \geqslant 0$. Thus, theorem 1 is proved.

Theorem 2. Any solution $\varrho(t)$ of eq. (7) is unit trace.

Proof. Because $\varrho(t)$ is a solution, $\varrho(0)$ is unit trace. Because it can be readily verified that $\mathrm{Tr}\,([H, \varrho]) = 0$ and $\mathrm{Tr}\,(D) = 0$, $\mathrm{d}\,\mathrm{Tr}\,(\varrho)/\mathrm{d}t = \mathrm{Tr}\,(\mathrm{d}\varrho/\mathrm{d}t) = 0$ and, therefore, $\mathrm{Tr}\,(\varrho(t)) = \mathrm{Tr}\,(\varrho(0)) = 1$. Thus theorem 2 is proved.

Theorem 3. If $\psi(t)$ is a solution of the Schrödinger equation

$$\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar} H\psi, \tag{12}$$

then $\varrho(t) = P_{\psi(t)}$ is a physical solution of eq. (7), where $P_{\psi(t)}$ is the projector onto the one-dimensional subspace of $\mathscr{H}$ spanned by vector $\psi(t)$.

Proof. Substituting projector $P_{\psi(t)}$ into eq. (7), we find that all entries of the first column of determinant $\tilde{D}$ (eq. (9)) vanish for every t because $\sqrt{P_{\psi(t)}}\ln P_{\psi(t)}$ is the null operator. With operator $\tilde{D}$ equal to the null operator, eq. (7) reduces for every t to the von Neumann equation which is satisfied by $P_{\psi(t)}$. Thus theorem 3 is proved.

If uniqueness of physical solutions were proved, then theorem 3 would be strengthened so that « given a solution $\varrho(t)$ with $\varrho(0) = P_{\psi(0)}$, then $\varrho(t) = P_{\psi(t)}$ for all times t ». In other words, for pure states eq. (7) would reduce to the Schrödinger equation.

Definition 1: *Constants of the motion.* A physical observable represented by a linear, self-adjoint operator C is said to be a constant of the motion of the system if and only if

$$\frac{\mathrm{d}c(\varrho)}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Tr}\,(C\varrho) = \mathrm{Tr}\left(C\,\frac{\mathrm{d}\varrho}{\mathrm{d}t}\right) = 0 \tag{13}$$

for all state operators ϱ.

Theorem 4. Each of the generators of the motion is also a constant of the motion of the system.

Proof. By virtue of eq. (7), the rate of change of the mean value $c(\varrho)$ of an observable with corresponding linear operator C is given by the relation

$$\mathrm{Tr}\left(C\frac{\mathrm{d}\varrho}{\mathrm{d}t}\right) = -\frac{i}{\hbar}\,\mathrm{Tr}\,([C,H]\varrho) - m(\varrho)/\tau\Gamma(\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, \dots, \sqrt{\varrho}R_z)\,, \tag{14}$$

where

$$m(\varrho) = \begin{vmatrix} (C, \ln\varrho) & (C, R_0) & (C, R_1) & \dots & (C, R_z) \\ (R_0, \ln\varrho) & (R_0, R_0) & (R_0, R_1) & \dots & (R_0, R_z) \\ (R_1, \ln\varrho) & (R_1, R_0) & (R_1, R_1) & \dots & (R_1, R_z) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (R_z, \ln\varrho) & (R_z, R_0) & (R_z, R_1) & \dots & (R_z, R_z) \end{vmatrix}\,. \tag{15}$$

When C is one of the generators of the motion, then the first term in the right-hand side of eq. (14) vanishes because C commutes with H and the second term vanishes because $\sqrt{\varrho}\,C$ is a linear combination of operators $\sqrt{\varrho}\,R_i$ and, therefore, the rows of determinant $m(\varrho)$ (eq. (15)) are linearly dependent. Thus theorem 4 is proved.

Theorem 4 shows that state property energy, $e(\varrho) = \mathrm{Tr}\,(H\varrho)$, is conserved. In addition, the change of this property in any adiabatic process is uniquely related to the amount of work involved in the process [3]. Hence, we conclude that the proposed equation of motion implies the first law of thermodynamics.

Theorem 5. A physical observable represented by a linear, self-adjoint operator C is a constant of the motion if and only if C is a linear combination of the generators of the motion, *i.e.*

$$C = \lambda_I I + \lambda_H H + \sum_{i=1}^{n} \lambda_i N_i\,, \tag{16}$$

where λ_I, λ_H and λ_i, for $i = 1, \dots, n$, are real scalar constants.

Proof. For C to be a constant of the motion, the right-hand side of eq. (14) must vanish for every ϱ. This occurs if and only if each of the two terms vanishes independently because the first term is a linear and the second a nonlinear functional of ϱ.

Condition (16) is sufficient. The first term vanishes because each generator of the motion in C commutes with H. The second term vanishes for every ϱ because the operator $\sqrt{\varrho}\,C$ can be expressed as a linear combination of operators $\sqrt{\varrho}\,R_i$ and, therefore, the first row of determinant $m(\varrho)$ (eq. (15)) is a linear combination of the other rows.

Condition (16) is also necessary for determinant $m(\varrho)$ to vanish for every ϱ. Indeed, for the particular strictly positive state operator

$$\varrho = \exp[C]/\mathrm{Tr}(\exp[C]),$$

$m(\varrho)$ equals the Gram determinant $\Gamma(\sqrt{\varrho}\,C, \sqrt{\varrho}\,R_0, \sqrt{\varrho}\,R_1, \dots, \sqrt{\varrho}\,R_z)$. Because a Gram determinant of vectors vanishes if and only if the vectors are linearly dependent ([11]), $m(\varrho)$ vanishes only if $\sqrt{\varrho}\,C$ is a linear combination of operators $\sqrt{\varrho}\,R_i$. Because operators $\sqrt{\varrho}\,R_i$ span the set $\{\sqrt{\varrho}\,I, \sqrt{\varrho}\,H, \sqrt{\varrho}\,N_1, \dots, \sqrt{\varrho}\,N_n\}$ and $(\sqrt{\varrho})^{-1}$ exists for $\varrho = \exp[C]/\mathrm{Tr}(\exp[C])$, it follows that C must be a linear combination of generators of the motion. Thus theorem 5 is proved.

Corollary 1. All the constants of the motion are also constants of the motion according to the von Neumann equation (eq. (2)).

This corollary is a direct consequence of theorem 5, because each constant of the motion C commutes with the Hamiltonian operator. In general, however, not all constants of the motion according to the von Neumann equation (eq. (2)) are constants of the motion according to eq. (7), because not all of them satisfy condition (16). For example, H^2 is a constant of the motion according to eq. (2), but not according to eq. (7). This is a physically meaningful quantum-thermodynamic result because energy fluctuations are not conserved. For example, an energy eigenstate with energy e has zero fluctuations, while a thermodynamic equilibrium state (theorem (10)) with the same mean energy e has nonzero fluctuations.

It follows that the generators of the motion are essential characteristics of the definition of the system because they specify its time invariants.

Theorem 6. For a single constituent of matter, state property $s(\varrho) = -k\,\mathrm{Tr}(\varrho \ln \varrho)$ is a nondecreasing function of time.

Proof. Using eq. (7), relations (8) to (11) and theorem 2, we find

$$\frac{\mathrm{d}s(\varrho)}{\mathrm{d}t} = -k\,\mathrm{Tr}\left(\frac{\mathrm{d}\varrho}{\mathrm{d}t}\ln\varrho\right) - k\,\mathrm{Tr}\left(\frac{\mathrm{d}\varrho}{\mathrm{d}t}\right), \tag{17a}$$

$$\frac{\mathrm{d}s(\varrho)}{\mathrm{d}t} = \frac{k}{\tau}\,\frac{\begin{vmatrix} (\ln\varrho, \ln\varrho) & (\ln\varrho, R_0) & (\ln\varrho, R_1) & \dots & (\ln\varrho, R_z) \\ (R_0, \ln\varrho) & (R_0, R_0) & (R_0, R_1) & \dots & (R_0, R_z) \\ (R_1, \ln\varrho) & (R_1, R_0) & (R_1, R_1) & \dots & (R_1, R_z) \\ \vdots & \vdots & \vdots & & \vdots \\ (R_z, \ln\varrho) & (R_z, R_0) & (R_z, R_1) & \dots & (R_z, R_z) \end{vmatrix}}{\Gamma(\sqrt{\varrho}\,R_0, \sqrt{\varrho}\,R_1, \dots, \sqrt{\varrho}\,R_z)}, \tag{17b}$$

$$\frac{\mathrm{d}s(\varrho)}{\mathrm{d}t} = \frac{k}{\tau}\,\frac{\Gamma(\sqrt{\varrho}\ln\varrho, \sqrt{\varrho}\,R_0, \sqrt{\varrho}\,R_1, \dots, \sqrt{\varrho}\,R_z)}{\Gamma(\sqrt{\varrho}\,R_0, \sqrt{\varrho}\,R_1, \dots, \sqrt{\varrho}\,R_z)}, \tag{17c}$$

$$\frac{\mathrm{d}s(\varrho)}{\mathrm{d}t} = \frac{k}{\tau}(\tilde{D}|\tilde{D}), \tag{17d}$$

where the last of relations (17) follows from the fact that $(\tilde{D}|\sqrt{\varrho}R_i) = 0$ for $i = 0, 1, ..., z$ and, therefore, $(\tilde{D}|\sqrt{\varrho}\ln\varrho) = (\tilde{D}|\tilde{D})$. The right-hand side of eq. (17*c*) is nonnegative because Gram determinants are nonnegative [11] and, by definition, $\Gamma(\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, ..., \sqrt{\varrho}R_z)$ is strictly positive. Similarly, the scalar product $(\tilde{D}|\tilde{D})$ in eq. (17*d*) is nonnegative [12]. Thus $ds(\varrho)/dt$ is nonnegative and theorem 6 is proved.

Theorem 6 is important because it is shown later that the functional $s(\varrho)$ represents the thermodynamic entropy of the single elementary constituent in state ϱ.

Definition 2: *Nondissipative states.* A state operator ϱ is said to be nondissipative if and only if, for that state, $ds(\varrho)/dt = 0$. Otherwise, the state operator will be called dissipative.

Theorem 7. A given state operator ϱ is nondissipative if and only if there exists a constant of the motion C (theorem 5) such that

$$\varrho\ln\varrho = \varrho C = C\varrho\,. \tag{18}$$

Proof. Using definition 2 and relation (17*c*), we find

$$\Gamma(\sqrt{\varrho}\ln\varrho, \sqrt{\varrho}R_0, \sqrt{\varrho}R_1, ..., \sqrt{\varrho}R_z) = 0\,. \tag{19}$$

The Gram determinant in eq. (19) vanishes if and only if operators $\sqrt{\varrho}\ln\varrho$, $\sqrt{\varrho}R_0, \sqrt{\varrho}R_1, ..., \sqrt{\varrho}R_z$ are linearly dependent, *i.e.* if and only if there exist real scalars α and $\gamma\lambda_i'$, not all zero, such that

$$\alpha\sqrt{\varrho}\ln\varrho - \gamma\sum_{i=0}^{z}\lambda_i'\sqrt{\varrho}R_i = 0\,. \tag{20}$$

Because operators $\sqrt{\varrho}R_i$ are linearly independent, we can set $\alpha \neq 0$ and $\alpha = \gamma = 1$. Because operators $\sqrt{\varrho}R_i$ span the set $\{\sqrt{\varrho}I, \sqrt{\varrho}H, \sqrt{\varrho}N_1, ..., \sqrt{\varrho}N_n\}$, there exist scalars λ_I, λ_H, λ_i such that

$$\sum_{i=0}^{z}\lambda_i'\sqrt{\varrho}R_i = \lambda_I\sqrt{\varrho}I + \lambda_H\sqrt{\varrho}H + \sum_{i=1}^{n}\lambda_i\sqrt{\varrho}N_i = \sqrt{\varrho}C\,, \tag{21}$$

where C is a constant of the motion (theorem 5). Therefore, $ds(\varrho)/dt = 0$ if and only if there is a C such that

$$\sqrt{\varrho}\ln\varrho = \sqrt{\varrho}C\,. \tag{22}$$

Taking the adjoint of eq. (22), we find that ϱ and C commute. Multiplying eq. (22) by $\sqrt{\varrho}$, we find that condition (18) is necessary for ϱ to be nondissipative. Using it directly in the evaluation of determinant (17*b*), we verify that the condition is also sufficient. Thus theorem 7 is proved.

Corollary 2. Any pure state operator $\varrho = P_\psi$ is nondissipative.

Indeed, for any pure state operator, $\varrho \ln \varrho$ is the null operator and condition (18) is satisfied for $C = 0$.

Corollary 3. A given state operator ϱ is nondissipative if and only if there exists a constant of the motion C and an idempotent operator B commuting with C such that

$$\varrho = B \exp [C] . \tag{23}$$

Because B is idempotent, it can be readily verified that $B \ln B$ is the null operator and that the ϱ given by eq. (23) satisfies condition (18) and, therefore, is nondissipative. Conversely, if ϱ is nondissipative, then condition (18) is valid for some C commuting with ϱ and we can define an idempotent operator B having the same set of eigenvectors as that shared by ϱ and C, and eigenvalues $b_i = 1$ if $p_i \neq 0$ and $b_i = 0$ if $p_i = 0$, where p_i is the i-th eigenvalue of ϱ. Because $\varrho \ln \varrho = \varrho C$, we find that $p_i = b_i \exp [C_i]$, $\varrho = B \exp [C]$ and, therefore, that condition (23) is satisfied.

Theorem 8. – A solution $\varrho_n(t)$ of the von Neumann equation is also a physical solution of eq. (7) if and only if $\varrho_n(0)$ is nondissipative.

Proof. Being a solution of eq. (2), $\varrho_n(t) = U(t)\, \varrho_n(0)\, U^{-1}(t)$, where the unitary transformation $U(t) = \exp [-itH/\hbar]$. If, for some t_0, $\varrho_n(t_0)$ is nondissipative, then condition (18) is satisfied by $\varrho_n(t)$ for every t and $\varrho_n(t_0)$ for the same constant of the motion C because $[C, H] = 0$. Therefore, $\varrho_n(t)$ is nondissipative for every t if and only if $\varrho_n(0)$ is nondissipative. Moreover, by virtue of relation (17*d*) and definition 2, each of the operators $\tilde{D}$ and D equals the null operator if and only if ϱ is nondissipative. Thus, if $\varrho_n(t)$ is nondissipative and satisfies eq. (2), then $\varrho_n(t)$ also satisfies eq. (7) because $D = 0$ for every t. Conversely, if $\varrho_n(t)$ is a solution of both eqs. (2) and (7), then $\varrho_n(t)$ is nondissipative because $D = 0$ and, therefore, $\tilde{D} = 0$ for every t. Thus, theorem 8 is proved.

If uniqueness of physical solutions were proved, then theorem 8 would be strengthened so that « if initially in a nondissipative state, a physical solution evolves only through such states. » In other words, for such initial states, eq. (7) would reduce to the von Neumann equation.

By virtue of corollary 3 and theorem 8, a solution of the form $\varrho_n(t) = B_n(t) \exp [C]$, with $B_n(t) = U(t) B_n(0)\, U^{-1}(t)$ and $[B_n(0), H] \neq 0$, can be regarded as a limit cycle.

It is seldom recognized that thermodynamics does not exclude the existence of states of isolated systems which undergo steady, oscillatory time evolution. These states are included in the proposed theory. Moreover, theorems 3 and 8 show that conventional quantum dynamics is included in the proposed quantum dynamics as a special case. Said differently, conventional quantum dynamics describes only unitary transformations of nondissipative states of quantum thermodynamics.

Definition 3: *Equilibrium states.* A state operator ϱ is said to represent an equilibrium state if and only if

$$\frac{d\varrho}{dt} = 0 . \tag{24}$$

If condition (24) is not satisfied, then ϱ represents a nonequilibrium state.

Theorem 9. A state operator ϱ represents an equilibrium state if ϱ commutes with the Hamiltonian operator H and is nondissipative.

Proof. The first term in the right-hand side of eq. (7) vanishes if ϱ commutes with H. The second term vanishes if ϱ is nondissipative. Thus theorem 9 is valid.

Theorem 10. For given mean values of the generators of the motion, there exists one and only one state operator ϱ_0 for which $s(\varrho_0) = -k\,\mathrm{Tr}\,(\varrho_0 \ln \varrho_0)$ is greater than $s(\varrho)$ of any other state operator corresponding to the same mean values. The state operator ϱ_0 is given by the relation

$$\varrho_0 = \exp\left[-\beta H - \sum_{i=1}^{n} \nu_i N_i\right] \Big/ \mathrm{Tr}\left(\exp\left[-\beta H - \sum_{i=1}^{s} \nu_i N_i\right]\right) , \tag{25}$$

where the coefficients β and ν_i, for $i = 1, 2, ..., n$, are determined by the given mean values.

The theorem is proved in the literature by imposing reasonable additional technical conditions of regularity on operators H and N_i ([15]). Relation (25) is a generalization of the known thermodynamic-equilibrium distributions.

By virtue of corollary 3 and theorem 9, it is clear that ϱ_0 is an equilibrium state. For given mean values of the generators of the motion, a system admits many equilibrium states. We will see, however, that not all of these are thermodynamic equilibrium states. This feature of the theory reflects even for a single constituent of matter innumerable experiences with macroscopic systems that remain for long periods of time in an equilibrium state far from thermodynamic equilibrium.

In what follows, we examine the stability of equilibrium states in a special sense that, we believe, captures the essence of the second law of thermody-

---

([15]) W. OCHS and W. BAYER: ref. ([13]); see also A. KATZ: *Principles of Statistical Mechanics* (W. H. Freeman, San Francisco, Cal., 1967), p. 45-51.

namics [3,16]. Specifically, we define a special stability concept and examine whether there exists one and only one stable equilibrium state for each set of values of the energy and the other constants of the motion. This inquiry differs from that in mechanics, classical or quantum, because in mechanics a system admits as a stable equilibrium state only that of lowest energy.

Definition 4: *subset* Ω. We denote by Ω the set of all the linear, self-adjoint, unit trace, nonnegative-definite operators ϱ on $\mathscr{H}$ that correspond to finite mean values of the generators of the motion H and N_i, *i.e.* such that $\mathrm{Tr}\,(H\varrho) < \infty$ and $\mathrm{Tr}\,(N_i\varrho) < \infty$, for $i = 1, \dots, n$.

By virtue of theorem 4 every physical solution $\varrho(t)$ with $\varrho(0)$ in Ω lies entirely in Ω.

Definition 5: *trace norm.* We denote by $\|\cdot\|$ the trace operator norm defined by $\|A\| \equiv \mathrm{Tr}\,|A|$, where $|A| \equiv (A^\dagger A)^{\frac{1}{2}}$.

Definition 6: *stable equilibrium states.* An equilibrium state ϱ_e in Ω is said to be stable if and only if for every $\varepsilon > 0$ there is a $\delta > 0$ such that any physical solution $\varrho(t)$ in Ω with $\|\varrho(0) - \varrho_e\| < \delta$ remains with $\|\varrho(t) - \varrho_e\| < \varepsilon$ for every $t > 0$.

Among all the self-adjoint (not necessarily definite) operators $\varrho(0)$ in the open neighbourhood $\|\varrho(0) - \varrho_e\| < \delta$ of an equilibrium state ϱ_e, this special concept of stability requires that only those that are in the set Ω and that correspond to a physical solution $\varrho(t)$ need be considered. This concept extends that of conditional or constrained stability considered by LIAPUNOFF [17] to a differential operator equation like eq. (7).

Theorem 11. For given finite mean values of the generators of the motion, the equilibrium state ϱ_0 corresponding to the maximum value $s(\varrho_0)$ of $s(\varrho)$ (theorem (10)) is stable.

The proof of this theorem is given in appendix A.

Definition 7: *unstable equilibrium states.* An equilibrium state ϱ_e in Ω is said to be unstable if and only if there is an $\varepsilon > 0$ such that, for every $\delta > 0$, there is a physical solution $\varrho(t)$ in Ω with $\|\varrho(0) - \varrho_e\| < \delta$ and $\|\varrho(t) - \varrho_e\| \geqslant \varepsilon$ after some $t > 0$.

Conjecture. For given finite mean values of the generators of the motion, all equilibrium states other than ϱ_0 of theorem 10 are unstable.

A discussion of this conjecture is given in appendix E.

The conjecture and its discussion in appendix E can be extended to all unitary motions of nondissipative, nonequilibrium states—limit cycles—to

---

(16) See also G. N. HATSOPOULOS and J. H. KEENAN: *Principles of General Thermodynamics* (Wiley and Sons, New York, N.Y., 1965), p. 30, 361.

(17) A. LIAPUNOFF: *Problème Général de la Stabilité du Mouvement*, in *Annals of Mathematics Studies*, Vol. **17** (Princeton University Press, Princeton, N.J., 1949), p. 210-213.

show that they are unstable. The definition and the discussion of unstable limit cycles would be identical to definition 7 and appendix E, respectively, except that we would be considering limit cycles $\varrho_n(t)$ (theorem 8) instead of equilibrium states ϱ_e.

Assuming that the conjecture can be proved, by virtue of theorem 11 we conclude that for given finite mean values of the generators of the motion a system of a single constituent admits one and only one stable equilibrium state. But this is a generalization of the statement of the second law of thermodynamics used by HATSOPOULOS and GYFTOPOULOS [3] in their unified theory. Hence, we further conclude that the proposed equation of motion implies the second law of thermodynamics.

From the second law and eq. (2) in the limit of unitary processes, it has been shown [3] that $-k\,\mathrm{Tr}\,(\varrho \ln \varrho)$ satisfies all the requirements that the thermodynamic entropy of a system must satisfy. Because all arguments of the proof are valid here, we conclude that $s(\varrho) = -k\,\mathrm{Tr}\,(\varrho \ln \varrho)$ represents the entropy also when the dynamics of a single constituent of matter is described by eq. (7). Other quantum-thermodynamic results for both equilibrium and nonequilibrium states are discussed in ref. [3].

4. – Conclusion.

We believe that the proposed equation of motion is consistent with both mechanics and thermodynamics. One of its important consequences is that the first law and, subject to the proof of the conjecture, the second law of thermodynamics emerge as manifestations of the inherent quantum-dynamical behaviour of the elementary constituents of matter. Therefore, these two laws need not be added explicitly to the foundations of the theory because the theory includes their implications.

Our present knowledge of the mathematical properties of the new equation is far from complete. On the one hand, we are excited by its overall conceptual elegance as a generalization of the traditional quantum law of motion which satisfies our desideratum of direct compatibility with the principles of thermodynamics. Thus, in our theory, no layer of statistical or information-theoretic reasoning is required to bridge the gap between mechanics and thermodynamics, for there is no such a gap. On the other hand, we remain quite perplexed by several unresolved technical mathematical issues related to unbounded operators on infinite-dimensional Hilbert space and to the general question of existence and uniqueness of physical solutions.

In further communications, other physical implications of the theory will be explored, including the derivation of the Boltzmann equation, the derivation of the Onsager phenomenological relations of irreversible thermodynamics, the classical limit ($\hbar \to 0$) of eq. (7), and the experimental determination of the numerical value of the time constant τ that must be assigned to each elementary constituent of matter [18].

* * *

The first author gratefully acknowledges financial support of the Thermo-Electron Corporation.

APPENDIX A

Proof of theorem 11.

On the set Ω (definition 4), we define the real nonnegative functional

$$V(\varrho) \equiv s(\varrho_0[\varrho]) - s(\varrho) = k\,\mathrm{Tr}\,(\varrho \ln \varrho) - k\,\mathrm{Tr}\,(\varrho_0[\varrho] \ln \varrho_0[\varrho])\,, \tag{A.1}$$

where $\varrho_0[\varrho]$ is the unique operator in Ω defined by theorem 10 and the finite mean values of the generators of the motion corresponding to operator ϱ. Functional $s(\varrho)$ is continuous on the set Ω with respect to the trace norm $\|A\| \equiv \mathrm{Tr}\,|A|$ because $\mathrm{Tr}\,(H\varrho) < \infty$. This point is discussed by WEHRL [19]. In particular, continuity at the states $\varrho_0[\varrho]$ implies that, given any $\eta > 0$, there is a $\delta > 0$ such that $|s(\varrho) - s(\varrho_0[\varrho])| = V(\varrho) < \eta$ for every ϱ in Ω with $\|\varrho - \varrho_0[\varrho]\| = \mathrm{Tr}\,|\varrho - \varrho_0[\varrho]| < \delta$.

Next we define the nonnegative function $a(x)$ by

$$a(x) = \inf_{\varrho \in \Omega_x} V(\varrho)\,, \tag{A.2}$$

where set Ω_x is such that

$$\Omega_x \equiv \{\varrho \,|\, \varrho \in \Omega,\ \|\varrho - \varrho_0[\varrho]\| = x\}\,. \tag{A.3}$$

Thus, for every ϱ in Ω,

$$a(\|\varrho - \varrho_0[\varrho]\|) \leqslant V(\varrho)\,. \tag{A.4}$$

Lemma A1. For every $\varepsilon > 0$ there is a $\delta > 0$ such that $V(\varrho) < a(\varepsilon)$ for every ϱ in Ω with $\|\varrho - \varrho_0[\varrho]\| < \delta$.

Proof. Using the continuity of functional $V(\varrho)$ at states $\varrho_0[\varrho]$ and selecting $\eta = a(\varepsilon)$ for every given ε, we find that $V(\varrho) < a(\varepsilon)$. Thus lemma A1 is proved.

Lemma A2. Function $a(x)$ is such that $a(x) < a(y)$ implies $x < y$.

---

[18] A referee suggested two other aspects of our theory that need further investigation and clarification. The first is to study the invariance properties of the new equation of motion under the usual symmetry groups. The second is to explore the implications of the nonlinear equation on the quantum theory of measurement.

[19] A. WEHRL: ref. [2], p. 241.

Proof. For $a(x) < a(y)$, if we assume $x > y$ and for each operator ϱ_x in Ω_x define the operator $\varrho_\varepsilon = \varepsilon\varrho_x + (1-\varepsilon)\varrho_0[\varrho_x]$, where $0 < \varepsilon = y/x < 1$, then $\varrho_0[\varrho_\varepsilon] = \varrho_0[\varrho_x]$ and we find that each ϱ_ε belongs to Ω_y and, therefore, is such that $V(\varrho_\varepsilon) \geqslant a(y)$. Moreover, from the concavity of $s(\varrho)$ and definition (A.1), it follows that $V(\varrho_\varepsilon) < \varepsilon V(\varrho_x)$. Thus, for every ϱ_x in Ω_x, we find that $V(\varrho_x) > a(y)/\varepsilon$ and, therefore, that $a(y)/\varepsilon$ is a lower bound of $V(\varrho)$ on Ω_x. Because the greatest lower bound of $V(\varrho)$ on Ω_x is $a(x)$ (definition (A.2)), we find $a(x) \geqslant a(y)/\varepsilon$ and, hence, $a(x) > a(y)$ which is a contradiction. If $x = y$, then set Ω_x coincides with Ω_y and, by definition, $a(x) = a(y)$ which again is a contradiction. We conclude that $x < y$ and, thus, lemma A2 is proved.

Proof of Theorem 11. For any physical solution $\varrho(t)$ of eq. (7), the mean values of the generators of the motion are invariant (theorem 4), $\varrho_0[\varrho(t)] = \varrho_0[\varrho(0)] = \varrho_0$, $\mathrm{d}V/\mathrm{d}t = -\mathrm{d}s/\mathrm{d}t \leqslant 0$ (theorem 6) and, therefore, $V(\varrho(t)) \leqslant V(\varrho(0))$ for every $t > 0$. By lemma A1, for every $\varepsilon > 0$ there is a $\delta > 0$ such that $V(\varrho(0)) < a(\varepsilon)$ for every physical solution $\varrho(t)$ with $\|\varrho(0) - \varrho_0\| < \delta$. Using eq. (A.4) for every t, we find

$$a(\|\varrho(t)-\varrho_0\|) \leqslant V(\varrho(t)) \leqslant V(\varrho(0)) < a(\varepsilon)\,. \tag{A.5}$$

By lemma A2, relations (A.5) imply that $\|\varrho(t) - \varrho_0\| < \varepsilon$. Thus we conclude that every ϱ_0 in Ω is stable (definition 6) and theorem 11 is proved.

Appendix B

A class of approximate phisical solutions.

As an example of nontrivial results, we find a particular class of non-unitary approximate physical solutions. We select an equilibrium state

$$\varrho_e = B\exp[C]\,, \qquad [B, C] = [B, H] = 0\,, \tag{B.1}$$

where B and C are defined in theorem 5 and corollary 3. For the same B and C, we consider states ϱ in the class defined by the relations

$$\varrho = \varrho B = B\varrho\,, \qquad [\varrho, C] = 0\,, \qquad \mathrm{Tr}\,(\varrho R_i) = \mathrm{Tr}\,(\varrho_e R_i) \qquad \text{for } i = 1, 2, \ldots, z \tag{B.2}$$

or, equivalently,

$$\varrho = \varrho_e(I + \varepsilon\Phi) = B(I + \varepsilon\Phi)\exp[C]\,, \tag{B.3}$$

where

$$\varepsilon\Phi = B(\varrho\exp[-C] - I)\,, \qquad [\Phi, C] = 0\,, \qquad \mathrm{Tr}\,(\varrho_e\Phi R_i) = 0\,. \tag{B.4}$$

In the limit as $\varepsilon \to 0$ and $\|\Phi\| = \mathrm{Tr}\,|\Phi| < \infty$, eq. (7) reduces to the form ([20])

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} \to -\frac{i}{\hbar}[H, \varrho] - \frac{\varrho - \varrho_e}{\tau}. \tag{B.5}$$

Thus

$$\varrho(t) \to \exp\left[-\frac{t}{\tau}\right] \exp\left[-\frac{itH}{\hbar}\right] \varrho(0) \exp\left[\frac{itH}{\hbar}\right] + \left[1 - \exp\left[-\frac{t}{\tau}\right]\right] \varrho_e. \tag{B.6}$$

Equation (B.5) has the same form as a Bloch relaxation equation. Its solution (eq. (B.6)) is physical and unique, remains in the class defined by relations (B.2), is analytic in t, conserves the nullity and rank of $\varrho(0)$, evolves from lower to higher entropy, *i.e.* $s(\varrho(0)) < s(\varrho(t)) < s(\varrho_e)$, and tends asymptotically to ϱ_e, *i.e.* $\varrho(t) \to \varrho_e$ for $t \to \infty$.

Appendix C

Existence and uniqueness of solutions.

We conjecture that eq. (7) admits a solution $\varrho(t)$ for each $\varrho(0)$ in the subset $\tilde{Q}$ of the linear, self-adjoint, unit-trace operators ϱ on $\mathscr{H}$. In support of this conjecture, we note that the right-hand side of eq. (7) is a linear combination of operators $\varrho \ln \varrho$, ϱR_i and their adjoints, for $i = 0, 1, \ldots, z$, with coefficients that involve trace functionals of the same operators. For a system with a finite-dimensional Hilbert space, these operators are continuous with respect to the trace norm ([21]). Continuity of $\mathrm{d}\varrho/\mathrm{d}t$ is an important necessary condition to guarantee the existence of continuous solutions $\varrho(t)$ for every $\varrho(0)$. We conjecture that, perhaps by imposing additional technical restrictions on the set $\tilde{Q}$ and on the generators of the motion R_i, the existence of solutions of eq. (7) can be proved.

We also conjecture that, given a $\varrho(0)$, we can find a unique $\varrho(t)$. In support of this conjecture, we first consider an ordinary nonlinear differential equation of the form

$$\frac{\mathrm{d}y}{\mathrm{d}t} = F(y) - \frac{1}{\tau} y \ln y, \tag{C.1}$$

where y is real, $F(y) < \infty$ for all y, $F(0) = 0$ and $\mathrm{d}F/\mathrm{d}y$ exists and is finite. It can be verified that the term $F(y)$ satisfies a Cauchy-Lipschitz condition

([20]) We find $I + \varepsilon\Phi \to \exp[\varepsilon\Phi]$; $\varrho \to \mathrm{B}\exp[\varepsilon\Phi + C]$; $\sqrt{\varrho}\ln\varrho \to \sqrt{\varrho}(\varepsilon\Phi + C)$; $(R_i, \ln\varrho) \to \varepsilon(R_i, \Phi) + (R_i, C)$ for $i = 1, 2, \ldots, z$, where $(\cdot, \cdot)$ is defined by relation (11); $(R_i, \Phi) = \mathrm{Tr}(\varrho_e \Phi R_i) + \varepsilon\,\mathrm{Tr}(\varrho_e \Phi^2 R_i) \to 0$; $\tilde{D} \to \varepsilon\sqrt{\varrho}\Phi$; $D \to \varepsilon\varrho\Phi \to \varepsilon\varrho_e\Phi = \varrho - \varrho_e$.

([21]) The continuity of operator $\varrho \ln \varrho$ is discussed, *e.g.*, by A. Wehrl: ref. ([2]), p. 251.

and the term $y \ln y$ an Osgood condition [22], *i.e.*

$$|y_1 \ln y_1 - y_2 \ln y_2| < K|y_1 - y_2| \ln \frac{1}{|y_1 - y_2|} \tag{C.2}$$

for $0 \leqslant y_1 < y_2 \leqslant e^{-1}$ and $K = 1$. It can be shown that eq. (C.1) admits a unique solution for each $y(0)$. In particular, despite the logarithmic singularity at $y = 0$, the solution $y(t) = 0$ is unique.

Next, we rewrite eq. (7) in the form

$$\frac{d\varrho}{dt} = f(\varrho) - \frac{1}{\tau}\varrho \ln |\varrho| , \tag{C.3}$$

where

$$f(\varrho) \equiv -\frac{i}{\hbar}[H, \varrho] - \frac{1}{\tau}(D - \varrho \ln |\varrho|) . \tag{C.4}$$

Thus

$$\frac{dp_j}{dt} = f_j(\{p_k\}) - \frac{1}{\tau} p_j \ln |p_j| , \tag{C.5}$$

where $f_j(\{p_k\}) = \langle\varphi_j|f(\varrho)|\varphi_j\rangle$ and $\{\varphi_k\}$ is an eigenbasis of ϱ.

For every ϱ in $\tilde{Q}$, we can verify that $f_j(\{p_k\})$ vanishes for $p_j = 0$, and admits a partial derivative with respect to each eigenvalue p_k. These observations suggest a similarity between eq. (C.1) and operator equation (C.3). In particular, eqs. (C.5) show the same type of logarithmic singularity as eq. (C.1). We conjecture that conditions analogous to the Cauchy-Lipschitz one for $f(\varrho)$ and to the Osgood one for $\varrho \ln \varrho$ can be established and that, perhaps by imposing additional technical restrictions on the set $\tilde{Q}$ and on the generators of the motion R_i, the uniqueness of solutions of eq. (7) can be proved.

Appendix D

Nonnegativity of solutions.

We conjecture that every solution $\varrho(t)$ with $\varrho(0)$ nonnegative definite is physical. In support of this conjecture, we write the self-adjoint, not necessarily definite, operator $\varrho(t)$ in $\tilde{Q}$ as

$$\varrho(t) = \sum_k p_k(t)|\varphi_k(t)\rangle\langle\varphi_k(t)| + \int p_k(t)|\varphi_k(t)\rangle\langle\varphi_k(t)|\,dk , \tag{D.1}$$

[22] See, *e.g.*, E. L. Ince: *Ordinary Differential Equations* (Dover, New York, N.Y., 1956), p. 62-72.

where $\{\varphi_k(t)\}$ and $\{p_k(t)\}$ are complete sets of orthonormal eigenvectors ($\langle\varphi_k(t)|\varphi_k(t)\rangle = 1$) and real eigenvalues of $\varrho(t)$. Therefore,

$$\text{(D.2)}\qquad \frac{d\varrho(t)}{dt} = \dot{\varrho} = \sum_k \dot{p}_k|\varphi_k\rangle\langle\varphi_k| + \sum_k p_k(|\dot{\varphi}_k\rangle\langle\varphi_k| + |\varphi_k\rangle\langle\dot{\varphi}_k|) + \\ + \int \dot{p}_k|\varphi_k\rangle\langle\varphi_k|\,dk + \int p_k(|\dot{\varphi}_k\rangle\langle\varphi_k| + |\varphi_k\rangle\langle\dot{\varphi}_k|)\,dk\,,$$

$$\text{(D.3)}\qquad \dot{p}_j = \langle\varphi_j|\dot{\varrho}|\varphi_j\rangle = -\frac{i}{\hbar}\langle\varphi_j|[H, \varrho]|\varphi_j\rangle - \frac{1}{\tau}\langle\varphi_j|D|\varphi_j\rangle\,,$$

where in writing the second equality in relation (D.3) we have used eq. (7).
Using eqs. (8)-(11) in eq. (D.3), we find [10]

$$\text{(D.4)}\qquad \dot{p}_j = -\frac{1}{\tau}\frac{\begin{vmatrix} 0 & p_j(R_0)_{jj} \dots p_j(R_s)_{jj} \\ \sum_n (R_0)_{nn}|p_n|\ln|p_n| & \\ \vdots & \Gamma \\ \sum_m (R_s)_{mm}|p_m|\ln|p_m| & \end{vmatrix}}{\Gamma} - \frac{1}{\tau}p_j\ln|p_j|\,,$$

where $(R_i)_{jj} = \langle\varphi_j|R_i|\varphi_j\rangle$.

Because $\varrho(t)$ is a solution, the set of functions $\{p_j(t)\}$ satisfies the system of equations (D.4). If these functions are differentiable to all orders, then they also satisfy the expressions for $d^2p_j/dt^2, \dots, d^np_j/dt^n, \dots$, that follow by differentiating eqs. (D.4) to all orders. Then, if in addition a function $p_j(t)$ is zero at some time t_0, we can readily verify that eqs. (D.4) imply that all the time derivatives of $p_j(t)$ vanish at t_0. Moreover, if the function $p_j(t)$ were analytic in t, then it would be identically zero for all times t.

If every solution $\varrho(t)$ were so «smooth» that each function $p_j(t)$ were analytic in t and at some time a function $p_j(t)$ were zero or strictly positive, then we would conclude that at all times $p_j(t)$ would remain zero or strictly positive, respectively. Indeed, by continuity, a strictly positive $p_j(t)$ could change sign only by becoming zero. But then it would be zero at all times. In other words, we would conclude that eq. (7) preserves the nonnegativity, rank and nullity of solutions.

The conclusion that the rank and nullity of $\varrho(t)$ are conserved would imply that every nonstrictly positive initial state would tend towards an (unstable) equilibrium state or a limit cycle and not a thermodynamic (stable) equilibrium state. In addition, it would be consistent with our underlying hypothesis that traditional unitary quantum dynamics should emerge as an exact special case of quantum thermodynamics.

For the present, however, all of this is conjectural because we have not found a rigorous proof that the solutions of eq. (7) are indeed analytic functions of time.

Appendix E

Discussion of unstable equilibrium.

Lemma E1. For given mean values of the generators of the motion, ϱ_0 (eq. (25)) is the only strictly positive, nondissipative state operator.

Proof. A state operator ϱ is strictly positive if and only if all its eigenvalues are positive. It is nondissipative if and only if it satisfies condition (18). By virtue of this condition, every strictly positive and nondissipative state operator can be expressed in the form

$$\varrho = \exp[C], \tag{E.1}$$

where

$$C = \sum_{i=0}^{z} \lambda_i R_i, \tag{E.2}$$

$$1 = \mathrm{Tr}\,(\exp[C]) \equiv \Lambda(\lambda_i) \tag{E.3}$$

and R_i, for $i = 0, 1, \ldots, z = n+1$, are all the generators of motion.

Moreover, it can be shown that

$$\frac{\partial \Lambda}{\partial \lambda_i} = \mathrm{Tr}\,(R_i \exp[C]) = \mathrm{Tr}\,(R_i \varrho) = r_i\,. \tag{E.4}$$

For given mean values $r_0, r_1, \ldots, r_z$ of the linearly independent generators of the motion ($r_0 = 1$), the only solution ([15]) of eq. (E.4) is ϱ_0. Thus lemma E1 is proved.

Next, we consider an arbitrary equilibrium state $\varrho_e \neq \varrho_0[\varrho_e]$ in Ω (definition 4) and the one-parameter family Ω_η of operators

$$\varrho_\eta = (1-\eta)\,\varrho_e + \eta\varrho_0[\varrho_e] \tag{E.5}$$

for $0 < \eta < 1$. Clearly, Ω_η lies entirely in Ω.

Lemma E2. If ϱ_η is a state operator, then it is dissipative.

Proof. Every operator ϱ_η in Ω_η is strictly positive ([23]). Therefore, by virtue of lemma E1, if ϱ_η is in the set Q of state operators, then it is dissipative because it differs from the unique $\varrho_0[\varrho_e]$. Thus, lemma E2 is proved.

([23]) An operator ϱ is nonnegative definite if and only if $\langle\psi, \varrho\psi\rangle \geqslant 0$ for all vectors ψ. An operator ϱ is strictly positive if and only if $\langle\psi, \varrho\psi\rangle > 0$ for all vectors $\psi \neq 0$. If ϱ_η were not strictly positive, a vector $\psi \neq 0$ would exist such that $\langle\psi, \varrho_\eta\psi\rangle \leqslant 0$, *i.e.* $(1-\eta)\langle\psi, \varrho_e\psi\rangle \leqslant -\eta\langle\psi, \varrho_0[\varrho_e]\psi\rangle$. But, for $0<\eta<1$, this would imply that $\langle\psi, \varrho_0[\varrho_e]\psi\rangle = 0$, because both ϱ_e and $\varrho_0[\varrho_e]$ are nonnegative definite, and $\psi = 0$ because $\varrho_0[\varrho_e]$ is strictly positive. Hence, ϱ_η must be strictly positive.

For given finite mean values of the generators of the motion and for each operator ϱ_η (eq. (E.5)), if there were a physical solution $\varrho(t)$ of eq. (7) such that $\varrho(0) = \varrho_\eta$ and if every initially strictly positive physical solution $\varrho(t)$ remained strictly positive for every $t > 0$ (appendix D), then equilibrium state ϱ_e would be unstable because ϱ_η is strictly positive. Indeed, $\varrho(t)$ would remain dissipative (lemma E1) and $\mathrm{d}s(\varrho(t))/\mathrm{d}t$ strictly positive (theorem 6) until $\varrho(t) = \varrho_0[\varrho_e]$ for some $t > 0$, finite or infinite. We conclude that $\varrho(t)$ with $\varrho(0) = \varrho_\eta$ would tend to $\varrho_0[\varrho_e]$. For $\varepsilon = \|\varrho_0[\varrho_e] - \varrho_e\|/n$ with $n > 1$ and any $\delta > 0$, we would select $\eta < \delta/\|\varrho_0[\varrho_e] - \varrho_e\|$ so that $\|\varrho(0) - \varrho_e\| = \eta\|\varrho_0[\varrho_e] - \varrho_e\| < \delta$. Because $\|\varrho(t) - \varrho_e\|$ would tend to $\|\varrho_0[\varrho_e] - \varrho_e\| = n\varepsilon$, there would be a $t > 0$ such that $\|\varrho(t) - \varrho_e\| > \varepsilon$ and, thus, we would conclude that ϱ_e is unstable.

This discussion could be repeated for a limit cycle $\varrho_n(t)$ (theorem 8) instead of an equilibrium state ϱ_e.

In complete analogy with the notions of unstable equilibrium and limit cycles in mechanics, if initially in an unstable equilibrium state or a limit cycle, a single isolated constituent of matter would never reach thermodynamic equilibrium. However, in any neighbourhood of that equilibrium state or limit cycle there would be a strictly positive, dissipative, nonequilibrium state from which the system proceeds towards thermodynamic or stable equilibrium.

● RIASSUNTO

Si propone una nuova equazione di evoluzione per sistemi quantistici composti da un singolo costituente materiale elementare. L'equazione è soddisfatta dall'evoluzione unitaria degli stati puri e di una sottoclasse di stati misti. Ma, in generale, essa genera un'evoluzione non unitaria dell'operatore di stato. L'equazione mantiene costante il valor medio dell'energia e causa aumenti di entropia finché il sistema non raggiunge uno stato di equilibrio oppure un ciclo limite.

Квантовая термодинамика. Новое уравнение движения для однокомпонентного вещества.

Резюме (*). — Для квантовых систем, состоящих из вещества, представляющего одну элементарную компоненту, предлагается новое нелинейное уравнение движения. Уравнение удовлетворяется для чистых состояний и для специального класса смешанных состояний. В общем случае, это уравнение генерирует неунитарную эволюцию оператора состояния. Это уравнение сохраняет энергию инвариантной, вызывает увеличение энтропии со временем, пока система не достигнет состояния равновесия.

(*) *Переведено редакцией.*