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Generalized Two-Level Quantum Dynamics. III. Irreversible Conservative Motion

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If the ordinary quantal Liouville equation $\mathscr{L}\rho = \dot{\rho}$ is generalized by discarding the customary stricture that $\mathscr{L}$ be of the standard Hamiltonian commutator form, the new quantum dynamics that emerges has sufficient theoretical fertility to permit description even of a thermodynamically irreversible process in an isolated system, i.e., a motion $\rho(t)$ in which entropy increases but energy is conserved. For a two-level quantum system, the complete family of time-independent linear superoperators $\mathscr{L}$ that generate such motions is derived; and a physically interesting example is presented in detail.

1. INTRODUCTION

A persistent enigma of theoretical physics inheres in the fact that entropy-increasing, energy-conserving processes in isolated systems are commonplace in nature but are strictly impossible within the framework of Hamiltonian mechanics, classical or quantal. We believe that the rational way to approach this dilemma—the famous problem of irreversibility—is to seek an elegant modification of basic quantum dynamics such that, from this new axiomatic structure, the second law of thermodynamics may be deduced as a theorem. In an earlier communication[(1)] (Part I of this series), after several fashionable alternative approaches had been examined, we developed a physical rationale for the hypothesis that the new quantum law of motion for a closed system ought to be of the form

$$\mathscr{L}\rho(t) = \dot{\rho}(t) \tag{1}$$

a natural generalization of the Liouville equation wherein the time-indepen-

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dent linear superoperator $\mathscr{L}$ (the generalized Liouvillian) is *not* restricted to the traditional Hamiltonian form

$$\mathscr{L}^H\rho = (1/i)[H, \rho] \tag{2}$$

Since the statistical operator (quantum state) $\rho(t)$ must at all times remain Hermitian, positive-semidefinite, and of unit trace, not every linear superoperator is an admissible candidate to be the generator $\mathscr{L}$ in (1). Necessary and sufficient mathematical conditions on $\mathscr{L}$ have been discussed recently by Kossakowski.[2]

To explore the theoretical fertility of the postulated law (1), we have focused attention on the simplest possible case—the two-level quantum system. Every Hermitian operator A associated with such a system may be represented as a real linear combination

$$A = \sqrt{2}\sum_{\alpha=0}^{3} a_\alpha \nu_\alpha = \sqrt{2}\left(a_0\nu_0 + \sum_{n=1}^{3} a_n\nu_n\right) \tag{3}$$

where the basis for operator space has been chosen for convenience to be

$$\{\nu_\alpha\} \equiv \{1/\sqrt{2}, \boldsymbol{\sigma}/\sqrt{2}\} \tag{4}$$

which obeys, because of the properties of the Pauli spin matrices $\boldsymbol{\sigma}$, the orthonormality relation

$$\mathrm{Tr}(\nu_\alpha\nu_\beta) = \delta_{\alpha\beta} \tag{5}$$

In this format every statistical operator is expressible in the form

$$\rho = \frac{1}{\sqrt{2}}\sum_\alpha s_\alpha\nu_\alpha = \frac{1}{\sqrt{2}}\left(s_0\nu_0 + \sum_n s_n\nu_n\right) = \frac{1}{\sqrt{2}}(s_0\nu_0 + \mathbf{s}\cdot\boldsymbol{\nu}) \tag{6}$$

where

$$s_0 = 1 \qquad \text{and} \qquad \mathbf{s}\cdot\mathbf{s} \leqslant 1 \tag{7}$$

From (6) and (7) we see that there is a one-to-one correspondence between the statistical operators of a two-level system and the points of the surface and interior of the unit sphere in an auxiliary 3-space $\mathscr{S}$ in which $\mathbf{s}$ is the radius vector.

The quantal mean value of an observable A in the state ρ is then given in terms of $\mathbf{a}$ and $\mathbf{s}$ as

$$\mathrm{Tr}(\rho A) = a_0 + \sum_n a_n s_n = a_0 + \mathbf{a}\cdot\mathbf{s} \tag{8}$$

Moreover, if we define matrix elements for the superoperator $\mathscr{L}$ by

$$\mathscr{L}_{\beta\alpha} \equiv \mathrm{Tr}(\nu_\beta \mathscr{L} \nu_\alpha) \tag{9}$$

then (1) is represented by

$$\sum_{\alpha} \mathscr{L}_{\beta\alpha} s_{\alpha} = \dot{s}_{\beta} \tag{10}$$

We have already noted that not every $\mathscr{L}$ will be acceptable; to be more explicit, we adopt the following terminology:

Definition 1. A linear superoperator $\mathscr{L}$ generates a *dynamical evolution* if and only if every solution $\rho(t)$ of $\mathscr{L}\rho = \dot{\rho}$ is a statistical operator if the initial condition $\rho(0)$ is a statistical operator.

In a previous paper[3] (Part II of this series) we derived the following criterion for determining the admissible $(\mathscr{L}_{\beta\alpha})$ matrices for a two-level system.

Theorem 1. A superoperator $\mathscr{L}$ generates a dynamical evolution for a two-level quantum system if and only if (a) $\mathscr{L}_{0\alpha} = 0$; (b) K_{mn}, the symmetric part of $\mathscr{L}_{mn}$, is a negative-semidefinite matrix; and (c) $\mathscr{L}_{m0}$ meets one of these requirements:

(i) If $\det(K_{mn}) < 0$, the ellipsoid in $\mathscr{S}$ described by $\sum_{mn} K_{mn} s_m s_n + \sum_m \mathscr{L}_{m0} s_m = 0$ must have no points external to the unit sphere in $\mathscr{S}$; or

(ii) If $\det(K_{mn}) = 0$, then $\mathscr{L}_{m0} = 0$.

Thus the most general admissible $\mathscr{L}$ is given in matrix form as

$$(\mathscr{L}_{\beta\alpha}) = \left(\begin{array}{c|ccc} 0 & 0 & 0 & 0 \\ \hline 0 & & & \\ 0 & & (J_{mn}) & \\ 0 & & & \end{array}\right) + \left(\begin{array}{c|ccc} 0 & 0 & 0 & 0 \\ \hline & & & \\ (\mathscr{L}_{m0}) & & (K_{mn}) & \\ & & & \end{array}\right) \tag{11}$$

where the symmetric and antisymmetric parts of $\mathscr{L}_{mn}$ are defined, respectively, by

$$J_{mn} \equiv \tfrac{1}{2}(\mathscr{L}_{mn} - \mathscr{L}_{nm}) \qquad \text{and} \qquad K_{mn} \equiv \tfrac{1}{2}(\mathscr{L}_{mn} + \mathscr{L}_{nm}) \tag{12}$$

The $\mathscr{L}_{m0}$ and K_{mn} in (11) are of course subject to the constraints of Theorem 1.

Now if the generalized equation of motion (1) is truly adequate for the incorporation of closed-system irreversibility into the framework of mechanics, there will have to be $(\mathscr{L}_{\beta\alpha})$ matrices of the form (11) that generate non-Hamiltonian motion in which *energy is conserved but entropy increases.* We shall find that such generators can in fact be constructed.

2. IRREVERSIBLE MOTION

First we seek conditions on the parameters in (11) such that entropy will increase with time. For the measure of entropy we take the standard Gibbs–von Neumann formula

$$S(\rho) = -k \operatorname{Tr} \rho \ln \rho \tag{13}$$

Normally the time rate of change of S is difficult to manipulate algebraically because it involves the logarithm of an operator. However, in case of a two-level system, a useful simplification is described by the next result:

Theorem 2. For a two level quantum system the motion $\rho(t) = (1/\sqrt{2}) \sum_\alpha s_\alpha(t)\, \nu_\alpha$ has (a) $\dot{S}(t) > 0$ or (b) $\dot{S}(t) = 0$ if and only if, respectively,

$$\text{(a)} \quad G(t) < 0 \qquad \text{or} \qquad \text{(b)} \quad G(t) = 0 \tag{14}$$

where

$$G(t) \equiv \sum_{\beta\alpha} s_\beta(t)\, \mathscr{L}_{\beta\alpha} s_\alpha(t) \tag{15}$$

Proof. In matrix form, (6) becomes

$$(\rho) = \tfrac{1}{2} \begin{pmatrix} 1 + s_3 & s_1 - is_2 \\ s_1 + is_2 & 1 - s_3 \end{pmatrix} \tag{16}$$

and the eigenvalues are readily found to be

$$r_\pm = \tfrac{1}{2}[1 \pm (\mathbf{s} \cdot \mathbf{s})^{1/2}] \tag{17}$$

In terms of these eigenvalues, (13) takes the simple form

$$S = -k(r_+ \ln r_+ + r_- \ln r_-) \tag{18a}$$

and since $r_+ + r_- = 1$, the time derivative of (18a) reduces to

$$\dot{S} = -k\dot{r}_+ \ln(r_+/r_-) \tag{18b}$$

It is apparent from (17) that for $|\mathbf{s}| > 0$, $r_+ > r_-$; hence from (18b) we conclude that $\dot{S}$ and $\dot{r}_+$ are always opposite in sign or else both are zero. The exception, $\mathbf{s} = 0$, which corresponds to $\rho = \tfrac{1}{2}1$, has $\dot{S} = 0$ regardless of the sign of $\dot{r}_+$.

To complete the proof, we note that (17) implies that $\dot{r}_+$ is zero or negative whenever $\mathbf{s} \cdot \dot{\mathbf{s}}$ is zero or negative, respectively. From (6), (7), and (10) we obtain

$$\mathbf{s} \cdot \dot{\mathbf{s}} = \sum_n s_n \dot{s}_n = \sum_\beta s_\beta \dot{s}_\beta = \sum_{\beta\alpha} s_\beta \mathscr{L}_{\beta\alpha} s_\alpha = G \tag{19}$$

In the exceptional case $\mathbf{s} = 0$, since $s_0 = 1$, we have

$$G = \sum_{\beta\alpha} s_\beta \mathscr{L}_{\beta\alpha} s_\alpha = \mathscr{L}_{00} = 0 \tag{20}$$

where the last equality is a consequence of Theorem 1. It follows that in all cases $G = 0$ is necessary and sufficient for $\dot{S} = 0$, while $G < 0$ if and only if $\dot{S} > 0$, and the theorem is proved.

Incidentally, from (17) and (18a) it is easy to see that the isentropic surfaces in the auxiliary space $\mathscr{S}$ are concentric spheres centered on the origin and ranging in size from a point ($S_{\max} = k \ln 2$) to the unit sphere ($S_{\min} = 0$).

To characterize the temporal variations in S that may be induced by the dynamical law (1), we introduce the following thermodynamic nomenclature:

Definition 2. A motion $\rho(t)$ is *reversible* if and only if for all t

$$dS[\rho(t)]/dt = 0 \tag{21}$$

Definition 3. A motion $\rho(t)$ is *thermodynamically irreversible* if and only if for all t

$$dS[\rho(t)]/dt \geqslant 0 \tag{22}$$

and during some time interval,

$$dS[\rho(t)]/dt > 0 \tag{23}$$

Using Theorem 2, we can find the subclass of superoperators satisfying Theorem 1 that describe irreversible motions. To do this, we first use the relations $s_0 = 1$ and $\mathscr{L}_{0\alpha} = 0$ to rewrite (15) as

$$G = \sum_m \mathscr{L}_{m0} s_m + \sum_{mn} s_m \mathscr{L}_{mn} s_n = \sum_m \mathscr{L}_{m0} s_m + \sum_{mn} s_m K_{mn} s_n \tag{24}$$

where the second equality followed from (12).

It follows from Theorem 2 and Definition 3 that the only superoperators $\mathscr{L}$ that generate irreversible motions exclusively are those for which

$$G = \sum_m \mathscr{L}_{m0} s_m + \sum_{mn} s_m K_{mn} s_n \leqslant 0 \tag{25}$$

for every $\mathbf{s}$ such that $\mathbf{s} \cdot \mathbf{s} \leqslant 1$. In particular, (25) must hold for

$$s_m = \epsilon \delta_{mr} \tag{26}$$

where

$$0 < |\epsilon| \leqslant 1 \tag{27}$$

Substituting (26) into (25) and rearranging, we obtain

$$\mathscr{L}_{r0}\epsilon \leqslant -K_{rr}\epsilon^2 \tag{28}$$

If $\epsilon > 0$, (28) implies

$$\mathscr{L}_{r0} \leqslant -K_{rr} \mid \epsilon \mid \tag{29}$$

whereas, if $\epsilon < 0$,

$$\mathscr{L}_{r0} \geqslant K_{rr} \mid \epsilon \mid \tag{30}$$

According to Theorem 1, (K_{mn}) must be negative-semidefinite and thus $K_{rr} \leqslant 0$. Therefore, since (29) and (30) must hold for arbitrarily small $\mid \epsilon \mid$, it follows that

$$\mathscr{L}_{m0} = 0 \tag{31}$$

for generators of thermodynamically irreversible motion. When (29) holds, (23) is automatically satisfied because of the negative-semidefiniteness of (K_{mn}). However, in order for the strict inequality in (25) and thus in (23) to be valid sometimes, it is essential that (K_{mn}) be nonzero. We summarize these results as follows:

Theorem 3. The general form $(\mathscr{L}_{\beta\alpha})$ for a generator of thermodynamically irreversible motion in a two-level quantum system is

$$(\mathscr{L}_{\beta\alpha}) = \left(\begin{array}{c|c} 0 & 0 \quad 0 \quad 0 \\ \hline \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} & (J_{mn}) \end{array}\right) + \left(\begin{array}{c|c} 0 & 0 \quad 0 \quad 0 \\ \hline \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} & (K_{mn}) \end{array}\right) \tag{32}$$

where J_{mn} is antisymmetric and K_{mn} is nonzero, symmetric, and negative-semidefinite.

Similarly, we may argue that the only superoperators $\mathscr{L}$ that generate reversible motions exclusively are those for which the equality holds in (25) for every admissible **s**. This implies not only (31) but also that the matrix (K_{mn}) vanishes; whence we have the following result:

Theorem 4. The general form $(\mathscr{L}_{\beta\alpha})$ for a generator of reversible motion in a two-level quantum system is

$$(\mathscr{L}_{\beta\alpha}) = \left(\begin{array}{c|c} 0 & 0 \quad 0 \quad 0 \\ \hline \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} & (J_{mn}) \end{array}\right) \tag{33}$$

where J_{mn} is antisymmetric.

3. CONSERVATIVE MOTION

In the ordinary Hamiltonian quantum dynamics of an isolated system, the energy operator H is defined as the generator of unitary time translation, so that the fundamental equation of motion has the form

$$\mathscr{L}^H \rho \equiv (1/i)[H, \rho] = \dot{\rho} \tag{34}$$

It is then easy to prove, by combining (13) and (34), that for every t,

$$dS[\rho(t)]/dt = 0 \tag{35}$$

and hence by Definition 2 all Hamiltonian motion is reversible.

When we deal with the non-Hamiltonian motions that are conceivable within the generalized dynamical framework in which $\mathscr{L}$ has the general form (11), a new theoretical definition of energy is needed.

Definition 4. For a two-level quantum system whose dynamical evolution is generated by an $\mathscr{L}$ of the general form (11), the *energy* operator H is given by

$$H = \sqrt{2} \sum_{\alpha} h_\alpha \nu_\alpha \tag{36}$$

with

$$h_m \equiv -\tfrac{1}{4} \sum_{rs} \epsilon_{mrs} \mathscr{L}_{rs} = -\tfrac{1}{4} \sum_{rs} \epsilon_{mrs} J_{rs} \tag{37}$$

where ϵ_{mrs} is the antisymmetric Levi-Civita symbol.

Just as in traditional quantum mechanics, where the evolution operator only determines H to within an additive c-number, Definition 4 does not yield h_0 from $\mathscr{L}$. The complete rationale for the form (37) was discussed in an earlier paper[3] (Part II of this series); there it was established that in the reversible limit of (11), when (K_{mn}) becomes null, we have

$$\mathscr{L}\rho \to \mathscr{L}^H \rho \equiv (1/i)[H, \rho] \tag{38}$$

provided that Definition 4 is used to find H from $\mathscr{L}$.

Having thus given a new definition for energy which reduces to the old one in the case of reversible motion, we may now meaningfully consider the notion of energy conservation.

Definition 5. A motion $\rho(t)$ is *conservative* if and only if for every t

$$(d/dt)\,\mathrm{Tr}[\rho(t)\,H] = 0 \tag{39}$$

The necessary and sufficient conditions for a conservative $(\mathscr{L}_{\beta\alpha})$ are then given by:

Theorem 5. The general form $(\mathscr{L}_{\beta\alpha})$ for a generator of conservative motion in a two-level quantum system with nondegenerate H is

$$(\mathscr{L}_{\beta\alpha}) = 2\left(\begin{array}{c|ccc} 0 & 0 & 0 & 0 \\ \hline 0 & 0 & -h_3 & h_2 \\ 0 & h_3 & 0 & -h_1 \\ 0 & -h_2 & h_1 & 0 \end{array}\right) + \left(\begin{array}{c|ccc} 0 & 0 & 0 & 0 \\ \hline 0 & & & \\ 0 & & (K_{mn}) & \\ 0 & & & \end{array}\right) \tag{40}$$

where K_{mn} is negative-semidefinite, and

$$\sum_m h_m K_{mn} = 0, \qquad n = 1, 2, 3 \tag{41}$$

Proof. By combining (39) with (1), (10), and (36), we obtain

$$\sum_{\beta\alpha} h_\beta \mathscr{L}_{\beta\alpha} s_\alpha = 0 \tag{42}$$

for every s_α satisfying (7).

Since $\mathscr{L}_{0\alpha} = 0$ and $s_0 = 1$, (42) reduces to

$$\sum_m h_m \mathscr{L}_{m0} + \sum_{mn} h_m \mathscr{L}_{mn} s_n = 0 \tag{43}$$

Noting that (43) must be true for all $\mathbf{s}$ such that $\mathbf{s} \cdot \mathbf{s} \leqslant 1$, we conclude that

$$\sum_m h_m \mathscr{L}_{m0} = 0 \tag{44}$$

$$\sum_m h_m \mathscr{L}_{mn} = 0, \qquad n = 1, 2, 3 \tag{45}$$

From (12) and (37) we have

$$J_{mn} = -2 \sum_p \epsilon_{mnp} h_p \tag{46}$$

so (45) becomes

$$\sum_m h_m K_{mn} = \sum_m \sum_p \epsilon_{mnp} h_m h_p\,, \qquad n = 1, 2, 3 \tag{47}$$

But the right side of (46) vanishes identically since ϵ_{mnp} is completely skew-symmetric, and we have

$$\sum_m h_m K_{mn} = 0, \qquad n = 1, 2, 3 \tag{48}$$

Because H is nondegenerate by hypothesis, all h_m cannot vanish; thus (47) can be valid if and only if $\det(K_{mn}) = 0$ which, by Theorem 1, implies that

$$\mathscr{L}_{m0} = 0 \tag{49}$$

Equations (40) and (41) then follow from (11), (37), (44), (45), and (48); and the theorem is proved.

The degenerate H excluded from consideration in Theorem 5 is trivially conserved for all $(\mathscr{L}_{\beta\alpha})$.

4. IRREVERSIBLE CONSERVATIVE MOTION

By comparing with the aid of (37) the general forms (32), (33), and (40) which occur in Theorems 3–5, we conclude that for any two-level quantum system, every conservative motion is either thermodynamically irreversible [(K_{mn}) nonnull] or reversible [(K_{mn}) null]. Conversely, every reversible motion is conservative. There are, however, irreversible motions that are not conservative; and there are of course motions that are neither reversible nor thermodynamically irreversible, and these cannot be conservative. Examples of such exotic possibilities were treated in a previous publication (Part II of this series).[3]

At present we are concerned only with the thermodynamically interesting case of *irreversible conservative motion*. It is now clear that generators $(\mathscr{L}_{\beta\alpha})$ for such motion do indeed exist, their properties being described by Theorem 5 with (K_{mn}) nonnull.

To obtain the general solution of the differential equation (10), viz.

$$\sum_{\alpha} \mathscr{L}_{\beta\alpha} s_\alpha = \dot{s}_\beta \tag{50}$$

when $(\mathscr{L}_{\beta\alpha})$ has the form (40), it is convenient to adopt a matrix representation in which $(\mathscr{L}_{\beta\alpha})$ has as many zero elements as is possible without loss of generality. This may be done by noting that the condition (41) is mathematically equivalent to a vector analysis problem where three vectors $\{\mathbf{K}_n\}$ must be found, each of which is orthogonal to a given vector $\mathbf{h}$, but not all of which are zero. Thus

$$\mathbf{h} \cdot \mathbf{K}_n = 0 \tag{51}$$

where the $\{h_m\}$ and $\{K_{mn}\}$ appearing in (40) and (41) are the components of $\mathbf{h}$ and $\mathbf{K}_n$, respectively. Since (51) is invariant under rotation, we lose no generality by choosing the 3-axis along $\mathbf{h}$ ($h_1 = h_2 = 0$), so that the $\mathbf{K}_n$ must then lie in the 1, 2 plane. Hence

$$K_{3n} = 0 = K_{n3} \tag{52}$$

where the second equality follows from the symmetry of (K_{mn}) and implies that only $\mathbf{K}_1$ and $\mathbf{K}_2$ may be nonzero. A suitably chosen rotation about the 3-axis, which can have no effect on the $\{h_m\}$, will then yield

$$K_{21} = 0 = K_{12} \tag{53}$$

We conclude therefore that without loss of generality we may study irreversible conservative motion by taking

$$(\mathscr{L}_{\beta\alpha}) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & K_1 & -\varDelta & 0 \\ 0 & \varDelta & K_2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{54}$$

where

$$\varDelta \equiv 2h_3\,, \qquad K_n \equiv K_n \leqslant 0 \tag{55}$$

and the representation has been selected such that

$$h_1 = h_2 = 0, \qquad K_{mn} = 0, \quad m \neq n, \qquad K_{33} = 0 \tag{56}$$

From (36), (55), and (56) it is easy to see that $\varDelta$ is the separation between the two eigenvalues of H.

Substituting (54) into (50), we obtain

$$\dot{s}_0 = 0 \tag{57}$$

$$\dot{s}_3 = 0 \tag{58}$$

and

$$\sum_{p,q=1}^{2} L_{pq} s_q = \dot{s}_p \tag{59}$$

where

$$(L_{pq}) \equiv \begin{pmatrix} K_1 & -\varDelta \\ \varDelta & K_2 \end{pmatrix} \tag{60}$$

Equation (57) expresses the constancy of $\mathrm{Tr}\,\rho$; and, since in this representation H has the diagonal form

$$H = \sqrt{2}\,(h_0 \nu_0 + h_3 \nu_3) \tag{61}$$

we have, using (6) and (8), that

$$\mathrm{Tr}(\rho H) = h_0 + h_3 s_3 \tag{62}$$

which implies that (58) expresses conservation of energy. The motion of $\mathbf{s}$ in the auxiliary space $\mathscr{S}$ is therefore confined to a circle and its interior, where the circle is the intersection of the plane $s_3 = s_3(0)$ with the unit sphere, the plane being perpendicular to **h**.

The motion within the circle is described by (59). To solve this differential equation in the standard way, we first note that the eigenvalues of (L_{pq}) are

$$\lambda_{\pm} = \gamma \pm (\delta^2 - \Delta^2)^{1/2} \tag{63}$$

where

$$\gamma \equiv \tfrac{1}{2}(K_1 + K_2), \qquad \delta \equiv \tfrac{1}{2}(K_1 - K_2) \tag{64}$$

Then $(e^{tL})_{pq}$ may be found by solving the two simultaneous equations

$$e^{t\lambda_{\pm}} = \alpha + \lambda_{\pm}\beta \tag{65}$$

and using the solutions α, β in the formula

$$(e^{tL})_{pq} = \alpha\delta_{pq} + \beta L_{pq} \tag{66}$$

Routine calculations now yield as the solution of (58)

$$\begin{bmatrix} s_1(t) \\ s_2(t) \end{bmatrix} = \frac{e^{\gamma t}}{\Omega} \begin{bmatrix} \delta \sin \Omega t + \Omega \cos \Omega t & -\Delta \sin \Omega t \\ \Delta \sin \Omega t & -\delta \sin \Omega t + \Omega \cos \Omega t \end{bmatrix} \begin{bmatrix} s_1(0) \\ s_2(0) \end{bmatrix} \tag{67}$$

where

$$\Omega \equiv (\Delta^2 - \delta^2)^{1/2} \tag{68}$$

If (K_{mn}) is null, then $\gamma = \delta = 0$ and the motion (67) reduces to

$$\begin{bmatrix} s_1(t) \\ s_2(t) \end{bmatrix} = \begin{bmatrix} \cos \Omega t & -\sin \Omega t \\ \sin \Omega t & \cos \Omega t \end{bmatrix} \begin{bmatrix} s_1(0) \\ s_2(0) \end{bmatrix} \tag{69}$$

which is the usual Hamiltonian motion of a two-level system, reversible and periodic with "Larmor frequency"

$$\Omega = \Delta \tag{70}$$

On the other hand, if (K_{mn}) is not null, then $\delta < 0$ and

$$\lim_{t \to \infty} \begin{bmatrix} s_1(t) \\ s_2(t) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{71}$$

Recalling that the insentropic surfaces in $\mathscr{S}$ are concentric spheres about the origin [cf. (17) and (18a)], we see that (58) and (67) describe motions in which *energy is conserved but entropy increases to the maximum value compatible with the fixed energy*, which is of course the classic textbook description of an irreversible process in an isolated thermodynamic system.

5. A SPECIFIC EXAMPLE

In attempting to set up a "physical" illustration of irreversible conservative quantum dynamics, naturally we have no prior intuition for the new parameters δ and γ. From (67) it is evident that γ determined the speed with which the thermodynamic equilibrium is attained, and thus we might dub γ the "serenity" of the system. The quantity δ does not admit of so simple an interpretation. Equation (68) does indicate one obvious meaning for δ—a measure of the departure of Ω from its reversible-case value Δ during irreversible motion. In fact, the formula (68) is reminiscent of the classical frequency of a damped harmonic oscillator, in which Δ would be the natural frequency and δ the adjustment due to damping. Unfortunately, such an analogy is flawed since in the damped oscillator case δ would also be the attenuation factor, whereas here the independent parameter γ plays that role.

To find a thermodynamically interesting interpretation for δ, we consider the time rate of change of entropy in the general motion described by (67). By combining (17) and (18b), we obtain

$$\dot{S} = -\frac{k}{2}\frac{d\,|\,\mathbf{s}\,|}{dt}\ln\frac{r_+}{r_-} = -k(\mathbf{s}\cdot\dot{\mathbf{s}})\ln\frac{1+|\,\mathbf{s}\,|}{1-|\,\mathbf{s}\,|} \tag{72}$$

Using (67) we then find that at $t = 0$,

$$\mathbf{s}\cdot\dot{\mathbf{s}} = \gamma(s_1^2 + s_2^2) + \delta(s_1^2 - s_2^2) \tag{73}$$

Hence $\dot{S}$ may be expressed generally in terms of $\mathbf{s}$ as follows:

$$\dot{S} = -k\left(\ln\frac{1+|\,\mathbf{s}\,|}{1-|\,\mathbf{s}\,|}\right)[\gamma(|\,\mathbf{s}\,|^2 - s_3^2) + \delta(s_1^2 - s_2^2)] \tag{74}$$

Now since values of S are in one-to-one correspondence with values of $|\,\mathbf{s}\,|$ through (17) and (18a), and s_3 is fixed at a value determined in (62) by the thermodynamic parameter

$$U \equiv \mathrm{Tr}(\rho H) \tag{75}$$

it follows from (74) that $\dot{S}$ will depend only on the extensive parameters S and U rather than on finer details of the microstate ρ if and only if $\delta = 0$. It would seem therefore that the case $\delta = 0$ would be of paramount interest in irreversible thermodynamics. The illustration to be discussed next falls in this category.

It is apparent from (69) that in reversible conservative motion generated by an $\mathscr{L}^H$ of the ordinary commutator form (2), the end point of $\mathbf{s}$ moves uniformly on a circle; in fact the equation of motion may be written as

$$\dot{\mathbf{s}} = 2\mathbf{h}\times\mathbf{s} \tag{76}$$

To describe an irreversible thermodynamic process, we need a motion in which the end point of **s** moves inward toward the axis where the entropy is a maximum for the given energy. This would involve an **s** velocity in the direction $\mathbf{h} \times (\mathbf{h} \times \mathbf{s})$, and one may therefore speculate that a term in $\mathscr{L}\rho$ of the form $-[H, [H, \rho]]$ would produce the desired motion. Motivated by this clue, we now propose to consider the following, more elaborate equation of motion:

$$\dot{\rho} = (1/\tau)(e^{-i\tau F}\rho e^{i\tau F} - \rho) \tag{77}$$

where τ is a parameter, and F is a traceless operator related to H but as yet not defined explicitly. When $\tau \to 0$, the exponentials converge rapidly, the dominant term being $-i[F, \rho]$ and the next term $-\frac{1}{2}\tau[F, [F, \rho]]$. We shall retain the complete series and make no assumption regarding the magnitude of τ.

To derive the matrix $(\mathscr{L}_{\beta\alpha})$ associated with (77), it is convenient to introduce the symbol

$$\boldsymbol{\theta} = \tau \mathbf{f} \tag{78}$$

where $\mathbf{f}$ is related to F by

$$F = \sqrt{2}\,(\mathbf{f} \cdot \boldsymbol{\nu}) = \mathbf{f} \cdot \boldsymbol{\sigma} \tag{79}$$

Then from the identity

$$(\boldsymbol{\theta} \cdot \boldsymbol{\sigma})^2 = |\boldsymbol{\theta}|^2\, 1 \tag{80}$$

it is easy to prove that

$$\exp(i\tau F) = \exp(i\boldsymbol{\theta} \cdot \boldsymbol{\sigma}) = 1 \cos\theta + i(\boldsymbol{\theta} \cdot \boldsymbol{\sigma}) \sin\theta/\theta \tag{81}$$

where $\theta \equiv |\boldsymbol{\theta}|$.

Substituting (6) and (81) into (77), we obtain

$$(\dot{\mathbf{s}} \cdot \boldsymbol{\sigma}) = \frac{1}{\tau}\Big\{(\mathbf{s} \cdot \boldsymbol{\sigma})(\cos^2\theta - 1) + i[\mathbf{s} \cdot \boldsymbol{\sigma}, \boldsymbol{\theta} \cdot \boldsymbol{\sigma}]\frac{\sin\theta\cos\theta}{\theta} + (\boldsymbol{\theta} \cdot \boldsymbol{\sigma})(\mathbf{s} \cdot \boldsymbol{\sigma})(\boldsymbol{\theta} \cdot \boldsymbol{\sigma})\frac{\sin^2\theta}{\theta^2}\Big\} \tag{82}$$

Using the standard formulas,

$$[\mathbf{a} \cdot \boldsymbol{\sigma}, \mathbf{b} \cdot \boldsymbol{\sigma}] = 2i(\mathbf{a} \times \mathbf{b}) \cdot \boldsymbol{\sigma} \tag{83}$$

and

$$(\mathbf{a} \cdot \boldsymbol{\sigma})(\mathbf{b} \cdot \boldsymbol{\sigma}) = \mathbf{a} \cdot \mathbf{b} + i(\mathbf{a} \times \mathbf{b}) \cdot \boldsymbol{\sigma} \tag{84}$$

we may convert (82) to the form

$$\tau\dot{s}_m = -(2/\theta^2)(\sin^2\theta)\Big(\theta^2 s_m - \sum_j s_j\theta_j\theta_m\Big) - (1/\theta)(\sin 2\theta)\sum_{kj} \theta_k s_j \epsilon_{jkm} \tag{85}$$

which is to be compared to (50) in order to find the $(\mathscr{L}_{mn})$ elements of the matrix $(\mathscr{L}_{\beta\alpha})$ associated with (77). It is obvious from the algebraic form of (77) that the $\mathscr{L}_{0\alpha}$ and $\mathscr{L}_{\alpha 0}$ vanish. Denoting the direction cosine of $\boldsymbol{\theta}$ (or $\mathbf{f}$) by

$$\xi \equiv \theta_1/\theta, \qquad \eta \equiv \theta_2/\theta, \qquad \zeta \equiv \theta_3/\theta \tag{86}$$

we have

$$\tau(\mathscr{L}_{\beta\alpha}) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 2(\sin^2\theta)(\xi^2 - 1) & 2\xi\eta\sin^2\theta - \zeta\sin 2\theta & 2\zeta\xi\sin^2\theta + \eta\sin 2\theta \\ 0 & 2\xi\eta\sin^2\theta + \zeta\sin 2\theta & 2(\sin^2\theta)(\eta^2 - 1) & 2\zeta\eta\sin^2\theta - \xi\sin 2\theta \\ 0 & 2\zeta\xi\sin^2\theta - \eta\sin 2\theta & 2\zeta\eta\sin^2\theta + \xi\sin 2\theta & 2(\sin^2\theta)(\zeta^2 - 1) \end{bmatrix} \tag{87}$$

If the representation is chosen to diagonalize F, we have $\zeta = 1$ and $\xi = \eta = 0$, and $\mathscr{L}_{\beta\alpha}$ becomes

$$\tau(\mathscr{L}_{\beta\alpha}) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -2\sin^2\theta & -\sin 2\theta & 0 \\ 0 & +\sin 2\theta & -2\sin^2\theta & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{88}$$

This is clearly an example of (54) with $K_1 = K_2$. Hence

$$\gamma = -(2/\tau)\sin^2\theta, \qquad \delta = 0, \qquad \Omega = \Delta = \sin 2\theta \tag{89}$$

Substituting (89) into (67), we have

$$\begin{aligned} s_1(t) &= \{\exp[-2(t/\tau)\sin^2\theta]\}\{\cos[(t/\tau)\sin 2\theta]\, s_1(0) \\ &\qquad - \sin[(t/\tau)\sin 2\theta]\, s_2(0)\} \\ s_2(t) &= \{\exp[-2(t/\tau)\sin^2\theta]\}\{\cos[(t/\tau)\sin 2\theta]\, s_2(0) \\ &\qquad + \sin[(t/\tau)\sin 2\theta]\, s_1(0)\} \end{aligned} \tag{90}$$

which describes a spiral motion that can be more easily visualized by noting that

$$s_1^2(t) + s_2^2(t) = e^{-2\gamma t}(|\,\mathbf{s}_0\,|^2 - s_3^2) \tag{91}$$

where $\mathbf{s}_0$ is the initial value of $\mathbf{s}$ and s_3 is constant.

The ultimately irreversible character of this motion becomes manifest when we note that the evolution matrix [cf. Part I,[1] Eq. (17)]

$$(T_{\beta\alpha}(t)) \equiv (e^{t\mathscr{L}_{\beta\alpha}}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & e^{\gamma t}\cos\Omega t & -e^{\gamma t}\sin\Omega t & 0 \\ 0 & e^{\gamma t}\sin\Omega t & e^{\gamma t}\cos\Omega t & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{92}$$

evidently approaches as $t \to \infty$ a matrix with two zero eigenvalues, hence a zero determinant and no inverse. The process described by $T(t)$ is therefore literally "irreversible" in the sense that once the destination (equilibrium) is reached, retrodiction becomes impossible.

Since F is diagonal in the chosen representation, we have

$$F = f\nu_3 \tag{93}$$

and the conserved energy associated with (88) is given by

$$H = (1/2\tau)[\sin(2\tau f)]\,\nu_3 = [1/(2\sqrt{2})\,\tau]\sin[(2\sqrt{2})\,\tau F] \tag{94}$$

In the limit when $\tau \to 0$, F and H become identical. Both are conserved in general. In terms of the parameters determing $\mathscr{L}$, we find that

$$\tau = -\gamma/[2(h_3^2 + \tfrac{1}{4}\gamma^2)] \tag{95}$$

Thus only in the reversible limit $\gamma \to 0$ does $\tau \to 0$.

If we imagine a spinning electron in a magnetic field of about 1G, the energy coefficient h_3 would be around 10^{-20} erg. Since such systems in isolation are not observed to evolve spontaneously toward states of higher entropy, we see that even if the hypothetical $\mathscr{L}$ of (88) were correct, $|\gamma|$ must be quite small—less, say, than 10^{-6} sec to guarantee that the spin would seem to execute ordinary Hamiltonian motion for months. Using these values in (95), and restoring Planck's constant, we see that it would be necessary to postulate a characteristic time τ of about 10^{-19} sec in this case. By contrast, a similar theory for macroscopic systems, which do as a matter of common experience exhibit thermodynamically irreversible behavior, would require a much larger τ. It should perhaps be emphasized that such a τ would not be a "relaxation time" but rather in the nature of an "interaction time" between the parts of the structured system. We believe that such a characteristic time exists for every isolated system and that it should appear naturally in a suitably generalized quantum mechanical description of the system. The present analysis of the two-level system, though not of direct practical utility, has nevertheless demonstrated that adoption of a dynamical postulate of the simple form (1) is a theoretically fertile hypothesis, for it permits the logical deduction of thermodynamically irreversible motion within a distinctly mechanical context.

NOTE ADDED IN PROOF

A referee has kindly called our attention to an interesting and related article on irreversibility [G. Ananthakrishna, E. C. G. Sudarshan, and V. Gorini, *Rep. Math. Phys.* **8**, 25 (1975)] and to some very recent papers that also appear to have some points of similarity with ours but which were published after our manuscript was communicated [G. Lindblad, *Commun. Math. Phys.* **48**, 119 (1976); V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, *J. Math. Phys.* **17**, 821 (1976)].

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