PHYSICAL REVIEW A, VOLUME 61, 052715

Quantum approach to rotation-state relaxation theory

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(Received 2 August 1999; published 14 April 2000)

The principles of the quantum theory of open systems are used to calculate the collisional relaxation parameters of the ground rotational transition for a dipole molecule. The conditions for a microwave-field saturation of the rotational transition are specified taking into account degeneracy of the excited state. A simple quantum model is used to illustrate the idea of rigorous substantiation of the second law of thermodynamics.

PACS number(s): 34.10.+x, 05.30.−d, 05.70.Ln, 42.50.Ct

I. INTRODUCTION

One major achievement over the last two decades is the awareness that the physical kinetics is part of the general theory of open systems [1–4]. From this stand point the irreversibility of relaxation processes is essentially of a quantum nature and is conditioned by interactions of the object in question with the external subsystems that are not measured after interaction. This approach was applied in Ref. [5] to the quantum models of interaction with exact solutions to obtain relations between the longitudinal and cross-relaxation times for a system with two energy levels.

Following the long established tradition nearly all principle calculations in atomic-molecular spectroscopy are done on the basis of the semiclassical Bloch equation (see Ref. [6]). This equation contains two empirical parameters: characteristic times of the longitudinal T_1 and cross T_2 relaxations. In terms of the formalism of density matrix, they correspond, respectively, to relaxation to equilibrium values of diagonal and nondiagonal matrix elements. With numerical values of T_1 and T_2 chosen from available experimental data, the Bloch equation is frequently employed for description of quantum transitions between degenerated energy levels, which is clearly not quite correct.

The use of a consistent quantum approach enables one to minimize the number of empirical parameters of the theory and calculate the T_2/T_1 ratio within the framework of the adopted physical model of relaxation. Particularly, for a nondegenerate quantum transition in the asymptotic limit of weak relaxation perturbations, one obtains $T_2/T_1=2$ [5].

The degeneracy of an excited state is a difficult problem in the relaxation theory of molecular rotational spectra. The available standard methods [6,7] either fail in this case or require application of arbitrary empirical assumptions. We propose a possible solution to this problem employing rigorous methods of the quantum theory of open systems that allow us to carry out the entire computational procedure without addressing the empirical phenomenology.

II. QUANTUM KINETIC EQUATION

Let us describe derivation of the kinetic equation in terms of the theory of open systems [4]. Consider an external impact on a quantum system (an object) with Hamiltonian $\hat{H}_s$. The external medium in our consideration is represented as a set of identical physical subsystems (a homogeneous flow) that alternately interact with the object. We are interested in the evolution of the object state under the action of external impacts.

We designate the Hamiltonian of a single external subsystem (element of the flow) through $\hat{H}_t$, and the system-object interaction by collision through $\hat{H}_{\rm int}$. We also introduce the energy conservation condition: $[H_{\rm int},\ H_s+H_t]=0$. In a particular case of relaxation when the object interacts with thermal radiation, the element of the flow acts as a field oscillator. A flow of arbitrary physical origin possessing equilibrium statistical properties is also referred to as a thermostat.

By $\hat{\rho}_0$ and $\hat{\sigma}_0$ we define the density operators of initial states for the object and the element of the flow, respectively, and suppose them to be statistically independent. We write the density matrix of the object after interaction in an ordinary form (see Ref. [4]):

$$\langle n|\rho_1|m\rangle=\sum_{\nu}\ \langle n,\nu|U\rho_0\sigma U^{+}|m,\nu\rangle. \tag{1}$$

Here and elsewhere through the paper, the eigenstates of the object are marked by Latin and those of the element of the flow by Greek letters. The unitary evolution operator $\hat{U}$ operates in the expanded Gilbert space including the states of both interacting subsystems (the direct product space, see Ref. [8]). If we describe the subsystems operators in the energy representation and the time evolution of states in collision in the interaction representation, we shall have to assume that

$$\hat{U}=\exp\{-i\hat{H}_{\rm int}t_c\}, \tag{2}$$

where t_c is the interaction time (in the system with $\hbar=1$). In our analysis of the models we shall sometimes specify the evolution operator $\hat{U}$ directly, omitting the corresponding $\hat{H}_{\rm int}$ in the explicit form.

1050-2947/2000/61(5)/052715(7)/$15.00

We use the subscript j to indicate successive interactions of the object with the elements of the flow, and the notation $\hat{\rho}_j$ for the density operator of the object state after the jth impact. Assuming the initial mixed states of all of the elements of the flow to be identical and mutually independent, from Eq. (1) we obtain

$$\langle n|\rho_{j+1}|m\rangle=\sum_{p,q}(n,m|p,q)\langle p|\rho_j|q\rangle. \tag{3}$$

Here,

$$(n,m|p,q)=\sum_{\mu,\nu,\lambda}\langle n,\mu|U|p,\nu\rangle\langle\nu|\sigma|\lambda\rangle\langle q,\lambda|U^{\dagger}|m,\mu\rangle. \tag{4}$$

Expression (3) is a quantum kinetic equation (a generalized Markov chain) in which the transition matrix $(n,m|p,q)$ does not necessarily have the probability meaning (see Ref. [9]).

For spectroscopic problems of collision-induced relaxation, this equation is used as follows. We identify one molecule as the object and describe its excitation by a resonance electromagnetic field. The other molecules in the gas volume under consideration are treated as an external flow responsible for relaxation of the object's excitations. The states of the molecules in the flow are assumed to be equilibrium ones (their weak excitation by the field is neglected). It can be easily seen that this is the only approximation that allows for the description of spectral excitation of a molecule using the linear theory.

To pass over to the differential form of the kinetic equation we need to make use of the ''course-grain'' averaging idea [2]. We suppose that over some time dt a molecule is exposed to multiple collisions, and denote the characteristic time between them by τ. Then, Eq. (3) can be rewritten as

$$\frac{d}{dt}\langle n|\rho|m\rangle=\tau^{-1}\left(\sum_{p,q}(n,m|p,q)\langle p|\rho|q\rangle-\langle n|\rho|m\rangle\right). \tag{5}$$

To make this equation complete, one has to account for the field-induced excitation. We shall define this excitation as the time-dependent operator $\hat{V}(t)$ that affects only the states of the object. The latter restriction is not imperative: actually, any nonequilibrium action can be described in terms of the open systems theory similarly to the relaxation thermal collisions (see Ref. [3]). However, the classical-field approximation proves to be sufficient for most problems of the atomic-molecular spectroscopy. With this in mind we finally write

$$\frac{d}{dt}\langle n|\rho|m\rangle=i\langle n|[\rho,V(t)]|m\rangle+\tau^{-1}\left(\sum_{p,q}(n,m|p,q)\langle p|\rho|q\rangle-\langle n|\rho|m\rangle\right). \tag{6}$$

III. ROTATION STATES

Let us model the principal mechanisms of relaxation by the collision of identical dipole symmetric molecules. Then, we shall study excitation of a molecule rotation state transition by a resonance electric field and discuss some peculiarities in the behavior of the absorption line for various conditions.

We designate by $\hat{\vec{L}}$ and $\hat{\vec{\Lambda}}$ the vector-operators of the rotational moments for the molecule object and molecule-element of the flow, respectively. The hamiltonians of the molecular rotation, omitting the additive terms that have no significance at rather low temperatures (see Ref. [10]), are written in the form:

$$\hat{H}_s=(2I)^{-1}\hat{L}^2;\quad \hat{H}_t=(2I)^{-1}\hat{\Lambda}^2, \tag{7}$$

where I is the moment of inertia. The energy levels of the molecules, $(2I)^{-1}\times L(L+1)$ and $(2I)^{-1}\Lambda(\Lambda+1)$, are degenerated $(2L+1)$- or $(2\Lambda+1)$-fold, where L $(\Lambda)=0,1,2,\ldots$. In our relaxation model we investigate only the two lower levels $L(\Lambda)=0,1$ and the transitions between them. It will be shown further that such a simplified approach is quite sufficient to describe inelastic relaxation for the above quantum transitions, but needs to be refined for the description of elastic collisions.

We now impose the conditions of conservation for the total energy in collision and for the total moment vector $\hat{\vec{L}}+\hat{\vec{\Lambda}}$. This means that the unitary operator of the collision evolution $\hat{U}$ must satisfy the conditions

$$[U,H_s+H_t]=0;\quad [U,\vec{L}+\vec{\Lambda}]=0. \tag{8}$$

In all other respects we follow the maximum simplicity criterion in deriving the explicit form of operator $\hat{U}$.

Let us label the states of a complete system of two dipole molecules with four quantum numbers $|L,m;\ \Lambda,\mu\rangle$. The semicolon is used to separate one-molecule states. Here, L and Λ take on the values 0,1 and number the energy levels; the z projections of the moments m and μ take on the values $0,\pm 1$ for $L(\Lambda)=1$, and 0 for $L(\Lambda)=0$. So, the expanded Gilbert space for description of molecular collision has 16 coordinates.

Next, we collect the multiplet distribution of the basis vectors $|L,m;\ \Lambda,\mu\rangle$; the states of each multiplet contain equal sums of the quantum numbers $L(L+1)+\Lambda(\Lambda+1)$ and of the quantities $m+\mu$ that remain unchanged in collision according to the conditions (8). For further discussion, it should be specified straightforward in which multiplets the transformation is induced by the elastic collisions and in which of them due to inelastic collisions.

(1) Singlets:

$$|0,0;0,0\rangle,|1,1;1,1\rangle,|1,-1;1,-1\rangle.$$

(2) Doublets:

$$\left.\begin{array}{l}|1,1;1,0\rangle,|1,0;1,1\rangle\\|1,-1;1,0\rangle,|1,0;1,-1\rangle\end{array}\right\}\text{ elastic transitions,}$$

$$\left.\begin{array}{l}|1,0;0,0\rangle,|0,0;1,0\rangle\\|1,1;0,0\rangle,|0,0;1,1\rangle\\|1,-1;0,0\rangle,|0,0;1,-1\rangle\end{array}\right\}\text{ inelastic transitions.}$$

(3) Triplet:

$$|1,1;1,-1\rangle,|1,0;1,0\rangle,|1,-1;1,1\rangle.$$

The transitions inside the only triplet are caused by elastic collisions. As follows from the above classification, the elastic processes here are understood as quantum transitions that feature no energy exchange between the molecules.

In order to satisfy the conditions (8) for the conservation of the additive invariants, it would be sufficient to take the transformation matrix

$$\langle L,m;\Lambda,\mu|U|L,n;\Lambda,\nu\rangle$$

in the block-diagonal form in which each block operates only in the subspace of the corresponding multiplet. In this case, the unitary blocks will effect transformation in the subspaces where matrix representations of the additive integrals of motion, $\hat{L}^2+\hat{\Lambda}^2$ and $\hat{L}_z+\hat{\Lambda}_z$, are multiples of the unit matrix, which will ensure fulfillment of Eq. (8).

Then, taking into account that the quantum phases cannot be observed, we can choose for the doublets the transformation with real parameters a and b. Note that parameter b which stands for the ''transformation depth'' is not necessarily equal for the elastic and inelastic processes. Further we will discuss this issue in greater detail, and meanwhile assume that all of the above doublets have identical block transformations

$$\langle L,m;\Lambda,\mu|U|L',n;\Lambda',\nu\rangle=\begin{pmatrix}a & b\\-b & a\end{pmatrix};\quad a^2+b^2=1. \tag{9}$$

It can be checked that the numbering order of the basis vectors inside the doublets does not affect the observable results.

Again, following the criterion of maximum simplicity in describing transitions inside the triplet, we choose the matrix of a three-dimensional representation of group SU(2) (see Ref. [8]) with the same parameters a and b as for the two-dimensional case

$$\langle 1,m;1,\mu|U|1,n;1,\nu\rangle=\begin{pmatrix}a^2 & ab\sqrt{2} & b^2\\-ab\sqrt{2} & a^2-b^2 & ab\sqrt{2}\\b^2 & -ab\sqrt{2} & a^2\end{pmatrix}, \tag{10}$$

where the triplet states have the same numbering order as above.

Now that we have completed modeling collision we pass over to calculations of the kinetic coefficients. As before, let us start with the relaxation of the off-diagonal element $\langle 0,0|\rho|1,0\rangle$ of the ground transition for a ''working'' molecule. For this we need to specify notation in the description of the equilibrium state of its ''collision partner.''

By σ_u we denote any equal eigenvalue of the density matrix related to the upper energy states

$$\sigma_u=\sigma_{1,1}=\sigma_{1,0}=\sigma_{1,-1}=(3+\exp\{\beta\})^{-1}, \tag{11}$$

where $\beta=(I\theta)^{-1}$ and the parameter I^{-1}, which is inverse to the inertia moment, in our system of units is exactly the energy difference between the states $L=1$ and $L=0$. In a similar way we write for the lower state $|0,0\rangle$

$$\sigma_l=\sigma_{0,0}=(1+3\exp\{-\beta\})^{-1}. \tag{12}$$

Calculation of the cross-relaxation coefficient by the formula (4) yields

$$\begin{aligned}&\frac{n}{(0,0:}\ \frac{m}{1,0|}\ \frac{p}{0,0;}\ \frac{q}{1,0)}\\&\quad=\sum_{\Lambda=0,1}\sum_{\nu=-\Lambda}^{\Lambda}\langle 0,0;\Lambda,\nu|U|0,0;\Lambda,\nu\rangle\sigma_{\Lambda,\nu}\\&\qquad\times\langle 1,0;\Lambda,\nu|U^{+}|1,0;\Lambda,\nu\rangle\\&\quad\simeq 1-b^2(1/2+3\sigma_u).\end{aligned} \tag{13}$$

The last expression in Eq. (13) is written to the accuracy of the term b^2 inclusive. By substituting this result into Eq. (5) we obtain the off-diagonal component of the relaxation equation for the density matrix

$$\frac{d}{dt}\langle 0,0|\rho|1,0\rangle=(-b^2/\tau)(1/2+f(\theta))\langle 0,0|\rho|1,0\rangle, \tag{14}$$

where $f(\theta)=3\sigma_u$.

Let us now calculate the ''longitudinal'' coefficients of relaxation. We bear in mind (see Ref. [4]) that the transition coefficients for the diagonal elements of the density matrix for the object exposed to a stationary homogeneous flow are, essentially, the transition probabilities of the Markov chain. Therefore, we write

$$P(L,m|L',n)=(L,m;L,m|L',n;L',n). \tag{15}$$

Calculations by analogy with the previous ones, i.e., to an accuracy of the terms $\sim b^2$ inclusive, yield

$$P(1,0|0,0)=P(1,1|0,0)=P(1,-1|0,0)=b^2\sigma_u, \tag{16}$$

$$P(0,0|1,0)=P(0,0|1,1)=P(0,0|1,-1)=b^2\sigma_l, \tag{17}$$

$$\begin{aligned}P(1,1|1,0)&=P(1,0|1,1)=P(1,-1|1,0)=P(1,0|1,-1)\\&=3b^2\sigma_u=b^2f(\theta),\end{aligned} \tag{18}$$

$$P(1,0|1,0)=1-b^2(1+f(\theta)), \tag{19}$$

$$P(0,0|0,0)=1-b^2f(\theta). \tag{20}$$

The transition probabilities satisfy the normalization conditions

$$\sum_{L,m} P(L,m|L',n)=1 \tag{21}$$

for all values of L' and n.

Let us derive the kinetic equations for calculations of the line shape following excitation of transition $0 \Leftrightarrow 1$ by an alternating near-resonance electric field that, without loss of generality, is supposed to be polarized along the z axis. Omitting extensive description of the excitation structure we just note (see Ref. [11]) that its resonance terms can be represented by a two-row matrix in the subspace $(|0,0\rangle, |1,0\rangle)$ with a nonzero element

$$\langle 0,0|V(t)|1,0\rangle=(V/2)\exp\{i\varepsilon t\} \tag{22}$$

and with the element Hermitian conjugate to it. Here, $\varepsilon=\omega-\omega_0$, ω is the frequency of the exciting field and $\omega_0=I^{-1}$ is the frequency of the quantum transition. The energy amplitude of the disturbance V is proportional to the field amplitude and to the matrix element of the dipole moment.

This disturbance does not change the equilibrium zero value of the relative population difference of the upper boundary states $|1,\pm 1\rangle$. With this in mind, we put in the variables

$$S(t)=\langle 1,1|\rho|1,1\rangle+\langle 1,-1|\rho|1,-1\rangle, \tag{23}$$

$$s(t)=\langle 0,0|\rho|0,0\rangle+3\langle 1,0|\rho|1,0\rangle. \tag{24}$$

Using the normalization condition

$$\sum_{L=0,1}\sum_{m=-L}^{L}\langle L,m|\rho|L,m\rangle=1, \tag{25}$$

one can easily express the quantity $r=\langle 0,0|\rho|0,0\rangle-\langle 1,0|\rho|1,0\rangle$ through S and s:

$$r=2(1-S)-s. \tag{26}$$

Then, by supplementing Eq. (14) and introducing $\tilde{\rho}=\langle 0,0|\rho|1,0\rangle\exp(-i\varepsilon t)$, we find employing Eq. (6) the equation

$$\frac{d\tilde{\rho}}{dt}=-(i\varepsilon+T_2^{-1})\tilde{\rho}+iV(1-S-s/2), \tag{27}$$

where $T_2^{-1}=(b^2/\tau)[1/2+f(\theta)]$. In a similar way, the substitution of the coefficients (16)–(20) and the excitation formula (22) into Eq. (6) yields

$$\frac{ds}{dt}=(-1/T_1)(s-1)+2V\,\mathrm{Im}\,\tilde{\rho}, \tag{28}$$

$$\frac{dS}{dt}=(-1/T_3)(S-2\sigma_u s), \tag{29}$$

where $T_1^{-1}=(b^2/\tau)[1+2f(\theta)]=2T_2^{-1}, T_3^{-1}=b^2/\tau$. Note that the polarization-to-energy relaxation times ratio $T_2/T_1=2$ is typical of the classical system of charged particles too, given weak viscous friction.

We now analyze the stationary solution to the system (27)–(29). Let us calculate the value of $\mathrm{Im}\,\tilde{\rho}$ because it is the dimensionless characteristic of the rate of field energy absorption by a molecule at $T_1^{-1}\neq 0$. Supposing all the time derivatives to be zero, we perform some simple algebraic calculations to obtain

$$\mathrm{Im}\,\tilde{\rho}=\frac{VT_2Y(\varepsilon)(1/2-2\sigma_u)}{1+2V^2T_1T_2Y(\varepsilon)(1/2+2\sigma_u)}, \tag{30}$$

where $Y(\varepsilon)=(1+\varepsilon^2T_2^2)^{-1}$. For weak saturation $2V^2T_1T_2<1$, the non-Lorentz addition to the standard form of the absorption line is defined as

$$(\Delta\,\mathrm{Im}\,\tilde{\rho})_{\text{non-Lor}}=2Y^2(\varepsilon)V^3T_2^2T_1(4\sigma_u^2-1/4). \tag{31}$$

This formula describes the smoothing of the line peak due to saturation, that accounts (within our model) for the elastic-inelastic relaxation between the sublevels of the degenerate excited state.

We have already mentioned that the relaxation parameters in elastic and inelastic processes are different in general. In order to understand how this is reflected in the equations we consider the ideal situation when only elastic transformations occur by collision. Note that we do not claim direct applicability of our calculations but attempt at providing a deeper insight into the mathematical structure of the theory.

Let all the three ‘‘inelastic’’ doublets (see the multiplet classification given above) break down into singlets, and the remaining two doublets and the triplet undergo conventional transformations with parameters a and b. Then, instead of the relation (13) we obtain

$$(0,0;1,0|0,0;1,0)=1-3b^2\sigma_u. \tag{32}$$

Further analysis of the relaxation coefficients and comparison of the results with Eqs. (27)–(29) lead to the expressions

$$T_2^{-1}=(b^2/\tau)f(\theta), \quad T_1^{-1}=0. \tag{33}$$

Although there is no absorption of the field energy in this case and the spectral line cannot therefore be observed under stationary conditions, the above example is of certain fundamental importance. It shows that, given degeneracy of the excited level, the cross relaxation can occur due to elastic processes irrespective of the longitudinal relaxation. Hence, there is no requirement that the relation $T_2=2T_1$ be fulfilled in the general case, even in the weak-collision approximation.

Physically, elastic processes may take place by collisions of a ‘‘working’’ molecule with other kinds of particles (buffer particles) that have no resonance transition at frequency ω_0. This also happens when the molecules collide with their ''own'' dipole molecules at higher excited levels. In this case, they are likely to exchange the moment projections but there is no energy exchange.

It follows from the above that a consistent analysis of the elastic relaxation must take account of all of the rotation states rather than of just two lower levels, even for a homogeneous gas. Therefore, some of the formulas derived here could be applied only to the case of very low temperatures, when thermal excitation of higher levels may be neglected. The translational degrees of freedom of the thermostat molecules will also contribute to the relaxation, but this mechanism is beyond the scope of the present paper.

All the difficulties involved in constructing the general theory are solely computational. Here, we have attempted to analyze only the cases allowing for easy-to-derive analytical solutions.

IV. INCREASE OF ENTROPY

The considered relaxation processes are a typical example of thermodynamic irreversibility described at the quantum-microscopic level. Therefore, in their investigation it is impossible to avoid basic issues involved with quantum-theoretical substantiation of the second law of thermodynamics.

Mathematical foundations of the consistent quantum approach to solution of thermodynamic problems were laid back in the prewar works by Klein [12] and Elsasser [13]. The logical origin for the increase of the sum of quantum entropies from the zero initial value due to two particles collision is revealed in the analysis of the famous Einstein-Podolsky-Rosen paradox [14] and is due to the appearance of specifically quantum nonlocal states.

We believe that further discussion of these problems by physicists of the German school could lead to a complete clarification of the situation already in the 1940's. But history reasoned differently, and the problem was considered again only at the end of the century [4].

A study of simple models also helps clarify the old problem on the overflow of heat from hot to cold. Consider, following the same scheme, a single interaction of a two-level atom with a thermal oscillator. Naturally, this process can be traced on other models, too, for example, by describing molecular collisions. Yet, since we discuss so general a question, we would rather choose a model of the interaction between subsystems of different physical nature.

Let us take a two-level object with energies E_1, E_2 and describe its interaction with a quantum oscillator of frequency $\omega = E_2 - E_1$ (in our system of units $\hbar = 1$, and the frequency has the dimension of energy). We introduce the oscillator's Hamiltonian $\hat{H}_t$ and its eigenvectors $|\nu\rangle$

$$\hat{H}_t|\nu\rangle = \omega(\mathbf{a}^\dagger \mathbf{a} + 1/2)|\nu\rangle = \omega(\nu + 1/2)|\nu\rangle \tag{34}$$

in the usual fashion. Here, $\mathbf{a}$ is the photon annihilation operator. Let us write the matrix of the dipole interaction between the object and the oscillator. In the energy representation the nonzero elements are

$$\langle 1,\nu|H_{\text{int}}|2,\nu-1\rangle = \gamma\sqrt{\nu} \tag{35}$$

and those Hermitian conjugate to them. The values $n = 1,2$ here correspond to the object energies E_1, E_2, and the constant γ is determined by the off-diagonal element of the dipole moment.

The problem of the dipole interaction of a two-level system with quantum oscillator permits an exact solution. The nonzero elements of the evolution unitary matrix have the form

$$\begin{pmatrix} \langle 1,\nu|U|1,\nu\rangle & \langle 1,\nu|U|2,\nu-1\rangle \\ \langle 2,\nu|U|1,\nu+1\rangle & \langle 2,\nu|U|2,\nu\rangle \end{pmatrix} = \begin{pmatrix} \cos\alpha\sqrt{\nu} & i\sin\alpha\sqrt{\nu} \\ i\sin\alpha\sqrt{\nu+1} & \cos\alpha\sqrt{\nu+1} \end{pmatrix}, \tag{36}$$

where $\alpha = \gamma t_c$.

Let the initial mixed states of the atom and oscillator be statistically independent and described by the Gibbs density operators with different temperatures θ_s and θ_t:

$$\langle n|p|m\rangle = (1+\exp\{-\beta_s\})^{-1}\exp\{-E_n/\theta_s\}\delta_{nm}, \tag{37}$$

$$\langle \nu|\sigma|\mu\rangle = (1-\exp\{-\beta_t\})\exp\{-\beta_t\nu\}\delta_{\mu,\nu}, \tag{38}$$

where, again, $n = 1,2$; $E_2 - E_1 = \omega$, and $\beta_{s,t} = \omega/\theta_{s,t}$. Without loss of generality, here and elsewhere we suppose $E_1 = 0$.

Now we apply the transform (36) to these states and calculate the energy transfer by collision in the limit $\alpha^2 \ll 1$:

$$\Delta\langle H_s\rangle = -\Delta\langle H_t\rangle = \sum_{n=1,2} E_n \Delta\rho_n = (1/2)\alpha^2\omega[\tanh(\beta_s/2)\coth(\beta_t/2) - 1]. \tag{39}$$

In a similar way we find a change in the entropies

$$\Delta S_s = \Delta\left(-\sum_n \rho_n \ln \rho_n\right) = S_s' - S_s = \alpha^2\beta_s[(\exp\{\beta_t\}-1)^{-1}\tanh(\beta_s/2) - (\exp\{\beta_s\}+1)^{-1}], \tag{40}$$

$$\Delta S_t = \Delta\left(-\sum_\nu \sigma_\nu \ln \sigma_\nu\right) = S_t' - S_t = \alpha^2\beta_t[(\exp\{\beta_s\}+1)^{-1} - (\exp\{\beta_t\}-1)^{-1}\tanh(\beta_s/2)], \tag{41}$$

using the definition $\Delta S = \Delta S_s' + \Delta S_t'$. Note that the sum of the resulting entropies of the subsystems $S_s' + S_t'$ is no longer equal to the quantum entropy of the complete system, which does not change because the system is closed. The fact is that in collision the subsystems lose their reciprocal statistical independence. Comparison of Eqs. (40) and (41) with Eq. (39) yields

$$\Delta S = \Delta \langle H_s \rangle \left(\frac{1}{\theta_s} - \frac{1}{\theta_t} \right). \tag{42}$$

It is of principle importance that ΔS is always non-negative. This is why a spontaneous energy transfer is always bound towards a colder object irrespective of the physical nature of interacting bodies.

The inequality $\Delta S \geqslant 0$ is easily tested in our model too, but here it has a much more general meaning. It can have a rigorous proof for subsystems of arbitrary physical origin in any initial states, the only condition being that these subsystems be statistically independent prior to interaction [4].

We present this proof here. We designate, as before, the density operators of independent initial states of the subsystem of interest (I) and of the external object (II) through $\hat{\rho}$ and $\hat{\sigma}$, respectively. We introduce the density operator of the complete system after the interaction of its parts

$$\hat{R} = \mathbf{U} \hat{\rho} \hat{\sigma} \mathbf{U}^{+}. \tag{43}$$

The entropy of the system is written in the usual fashion

$$S = -\operatorname{Tr} \hat{R} \ln \hat{R} = -\operatorname{Tr} \hat{\rho} \ln \hat{\rho} - \operatorname{Tr} \hat{\sigma} \ln \hat{\sigma}. \tag{44}$$

We then calculate the resulting density operators for the subsystems

$$\hat{\rho}' = \operatorname{Tr}_{\mathrm{II}} \hat{R}, \quad \hat{\sigma}' = \operatorname{Tr}_{\mathrm{I}} \hat{R}, \tag{45}$$

where the traces are calculated for an arbitrary complete set of quantum numbers of subsystems II and I, respectively.

Let us designate through $\hat{L}$ and $\hat{\Lambda}$ the operators of the physical variables of the subsystems (or complete sets) for which operators $\hat{\rho}'$ and $\hat{\sigma}'$ have diagonal matrices. When the initial states are stationary and the energy is conserved, these operators commute or coincide with the Hamiltonians of the subsystems. By labeling, again, by Greek or Latin letters the corresponding sets of quantum numbers we write

$$\langle l | \rho' | m \rangle = \rho_l' \delta_{lm}, \quad \langle \lambda | \sigma' | \mu \rangle = \sigma_\lambda' \delta_{\lambda\mu}. \tag{46}$$

The resulting entropy of the subsystems will then be written as

$$S_{\mathrm{I}}' = -\sum_l \rho_l' \ln \rho_l', \quad S_{\mathrm{II}}' = -\sum_\lambda \sigma_\lambda' \ln \sigma_\lambda'. \tag{47}$$

According to Shannon's theory [15],

$$S_{\mathrm{I}}' + S_{\mathrm{II}}' + \sum_{l,\lambda} \langle l,\lambda | R | l,\lambda \rangle \ln \langle l,\lambda | R | l,\lambda \rangle \geqslant 0. \tag{48}$$

In addition, from Klein's lemma [12,16] follows

$$-\sum_{l,\lambda} \langle l,\lambda | R | l,\lambda \rangle \ln \langle l,\lambda | R | l,\lambda \rangle \geqslant S. \tag{49}$$

By combining Eqs. (48) and (49) we obtain

$$\Delta S = S_{\mathrm{I}}' + S_{\mathrm{II}}' - S \geqslant 0. \tag{50}$$

The inequality is proved.

Now it is absolutely certain that the inequality $\Delta S \geqslant 0$ as specified above is exactly the logical equivalent of the second law of thermodynamics in a rigorous quantum theory. The expression (42) also proves to be general enough. Consider a physical object with an arbitrary energy spectrum E_n (it does not matter whether this range includes equal energies) interacting with the environment. It can be easily shown that, for $[H_{\mathrm{int}}, H_s + H_t] = 0$, this interaction does not influence the initial stationary character of states of the subsystems $[\rho, H_s] = [\sigma, H_t] = 0$. If the initial mixed state of the object is a Gibbs state at temperature θ and the changes of the eigenvalues of the density matrix $\Delta \rho_n$ are not appreciable in the interaction with the environment, we can write

$$\Delta S_s = -\sum_n (\Delta \rho_n) \ln \rho_n = \theta^{-1} \sum_n E_n \Delta \rho_n. \tag{51}$$

It is quite obvious that this expression is equivalent, to an accuracy of notation, to the differential definition of entropy in thermodynamics [17]. Then, with account of the inequality $\Delta S \geqslant 0$ and the law of energy conservation, the complete theory of quasiequilibrium processes can be constructed solely on the axiomatic basis. We believe that the above study provides sufficient proof of the quantum origin of the second law of thermodynamics.

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