

On Theoretical Treatment of Chemical Reaction

Part 3 Relations to Statistical Mechanics and Quantum Mechanics Partially

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Introduction

The other part of relation between chemical reaction and statistical mechanics that could not describe on the previous paper is reported on this paper. Moreover, one part of relation between chemical reaction and quantum mechanics is reported on this paper except the rest that could not describe according to the space of this paper.

At first, in classical statistical mechanics, H-theorem is treated with the Ehrenfest's consideration that is modified by the author against the irreversibility in natural phenomenon. The relation among fine-grained density, coarse-grained density, ensemble, and assembly are considered as the following description. The quantity H is defined by coarse-grained density. The relation between H and time is considered. And the H that decreases with time is proved.

At second, the basis of quantum mechanics is considered including the uncertainty principle of Heisenberg. And quantum mechanics is treated on the viewpoint of wave mechanics. (1) Among probability W , probability amplitude Ψ and its conjugate one Ψ^* , the relation in them is considered. (2) Hermitian operator against coordinate q_i , momentum p_i , and time t is considered. As the operator becomes linear Hermitian, q_i , p_i , t is replaced with the operator. Ψ decides the quantum mechanical state, the physical quantity in classical mechanics is compared with the mean value of the physical property in quantum mechanics. (3) The time-like change of Ψ is given by Schrödinger's equation. Hermitian operator in quantum mechanics cor-

responds Hamilton function in classical mechanics. The important property in quantum mechanics, Principle of superposition, is considered.

The mean value by the determination of the mechanical quantity is considered according to eigenvalue. The operator \mathbf{H} that corresponds to energy of mass is considered. The continuity, uncontinuity, or mixed both properties of eigenvalue and the eigenfunction are considered. And the two characteristic states (k, j) are considered with the cases $j = k$, $j \neq k$, $j \neq k$; $F_j = F_k$ (degeneration). And eigenfunction is normalized by an usage of principle of superposition. Moreover, normalized orthogonal function system is used in development of function. So, probability amplitude is developed with eigenfunction.

Then, energy is selected as eigenvalue against the conservative system.

Experimental and Results, Gedanken Experiment

H-theorem in classical statistical mechanics: As the hypothesis of a priori probability is approved as shown on the previous paper,¹⁾ Gibbs' H-theorem that corresponds to the irreversibility in natural phenomenon is obtained after several preparations as follows. Namely, the necessity that the fine-grained density is separated from the coarse-grained density according to the method of Ehrenfest²⁾ must be mentioned at first.

The exact state of ensemble is represented by density ρ as shown on the previous paper.¹⁾

N is assumed to point the total number of representative point of the ensemble. If ρ is normalized, so the relation is represented by eq. (III-1).

$$\frac{\delta N}{N} = \rho(q_1, \dots, p_f, t) \delta q_1 \dots \delta p_f \quad (\text{III-1})$$

Namely, ρ shows the probability that the representative point exists in the range of differential refinement of the phase space. So, it is called as fine-grained density.

However, when the observation that becomes the problem in statistical mechanics in regard to coordinate and momentum of dynamical system is carried on, the value cannot be decided exactly. Therefore, the probability that the representative point exists in the finite size of region $\Delta q_1 \dots \Delta p_f$ becomes the problem. So, coarse-grained density P is defined by the following equation, eq. (III-2).

$$P = \frac{\int^{\Delta} \dots \int \rho dq_1 \dots dp_f}{\Delta q_1 \dots \Delta p_f} \quad (\text{III-2})$$

Here, the integration is carried on about the finite region $\Delta q_1 \dots \Delta p_f$. Namely, P is arithmetic mean of ρ in the region $\Delta q_1 \dots \Delta p_f$. So, eq. (III-3) is given against the probability that the representative point exists in the region $\Delta q_1 \dots \Delta p_f$.

$$\frac{\Delta N}{N} = \int^{\Delta} \dots \int \rho dq_1 \dots dp_f = P \Delta q_1 \dots \Delta p_f \quad (\text{III-3})$$

Moreover, if the phase space is divided into the same size of region $\Delta q_1 \dots \Delta p_f$, the relation is given by eq. (III-4) clearly.

$$\sum_k P_k \Delta q_1 \dots \Delta p_f = 1 \quad (\text{III-4})$$

Here, P_k is coarse-grained density against k th of the region. Also, the sum is calculated about the total region of such region k . On the other hand, if the sum is rewritten as the form of integration about the total phase space, eq. (III-5) is obtained.

$$\int \dots \int P dq_1 \dots dp_f = 1 \quad (\text{III-5})$$

Then, quantity H is defined with an usage of coarse-grained density ρ as follows.

$$H = \sum_k P_k \log P_k \Delta q_1 \dots \Delta p_f \quad (\text{III-6})$$

Here, the sum is calculated about the total region of the finite region k . Also, if the sum is rewritten as the form of integration about the total phase space, eq. (III-7) is obtained.

$$H = \int \dots \int P \log P dq_1 \dots dp_f \quad (\text{III-7})$$

Moreover, P , and resultant $\log P$ is constant in the region $\Delta q_1 \dots \Delta p_f$ respectively. Therefore, eq. (III-8) is obtained according to eq. (III-3).

$$H = \int \dots \int \rho \log P dq_1 \dots dp_f \quad (\text{III-8})$$

Then, H that is defined as such process decreases with time. Now, the proof that the quantity H is a function of time requires several related equations to understand easily.

(1) If ρ and P are positive quantities, $Q = \rho \log \rho - \rho \log P - \rho + P$, is positive or zero. And, against a defined random value of P , the following relations are obtained

$$\left(\frac{\partial Q}{\partial \rho} \right)_P = \log \rho - \log P \quad (\text{III-9})$$

$$\left(\frac{\partial^2 Q}{\partial \rho^2} \right)_P = \frac{1}{\rho} \quad (\text{III-10})$$

Here, as $\partial^2 Q / \partial \rho^2$ is always positive, when $\partial Q / \partial \rho$ is zero, namely $\partial Q / \partial \rho = 0$, Q becomes minimal.

In the other case, it must be positive. Namely, eq. (III-11) is obtained as follows.

$$Q = \rho \log \rho - \rho \log P - \rho + P \geq 0 \quad (\text{III-11})$$

(2) ρ in the neighborhood of the representative point that moves according to the principle of density conservation does not change with time. Consequently, the integration, $\int \dots \int \rho \log \rho dq_1 \dots dp_f$, about the total phase space that includes the all representative point does not change with time.

Namely,

$$\frac{d}{dt} \int \dots \int \rho \log \rho dq_1 \dots dp_f = 0 \quad (\text{III-12})$$

The quantity H that corresponds to the representative ensemble decreases with time. The unchangeable relation tries to be proved with usage of the two relations.

At first, the state of assembly at the time t_1 is observed approximately. And the ensemble that represents

the observed results is considered at the next time. This representative ensemble is obtained with homogenous distribution of the representative point in the region of the phase space according to the hypothesis of a priori probability. However, the phase space must correspond equally to the observed result. As the determination that becomes the problem in statistical mechanics is approximate, it becomes that such region has a finite magnitude. Moreover, ρ is equal to P in such region. Consequently, if the value at time t_1 is pointed with a supplementary note of suffix 1, it becomes that each point existed in the finite region $\Delta q_1 \cdots \Delta p_f$ moves variously with passage of time. So, the relation is shown as eq. (III-13).

$$H_1 = \int \cdots \int \rho_1 \log \rho_1 dq_1 \cdots dp_f \quad (\text{III-13})$$

Also, the magnitude of the region does not change according to the principle of volume conservation,²⁾ but the form of the region changes. $\frac{d}{dt}(\delta v) = 0$

In consequence, it becomes as follows; the representative point existed in the region $\Delta q_1 \cdots \Delta p_f$ at the beginning distributes into many regions that divides the phase space at the latter time t_2 . And, in the region that the form changes, distribution density is equal to the original value, ρ_1 , according to $d\rho/dt = 0$. Therefore, if a finite region $\Delta q_1 \cdots \Delta p_f$ is considered in the correspondence of the observation in statistical mechanics at the latter time t_2 , it becomes that the fine-grained density points the various different values. Generally, ρ_2 is not equal to P_2 , $\rho_2 \neq P_2$. So, the relation is shown as eq. (III-14).

$$H_2 = \int \cdots \int \rho_2 \log P_2 dq_1 \cdots dp_f \quad (\text{III-14})$$

Here, suffix 2 points the value at the time t_2 .

From eq. (III-13) and eq. (III-14), eq. (III-15) is obtained.

$$H_1 - H_2 = \int \cdots \int (\rho_1 \log \rho_1 - \rho_2 \log P_2) dq_1 \cdots dp_f \quad (\text{III-15})$$

And, according to eq. (III-12), eq. (III-16) is obtained.

$$H_1 - H_2 = \int \cdots \int (\rho_2 \log \rho_2 - \rho_2 \log P_2) dq_1 \cdots dp_f \quad (\text{III-16})$$

Moreover, from $1 = \int \cdots \int \rho dq_1 \cdots dp_f$ and eq. (III-5), eq. (III-17) is obtained.

$$H_1 - H_2 = \int \cdots \int (\rho_2 \log \rho_2 - \rho_2 \log P_2 - \rho_2 + P_2) dq_1 \cdots dp_f \quad (\text{III-17})$$

However, from eq. (III-11), eq. (III-18) is obtained.

$$\rho_2 \log \rho_2 - \rho_2 \log P_2 - \rho_2 + P_2 \geq 0 \quad (\text{III-18})$$

Consequently, the following relation is shown as eq. (III-19).

$$H_2 \leq H_1 \quad (\text{III-19})$$

Namely, H decreases with time. This result is called as H -theorem of Gibbs.

Quantum mechanics: This contents is one part of the preparation of deduction to quantum statistical mechanics. According to the principle of uncertainty proposed by Heisenberg, at a certain decided time, the position q_i and the conjugate momentum p_i in a certain dynamical system cannot be determined exactly at the same time. Moreover, the energy of free particle E and the time t that the particle passes through a certain boundary cannot be determined together at the same time. If this principle is expressed by other form, it is shown by eq. (III-20) that expresses the relation between the product of uncertainty Δ of these quantities and Planck constant h .

$$\Delta q_i \Delta p_i \sim h, \Delta E \Delta t \sim h \quad (\text{III-20})$$

Namely, this principle points that the product is at a degree of Planck constant h . And, quantum mechanics is based on this principle, and is constructed with it. Also, the partial interpretation of quantum mechanics is tried to be shown by one special form that places emphasis on so-called wave mechanics.

The fundamental assumption against the description

of dynamical system in quantum mechanics can be expressed as follows;

(1) When the coordinate q_1, \dots, q_f of dynamical system that the degree of freedom is f exists in the range of differential refinement shown at each time t , the existence of the probability that the coordinate exists in the range is considered as one important basic assumption. And, the probability is expressed as the following form.

$$W(q_1, \dots, q_f, t) dq_1, \dots, dp_f$$

Then, W is positive quantity. Therefore, this relation can be formed as the following expression.

$$W(q_1, \dots, q_f, t) = \Psi(q_1, \dots, q_f, t) \Psi^*(q_1, \dots, q_f, t) \quad (\text{III-21})$$

Here, Ψ is called as probability amplitude, and is generally complex function that Ψ itself cannot be observed. Ψ^* is the conjugate complex function. As Ψ has such a physical meaning, at all position that variable q exists, it is not only single-valued function but also is continuous function.

The value that the square, $\Psi \Psi^*$, of the absolute value is integrated in a certain domain must be finite. And, when W is integrated over the total region, the integrated value becomes 1. Namely,

$$\int \dots \int W(q, t) dq_1, \dots, dp_f = \int \dots \int \Psi(q, t) \Psi^*(q, t) dq_1, \dots, dp_f = 1 \quad (\text{III-22})$$

(2) The linear Hermitian operator that is given as the following expression corresponds to each physical quantity in quantum mechanics. Then, some descriptions about operator are shown to help understanding the development of this theoretical treatment.

1) Operator: When a certain function u is changed to the new function v of the same or the other variable by the application of a certain constant rule \mathbf{A} that is called a operator, the process is called as operation. And, it is expressed as the following eq. (III-23).

$$v = \mathbf{A} u \quad (\text{III-23})$$

The sum of two operators, $\mathbf{A} + \mathbf{B}$ is defined by the following relation as shown eq. (III-24).

$$\mathbf{S} = (\mathbf{A} + \mathbf{B}) u = \mathbf{A} u + \mathbf{B} u \quad (\text{III-24})$$

Also, the product, $\mathbf{A} \mathbf{B}$ is defined by the following relation as shown eq. (III-25).

$$\mathbf{P} u = \mathbf{A} \mathbf{B} u = \mathbf{A} (\mathbf{B} u) \quad (\text{III-25})$$

Namely, u is operated with \mathbf{B} at the first step. Successively, the result is operated with \mathbf{A} at the second step.

Generally, the product $\mathbf{A} \mathbf{B}$ is different from the product $\mathbf{B} \mathbf{A}$. If $\mathbf{A} \mathbf{B}$ is equal to $\mathbf{B} \mathbf{A}$, $\mathbf{A} = \mathbf{B}$, it is said that \mathbf{A} is able to exchange with \mathbf{B} each other.

2) Linear operator: The operator that has the following character is said as linear. Also, it is said that the character is equivalent to the definition. The character is shown as eq. (III-26). Namely,

$$\mathbf{A}(c_1 u_1 + c_2 u_2) = c_1 \mathbf{A} u_1 + c_2 \mathbf{A} u_2 \quad (\text{III-26})$$

Here, c_1 and c_2 are real or imaginary random constant.

Therefore, the sum and the product that are made up of two operators, \mathbf{A} and \mathbf{B} , are also linear. These relations that are shown as eq. (III-27) can be induced from the definition.

$$\mathbf{S} = c_1 \mathbf{A} + c_2 \mathbf{B}, \quad \mathbf{P} = c_3 \mathbf{A} \mathbf{B} \quad (\text{III-27})$$

If it is assumed that u_1 and u_2 are two solutions of the equation, $\mathbf{A} u = 0$, the following relations, $\mathbf{A} u_1 = 0$, $\mathbf{A} u_2 = 0$, are obtained. However, the equation includes linear operator \mathbf{A} .

Consequently, the relation is obtained from eq. (III-26), and is shown as eq. (III-28).

$$\mathbf{A}(c_1 u_1 + c_2 u_2) = 0 \quad (\text{III-28})$$

Namely, the linear combination of solution is the solution.

3) Hermitian operator: When the function u_1, u_2 of the variable, x_1, \dots, x_n are integrated over the total domain, the integral is shown as eq. (III-29).

$$\int \dots \int u_1(x_1, \dots, x_n)^* \mathbf{A} u_2(x_1, \dots, x_n) dx_1, \dots, dx_n$$

$$= \int \dots \int u_2(x_1, \dots, x_n) [\mathbf{A}u_1(x_1, \dots, x_n)]^* dx_1 \dots dx_n \quad (\text{III-29})$$

On the other hand, when its form is simplified, the following expression as shown eq. (III-30) is possible also.

$$\int u_1^* \mathbf{A}u_2 dx = \int u_2 [\mathbf{A}u_1]^* dx \quad (\text{III-30})$$

Then, when the above described relation is set up, it is said that \mathbf{A} is Hermitian.

If \mathbf{A} and \mathbf{B} are two Hermitian operators that are used to two functions, u_1 and u_2 , the sum, $c_1\mathbf{A} + c_2\mathbf{B}$, is also clearly Hermitian from the definition.

And, according to eq. (III-30), the following relations are induced as shown eq. (III-31) and eq. (III-32).

$$\int (\mathbf{A}u_1)^* \mathbf{B}u_2 dx = \int u_2 (\mathbf{B}\mathbf{A}u_1)^* dx \quad (\text{III-31})$$

$$\int (\mathbf{B}u_2)^* \mathbf{A}u_1 dx = \int u_1 (\mathbf{A}\mathbf{B}u_2)^* dx \quad (\text{III-32})$$

As the left side of eq. (III-31) is conjugated with the left side of eq. (III-32), the following relation is obtained as shown eq. (III-33).

$$\int u_1^* \mathbf{A}\mathbf{B}u_2 dx = \int u_2 (\mathbf{B}\mathbf{A}u_1)^* dx \quad (\text{III-33})$$

If \mathbf{A} is able to change with \mathbf{B} , it is understood that the product, $\mathbf{A}\mathbf{B} = \mathbf{B}\mathbf{A}$, is Hermitian. In consequence, \mathbf{A}^n is Hermitian. Therefore, the sum that is made up of these element is also Hermitian. The sum can be expressed as polynomial of \mathbf{A} .

On the other hand, in analogy with eq. (III-33), when the following equation, eq. (III-34), is added to eq. (III-33), the following relation is obtained. Namely,

$$\int u_1^* \mathbf{B}\mathbf{A}u_2 dx = \int u_2 (\mathbf{A}\mathbf{B}u_1)^* dx \quad (\text{III-34})$$

$$\int u_1^* (\mathbf{A}\mathbf{B} + \mathbf{B}\mathbf{A})u_2 dx = \int u_2 [(\mathbf{A}\mathbf{B} + \mathbf{B}\mathbf{A})u_1]^* dx \quad (\text{III-35})$$

That is to say, the symmetric sum of Hermitian operator \mathbf{A} and \mathbf{B} is Hermitian.

4) Operator against physical quantity: The operators, q_i and $h/2\pi i \partial/\partial q_i$, of coordinate q_i and momentum p_i

that are operated against probability amplitude $u(q)$ are clearly linear together from the definition. Also, as the $q_i = q_i$ is real number, the following relation as shown eq. (III-36) is valid.

$$\int u_1^* q_i u_2 dq = \int u_2 (q_i u_1)^* dq \quad (\text{III-36})$$

So, it is Hermitian. Moreover, against $\mathbf{P}_i = h/2\pi i \partial/\partial q_i$ the following eq. (III-37) is valid.

$$\begin{aligned} & \int \dots \int u_1^* \frac{h}{2\pi i} \frac{\partial u_2}{\partial q_i} dq_1 \dots dq_f \\ &= \int \dots \int \left[u_1^* \frac{h}{2\pi i} u_2 \right]_{q_i=-\infty}^{q_i=+\infty} dq_1 \dots dq_f \\ & - \int \dots \int u_2 \frac{h}{2\pi i} \frac{\partial u_1}{\partial q_i} dq_1 \dots dq_f \\ &= \int \dots \int u_2 \left(\frac{h}{2\pi i} \frac{\partial u_1}{\partial q_i} \right)^* dq_1 \dots dq_f \end{aligned} \quad (\text{III-37})$$

So, this is found to be Hermitian. Here, the case that the last equation becomes a problem physically is the following case. Namely, it is the case of the $u=0$ at the limit, $q_i = \pm\infty$. So, against this problem, the last equation can be obtained by an elimination of the first term of the second equation.

If \mathbf{Q} and \mathbf{P} are linear and Hermitian operators that are the function of \mathbf{q} and \mathbf{p} respectively, \mathbf{F} is linear, Hermitian in the following case. Namely, the case that the operator \mathbf{F} of $F(q, p) = \sum c QP$ is made a symmetric form as shown eq. (III-38).

$$\mathbf{F}(q, p) = \sum \frac{1}{2} c (\mathbf{Q}\mathbf{P} + \mathbf{P}\mathbf{Q}) \quad (\text{III-38})$$

Then, a role of linear Hermitian is quantum mechanics is considered again, as the author made some preparations ready for operator.

The operators against coordinate q_i , momentum p_i , and time t are given respectively as shown eq. (III-39).

$$q_i = q_i x, \quad \mathbf{P}_i = \frac{h}{2\pi i} \frac{\partial}{\partial q_i}, \quad \mathbf{t} = t x \quad (\text{III-39})$$

And, one condition is considered as follows; the operator, $\mathbf{F}(\mathbf{q}, \mathbf{p}, \mathbf{t})$ against a certain quantity $F(q, p, t)$ that is function of coordinate, momentum, and time is obtained by the following operation. It is the operation that variables q_i, p_i, t are replaced with operators $q_i,$

\mathbf{P}_i, t to become linear, Hermitian. So, this relation is shown as eq. (III-40).

$$\mathbf{F}(q, \mathbf{P}, t) = F(q, \frac{h}{2\pi i} \frac{\partial}{\partial q}, t) \quad (\text{III-40})$$

Then, the quantity $F(q, p, t)$ that is function of coordinate, momentum, time is related to a problem of the physical quantity, spin, if one example related it is selected.

However, there is a necessity of one kind of attention on the operation mentioned above. Even if it is the same dynamical quantity, there is the case that arrives at the different operator by the method of expression. But, fortunately, the operator can be decided usually unqualifiedly in the case that orthogonal coordinate is applied at conservative system.

Thus, the mean value of physical quantity $F(q, p, t)$ at a certain time t_0 is given by the integral over the obtained total coordinate region that operated the corresponding operator F on Ψ . And, the integral is shown as eq. (III-40).

$$\mathbf{F}(q, \mathbf{P}, t) = F(q, \frac{h}{2\pi i} \frac{\partial}{\partial q}, t) \quad (\text{III-40})$$

Then, as the \mathbf{F} is Hermitian, the following relation shown as eq. (III-41) is obtained.

$$\int \Psi^* \mathbf{F} \Psi dq = \int \Psi (\mathbf{F} \Psi)^* dq \quad (\text{III-41})$$

Namely, the mean value of F is equal to the conjugate value. Consequently, the mean value is real number. It is one of physical quantity must be Hermitian.

Thus, when the state is decided in classical mechanics, the physical quantity is decided. However, when Ψ is given in quantum mechanics, the mean value of physical quantity is decided, namely, the quantum mechanical state of the system is decided by the Ψ . In consequence, here, when the system exists at defined quantum mechanical state, the mean value has the meaning that is the mean value of the results of a series of determination.

Moreover, to determine two quantities together, the condition that the corresponding operator is able to exchange is necessary and sufficient condition at the first step. However, the condition must be proved at the second step.

(3) The time-like change of probability amplitude $\Psi(q, t)$ is given by Schrödinger's equation as shown eq. (III-42).

$$\mathbf{H}\Psi + \frac{h}{2\pi i} \frac{\partial \Psi}{\partial t} = 0 \quad (\text{III-42})$$

Here, \mathbf{H} is linear, Hermitian operator against Hamiltonian function in classical mechanics. As the two operators, $\frac{h}{2\pi i} \frac{\partial}{\partial t}$ and \mathbf{H} in this equation are linear together, if $\Psi_1(q, t)$ and $\Psi_2(q, t)$ are solutions of this equation, the linear combination, $\Psi(q, t) = c_1 \Psi_1(q, t) + c_2 \Psi_2(q, t)$ is also solution. This result is important character of quantum mechanics, is called as the principle of superposition.

Here, quantum mechanical state is decided by giving the Ψ . And, after the boundary condition is decided as the state at initial time t_0 becomes $\Psi(q, t_0)$, if the Schrödinger's equation is solved under the decided condition, the Ψ at later time is given.

Eigenvalue, characteristic value: The problem of the mean value that is obtained by the determination of a certain mechanical quantity $F(q, p, t)$ mentioned above is considered in conception of so-called "Eigenvalue".

$\Psi(q, t_0)$ at a certain defined time t_0 is expressed with $u(q)$. Now, if \mathbf{F} and F_e are the corresponding operator of F and a certain value respectively, the single-valued, continuous finite function $u(q)$ at the total coordinate region that is satisfied to the boundary condition and the following related equation shown as eq. (III-43) exists only against the specific value, eigenvalue.

$$\mathbf{F}u(q) = F_e u(q) \quad (\text{III-43})$$

This related equation becomes partial differential equation in many cases. When the quantity F is determined exactly the value that is found is certainly one of eigenvalue of the corresponding operator. For example, the operator \mathbf{H} against the energy of one simple particle that exists in rectangular parallelepiped of three sides, $a, b,$ and $c,$ is given by the following equation, eq. (III-44). And, the particle of mass m that is free from external pressure exists in the box mentioned above.

$$\mathbf{H} = \frac{1}{2m}(\mathbf{P}_x^2 + \mathbf{P}_y^2 + \mathbf{P}_z^2) + V(x, y, z) \\ = -\frac{h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \quad (\text{III-44})$$

Consequently, if F_e is expressed with E , the eq. (III-43) becomes the following equation, eq. (III-45).

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = -\frac{8\pi^2 m}{\hbar^2} (E - V)u \quad (\text{III-45})$$

Here, the single-valued, continuous finite function, $u(q)$ satisfies this partial differential equation. Moreover, this single-valued, continuous finite function, $u(q)$, is single-valued, continuous in regard to the total coordinate region that satisfies the condition. And the condition is as follows; V is zero, 0, in the box, and is infinite, ∞ , outside of the box.

$$E = \frac{\hbar^2}{8m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad (\text{III-46})$$

Here, n_1 , n_2 , and n_3 are natural number respectively. In consequence, if the energy of this particle is determined, one of E of eq. (III-46) can be found.

Then, eigenvalue is uncontinuous in such case shown by this example. Or there is the case that eigenvalue is continuous also. Moreover, there is the mixed case that eigenvalue is not only continuous but also uncontinuous.

Now, the eigenvalue of energy of conservative system that has a constant volume is uncontinuous. The conservative system having a constant volume is objective mainly in this consideration. Moreover, this defined system is treated comparatively simply. Therefore, the character of eigenfunction in the uncontinuous case is considered and is treated theoretically. Also, the continuous case can be considered as a limit of the uncontinuous case for the present.

Then, as two characteristic state are expressed with k and j , the following relations, eq. (III-47) and eq. (III-48), are obtained according to eq. (III-43).

$$\mathbf{F}u_k = F_k u_k \quad (\text{III-47})$$

$$(\mathbf{F}u_j)^* = F_j^* u_j^* \quad (\text{III-48})$$

After multiplying eq. (III-47) by u_j^* and also multiplying eq. (III-48) by u_k , when the integral over the total region of each variable is carried on, the following relations as shown the following eq. (III-49) and eq. (III-50) are obtained.

$$\int u_j^* \mathbf{F}u_k dq = F_k \int u_j^* u_k dq \quad (\text{III-49})$$

$$\int u_k (\mathbf{F}u_j)^* dq = F_j^* \int u_k^* u_j dq \quad (\text{III-50})$$

Here, as \mathbf{F} is Hermitian, the left sides of the both equations are equal. Consequently, the relation as shown eq. (III-51) is obtained.

$$(F_k - F_j^*) \int u_j^* u_k dq = 0 \quad (\text{III-51})$$

From this eq. (III-51), the following important conclusions are obtained.

1) If j is equal to k , $j=k$, as $\int u_k^* u_k dq$ is positive real number, the following relation, eq. (III-52) is obtained.

$$F_k = F_k^* \quad (\text{III-52})$$

It is found that eigenvalue is all real number.

2) If j is not equal to k , $j \neq k$, and if F_j is not equal to F_k at the same time, $F_j \neq F_k$, the following relation, eq. (III-53) is obtained.

$$\int u_j^* u_k dq = 0 \quad (\text{III-53})$$

The fact is said that eigenfunction against different eigenvalue is orthogonal.

3) If j is not equal to k , $j \neq k$, and if F_j is equal to F_k , $F_j = F_k$, eq. (III-53) is not always valid. Namely, in the case that the characteristic state degenerates and two and more eigenfunctions correspond to the same eigenvalue, eq. (III-53) is not always valid. However, the new g pieces of eigenfunction that is orthogonal each other can be made invariably from g pieces of different eigenfunction by the linear combination according to the principle of superposition. Consequently, the following relation shown as eq. (III-54) is valid in any event.

$$\int u_j^* u_k dq = 0 \quad (\text{III-54})$$

Then, the any eigenvalue against the degenerated g pieces of eigenfunction does not be expressed with F_k to simplify the following treatment. Each one is expressed with F_k, F_l, \dots that affixes each separate suffix.

As the one that the eigenfunction multiplied by a certain constant is also clear eigenfunction according

to the principle of superposition, the eigenfunction is made to normalize after the constant is selected as eq. (III-55).

$$\int u_k^* u_k dq = 1 \quad (\text{III-55})$$

When j is equal to k , $j=k$, if the $\delta_{j,k}$ is defined as the quantity that is 1, and, when j is not equal to k , $j \neq k$ if the $\delta_{j,k}$ is defined as the quantity that is zero, eq. (III-54) and eq. (III-56) are expressed with only one equation shown as eq. (III-56).

$$\int u_j^* u_k dq = \delta_{j,k} \quad (\text{III-56})$$

Generally, the arbitrary function, $f(g)$, that the finite $\int |f(q)|^2 dq$ exists can be developed with an usage of such normalized orthogonal function system. Consequently, the probability amplitude $\Psi(q,t)$ is developed with usage of eigenfunction $u_k(q)$. Namely, this relation is shown as eq. (III-57).

$$\Psi(q,t) = \sum_k a_k(t) u_k(q) \quad (\text{III-57})$$

Here, $a_k(t)$ is a coefficient of development.

After the both sides of eq. (III-57) multiplied by $u_k^*(q)$, when the integral over the total region of variable q is carried on, $a_k(t)$ is given by the following equation, eq. (III-58) from eq. (III-56).

$$a_k(t) = \int u_k^*(q) \Psi(q,t) dq \quad (\text{III-58})$$

It is found that $a_k(t)$ is equivalent to $\Psi(q,t)$ physically in comparison with the both equations, eq. (III-57) and eq. (III-58). Namely, the quantum mechanical state is given by $a_k(t)$ also.

If the physical quantity is determined exactly as mentioned above, one of eigenvalue can be found invariably, but, when a certain physical quantity about the system existed in the same quantum system $\Psi(q,t)$, is determined many times at the defined time, the probabilities that the various eigenvalues are found is trying to be considered to develop this theoretical treatment.

As $u_k(q)$ is normalized orthogonal function system, the n th power of mean value of the physical quantity F

is given by the following relations shown as the following equation, eq. (III-59).

According to eq. (III-40),

$$\begin{aligned} & \int \Psi^*(q,t) \mathbf{F}^n \Psi(q,t) dq \\ &= \int \sum_l a_l^*(t) u_l^*(q) \left(\sum_k a_k(t) \mathbf{F}^n u_k(q) \right) dq \\ &= \sum_{k,l} a_l^*(t) a_k(t) \int u_l^*(q) (F_k)^n u_k(q) dq \\ &= \sum_k a_k^*(t) a_k(t) (F_k)^n \end{aligned} \quad (\text{III-59})$$

As this equation is valid against arbitrary integer, n , so the probability, $W(F_k,t)$, that F_k is found by the determination can be expressed as the shown following equation, eq. (III-60).

$$W(F_k,t) = |a_k(t)|^2 \quad (\text{III-60})$$

Then, Schrödinger's equation can be normalized with an usage of $a_k(t)$ that has such physical meaning. According to eq. (III-42).

$$\mathbf{H} \Psi(q,t) + \frac{\hbar}{2\pi i} \frac{\partial \Psi(q,t)}{\partial t} = 0 \quad (\text{III-61})$$

Therefore, the relation is expressed by the following equation, eq. (III-62).

$$\sum_k a_k(t) \mathbf{H} u_k(q) + \frac{\hbar}{2\pi i} \sum_k \frac{\partial a_k(t)}{\partial t} u_k(q) = 0 \quad (\text{III-62})$$

After multiplying $u_l(q)$ by the both sides of this equation, when the integral over the total region of q is carried on, the following equation, eq. (III-63), is obtained from eq. (III-56).

$$\sum_k a_k(t) \int u_l^*(q) \mathbf{H} u_k(q) dq + \frac{\hbar}{2\pi i} \frac{\partial a_l(t)}{\partial t} = 0 \quad (\text{III-63})$$

Consequently, against the time differential of $a_l(t)$, the following equation, eq. (III-64), is obtained.

$$\frac{\partial a_l(t)}{\partial t} = -\frac{2\pi i}{\hbar} \sum_k a_k(t) H_{l,k} \quad (\text{III-64})$$

Here, $H_{l,k}$ is defined as the shown following equation, eq. (III-65).

$$H_{l,k} = \int u_l^*(q) \mathbf{H} u_k(q) dq \quad (\text{III-65})$$

As \mathbf{H} is Hermitian, the relation is obtained as the following equation, eq. (III-66).

$$H_{l,k} = H_{k,l}^* \quad (\text{III-66})$$

Then, in the case that the energy is selected as the eigenvalue against conservative system, those theories are trying to be applied as follows. So, the relation is obtained as the shown following equation, eq. (III-67).

$$H_{l,k} = E_k \delta_{j,k} \quad (\text{III-67})$$

Consequently, eq. (III-64) becomes the following equation, eq. (III-68).

$$\frac{\partial a_l(t)}{\partial t} + \frac{2\pi i}{h} a_l(t) E_l = 0 \quad (\text{III-68})$$

Then, the solution of this differential equation is shown as the following equation, eq. (III-69).

$$a_l(t) = c_l e^{-(2\pi i/h) E_l t} \quad (\text{III-69})$$

Here, c_l is constant. And eq. (III-56) becomes the following equation, eq. (III-70).

$$\Psi(q, t) = \sum_k c_k u_k(q) e^{-(2\pi i/h) E_k t} \quad (\text{III-70})$$

Here, c_k is given as the integral over the total domain according to multiplying $u_k^*(q) e^{+(2\pi i/h) E_k t}$ by the both sides of this equation. The relation is shown as the following equation, eq. (III-71).

$$c_k = \int u_k^*(q) e^{+(2\pi i/h) E_k t} \Psi(q, T) dq \quad (\text{III-71})$$

Moreover, the probability $W(E_k, t)$ that the energy E_k is determined becomes the following relation shown as the following equation, eq. (III-72). The probability does not relate to time.

$$W(E_k, t) = |a_k|^2 = |c_k|^2 \quad (\text{III-72})$$

Discussion and Conclusion

H-theorem in classical statistical mechanics: After the hypothesis of a priori probability is recognized at

the first step, Gibbs H-theorem is derived to correspond to the irreversibility in natural phenomenon. A fine-grained density is classified from a coarse-grained density according to the consideration of Ehrenfest. So, two densities are defined by the probability of existence of the representative point in the phase space. Moreover, normalization method is applied to them effectively. When statistical mechanics treats coordinate and momentum in the mechanical system, the probability of existence of the representative point in the finite region becomes the objective point. So, coarse-grained density that is arithmetic mean of fine-grained density in the finite region is defined. Successively, after the phase space is fractionated to the same region, the phase space is integrated. So, the quantity H is defined by the usage of coarse-grained density. Then, in the relation between H and time, H decreases with time. Next, the state of the assembly at the initial time t_1 is determined approximately. And the ensemble that represents the determined result is composed. This representative ensemble is distributed homogeneously to the region of the phase space that corresponds well to the determined result according to the hypothesis of a priori probability. In statistical mechanics, fine-grained densities equal to coarse-grained density in the region that is finite magnitude for the approximate determination. Consequently, at the late time t_2 , the representative point existed in the initial region distributes homogeneously to many regions of the fractionated phase space. In such changed region, the density at the neighborhood of one moving representative point does not change. So, the distribution density is equal to the original value. Then, from the difference between H_1 (H_1 is H at the time 1, t_1) and H_2 (H_2 is H at the time 2, t_2), H decreases with time.

Quantum mechanics: According to the principle of uncertainty of Heisenberg, both position q_i and its conjugated momentum p_i in a certain dynamical system at a certain decided time cannot be determined exactly at the same time. Both the energy of the free particle and the time that its particle passes through a boundary cannot be determined together at the same time. Quantum mechanics is composed on the basis of the principle. And quantum mechanics is treated as one form of the so-called wave mechanics on the view

point that is not relativistic.

(1) When the probability W that coordinate of a certain dynamical system of freedom f exists at differential range at each time is integrated over total region, the relation is valid and becomes 1. Also, the product $\Psi\Psi^*$ of both probability amplitude Ψ of complex function itself that cannot be determined generally and conjugate complex function Ψ^* , the integrated value of $\Psi\Psi^*$ in a certain domain must be finite.

(2) In quantum mechanics, linear Hamiltonian operator corresponds to the physical quantities, coordinate q_i , momentum p_i , and time t . And the operator corresponds to the function $F(q, p, t)$ that of coordinate, momentum, and time is obtained by the substitution of variable q_i, p_i, t to the operator $\mathbf{q}_i, \mathbf{p}_i, t$ under the condition of being the linear Hermitian. The mean value of the physical quantity $F(q, p, t)$ at the time t_0 is obtained by integration over total coordinate region. In classical mechanics, the decision of state decides the value of physical quantity. In quantum mechanics, the decision of Ψ decides the mean value of physical quantity. Namely, Ψ decides the quantum mechanical state of system.

(3) The time-like change of the probability amplitude is given by Schrödinger's equation. \mathbf{H} is linear Hermitian operator corresponds to Hamiltonian function in classical mechanics. And the important principle is obtained by the theoretical derivation. It is principle of superposition.

Ψ decides the quantum mechanical state, and the solution of Schrödinger's equation gives Ψ at the late time under the boundary condition that the state at the initial time t_0 becomes $\Psi(q, t_0)$.

Eigenvalue: On the basis of the concept relating to quantum mechanics, the problem of mean value obtained from the mechanical quantity $F(q, p, t)$ is considered against eigenvalues.

$\Psi(q, t_0)$ at definite time t_0 is expressed by $u(q)$. If \mathbf{F} and F_e are corresponding operator of F and a certain numerical value respectively, one single-valued, continuous finite function $u(q)$ exists only to specific value (eigenvalue, characteristic value) of F . When the quantity F is determined exactly, the obtained value is one of eigenvalue of corresponding operator.

And there are three conditions as follows; (a) eigenvalue is continuous (b) eigenvalue is uncontinuous (c) eigenvalue is mixed property of continuity and uncontinuity. Then, the property of eigenfunction in the case of (b) is considered among three conditions. Because, the continuous case is considered as the limit of the uncontinuous case. Now, the two characteristic states are considered, and are integrated over total region of each variable. Under the consideration that \mathbf{F} is Hermitian, the important conclusion is obtained as follows; (d) eigenvalue is real number (e) eigenfunction against different eigenvalue is orthogonal (f) if characteristic state degenerates and two and more eigenfunctions correspond to the same eigenvalue, it is not always valid that eigenfunction against different eigenvalue is orthogonal. However, according to the principle of superposition, new eigenfunction that is orthogonal each other can be made by linear combination from g pieces of different eigenfunction against one eigenvalue. And the normalization method is applied in this case. Generally, the arbitrary function $f(g)$ that the finite $\int |f(g)|^2 dq$ exists can be developed under normalized orthogonal function system. So, probability amplitude $\Psi(q, t)$ is developed with eigenfunction $u_k(q)$. And if coefficient of development is $a_k(t)$ in this development, $\Psi(q, t)$ is equivalent to $a_k(t)$. Namely, quantum mechanical state is given by $a_k(t)$.

The exact determination of the physical quantity can find certainly one of eigenvalue. As $u_k(q)$ is normalized orthogonal function system, the mean value of n th power of physical quantity is obtained by

$$\int \Psi^*(q, t) \cdot \mathbf{F}^n \Psi(q, t) = \sum_k a_k^*(t) a_k(t) (F_k)^n.$$

As this equation is valid against arbitrary integer n , the probability $W(F_k, t)$ of finding F_k is obtained as $W(F_k, t) = |a_k(t)|^2$.

On the other hand, Schrödinger's equation is generalized. Like the description of paragraph of eigenvalue of gedanken experiment, the equation A, $\frac{\partial a_l(t)}{\partial t} =$

$$-\frac{2\pi i}{h} \sum_k a_k(t) H_{l,k},$$

is obtained against time differentiation of $a_l(t)$. As \mathbf{H} is Hermitian. So, $H_{e,k} = \mathbf{H}^*_{k,l}$. Then, when energy is selected as eigenvalue against the conservative system, $H_{l,k} = E_k \delta_{j,k}$ is obtained. So,

$$\text{the equation A is renewed as } \frac{\partial a_l(t)}{\partial t} + \frac{2\pi i}{h} a_l(t) E_l = 0.$$

So, the solution of differential equation is $a_l(t) = c_l e^{-(2\pi i/h)E_l t}$.

$$\Psi(q, t) = \sum_k a_k(t) u_k(q) \text{ is renewed as } \Psi(q, t) = \sum_k c_k u_k(q) e^{-(2\pi i/h)E_k t}.$$

Moreover, the probability $W(E_k, t)$ that energy E_k is determined can be expressed as $W(E_k, t) = |a_k|^2 = |c_k|^2$. It is not a function of time.

Summary

After the hypothesis of a priori probability is recognized, Gibb's H-theorem corresponding to the irreversibility in natural phenomenon is obtained. A fine-grained density and a coarse-grained density are considered with some modifications. The quantity H is defined by coarse-grained density. The Gibbs' H-theorem that decreases with time is derived by this concept.

The concept in classical statistical mechanics is compared with the concept in quantum statistical mechanics. So, the basic concept in quantum mechanics is considered on the viewpoint of wave mechanics.

The basic assumption for mechanical system in quantum mechanics is considered. The probability, probability amplitude, complex function, conjugate complex function, Hermitian operator and Hamiltonian function in classical mechanics are considered.

Next, eigenvalue is considered with the mean value of mechanical quantity. Operator \mathbf{H} against energy of particle is considered. These concepts are derived into the case that energy is selected as eigenvalue against the conservative system.

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化学反応の理論的取扱

第3報 統計力学および量子力学一部との関係

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(昭和58年7月9日受理)*

統計力学, 量子力学, 熱力学を基にし, 新しい理論的取扱を思考実験として化学反応につき試み, 既報に続き, 本報では統計力学(未報部分)と量子力学の一部(紙面の都合上)に関し報告する。古典力学, 古典統計力学の思考と量子力学, 量子統計力学の思考との関係性の検討を試み, それらを基にし, 次の項に関し合せて記した。(1)古典統計力学におけるH定理, (2)量子力学, (a)確率振幅, (b)線型 Hermit 型演算子—演算子, 線型演算子, Hermit 型演算子, 物理量に対する演算子, (3)確率振幅の時間的变化。

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