

On Theoretical Treatment of Chemical Reaction

Part 4 Relation to Quantum Mechanics Partially

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Introduction

The relation between chemical reaction and quantum mechanics is reported on this paper according to the space of this paper. Of course, the rest part that could not be reported might be published on the next paper successively. The concept in classical statistical mechanics is applied to quantum statistical mechanics.

At first, the hypothesis of a priori probability in quantum statistical mechanics is considered. In statistical mechanics, with an usage of the representative ensemble that is the same composition to the objective assembly, its mean behavior and property are studied. The component of ensemble must be distributed corresponding to unsatisfactory knowledge. So, in quantum statistical mechanics as similar as classical statistical mechanics, the hypothesis of a priori probability is necessary to be deduced as a postulate. The future behavior is decided by Schrödinger's equation. This assumption hypothesis of a priori probability, is introduced to quantum statistical mechanics. So, this proper fact is recognized by the fact that the introduced conclusion agrees to the experience.

Density matrix: In quantum mechanics, the state of mechanical system at a certain time is decided by probability amplitude Ψ . The time-like change of Ψ is decided by Schrödinger's equation. So, in principle, the change of state of mechanical system in quantum mechanics can be pursued exactly at least like classical mechanics. In classical mechanics, the state of ensemble is indicated by the distribution density ρ of the representative point in phase space. And, in quantum mecha-

tics, density matrix plays a similar role to distribution density. The concept in classical statistical mechanics is compared with the concept in quantum statistical mechanics. The former corresponds well to the latter.

H-theorem: The H-theorem is classical statistical mechanics is compared with the H - quantum statistical mechanics. H-theorem in quantum statistical mechanics is proved with the hypothesis of a priori probability. Fine-grained density and coarse-grained are considered separately. Density matrix of diagonal element gives the probability that assembly exists at the state k . In statistical mechanics, the case that the limitation exists in accuracy of determination becomes the problem. So, coarse-grained density P_k is defined. The quantity H against ensemble is defined by the quantity P_k . And, like the consideration in classical statistical mechanics, the component of ensemble is distributed homogeneously to the decided state according to the hypothesis of a priori probability. H decreases with time, and becomes minimum value. After these considerations are developed, canonical ensemble expresses the assembly that the statistical mean value of energy of the representative ensemble is constant under being at statistical equilibrium. In quantum statistical mechanics, the exact circumstances in quantum statistical mechanics is described with the density matrix. The time-like change of density matrix is considered. With the generalized Schrödinger's equation, Liouville theorem is derived. The assembly represented by the ensemble that distributes to various quantum states without time-like change exists at statistical equilibrium. Especially, the case that density matrix is a function of energy is interested in statistical mechanics. So, micro-canonical ensemble and canonical ensemble are con-

sidered at various viewpoints.

Caninical ensemble is satisfactory for represent the assembly that exists at constant temperature, and is especially important to consider the relation between statistical mechanics and thermodynamics.

Pauli's principle: To explain anomalous Zeeman effect, Uhlenbeck and Goudsmit deduced position, momentum, new physical quantity (spin) to electron. Spin cannot be found in classical mechanics. Spin is characteristic angular momentum and magnetic efficiency. Then, the multiplicity of atomic spectrum is magnetic interaction between spin of electron and orbital momentum. Also, spin is found in positron, proton, neutron. Spin has characteristic momentum of $+\frac{1}{2}h/2\pi$ or $-\frac{1}{2}h/2\pi$. In general case, Hamilton function does not be affected by magnetic interaction of spin and orbital momentum.

Pauli assumed that only one electron existed at the same quantum state and could explain the periodic law under restriction of rearrangement of electron in atom. This pauli's principle is developed to electron, proton, chemical species composed with odd number of elementary particle, and to photon, meson, chemical species composed with even number of elementary particle at the same time.

Experimental and Results, Gedanken Experiment

Hypothesis of a priori probability: In statistical mechanics, the mean behavior and property are studied with an usage of the suitable selected representative ensemble that has the same composition to the assembly in question. But, of course, to compose such representative ensemble, the component of the ensemble must be distributed over the state that the insufficient knowledge relating to the state of the objective assembly corresponds. Nevertheless, to distribute the component of ensemble over the state that corresponds well similarly such insufficient knowledge, the hypothesis of a priori probability must be derived newly as the postulate in quantum statistical mechanics similarly in classical statistical mechanics. And it is necessary to derive the hypothesis of a priori probability in modern statistical mechanics as the basic point.

Consider a certain physical quantity F of a certain mechanical system. The eigenvalue and eigenfunction of F are decided by eq. (IV-1) according to $Fu(q) =$

$$F_e u(q)^1).$$

$$Fu_k(q) = F_k u_k(q) \quad (IV-1)$$

And the probability amplitude Ψ is represented by eq. (IV-2) with the usage of this eigenfunction according to $\Psi(q, t) = \sum_k a_k(t) u_k(q)^1)$

$$\Psi(q, t) = \sum_k a_k(t) u_k(q) \quad (IV-2)$$

If it is found that the value is one of eigenvalue F_k after the physical quantity F is determined exactly at a certain time, namely if the system is at the state corresponding to F_k , the following eq. (IV-3) is valid at the time t_0 .

$$a_k^*(t_0) a_k(t_0) = 1 \quad (IV-3)$$

The property of the system at the time t_0 can be decided by the method of quantum mechanics with the usage of the above described equation, eq. (IV-3). Moreover, the future behavior of system is decided by Schrödinger's equation, eq. (IV-4).

$$\frac{\partial a_t}{\partial t} = -\frac{2\pi i}{h} \sum_n a_n(t) H_{l,n} = -\frac{2\pi i}{h} a_k(t) H_{l,k} \quad (IV-4)$$

On the other hand, it is assumed as follows: the determination is approximate and the state of assembly is well represented by any one of the contiguous g pieces of eigenstate corresponding to each eigenvalue $F_1, \dots, F_k, \dots, F_g$. In this case, the representative ensemble of the objective assembly must be composed with them by the usage of the method of statistical mechanics. About the representative ensemble of the assembly that the state is known only such uncertainly, the distribution matrix $\rho_{k,l}$ is composed like the expression of the following eq. (IV-5) against one k of any one of these g pieces of eigenstate

$$\rho_{k,l} = a_l^* a_k = \rho_0 \delta_{k,l} \quad (IV-5)$$

The distribution matrix $\rho_{k,l}$ is composed like the expression of the following eq. (IV-6) against the other

characteristic state.

$$\rho_{k,l} = 0 \quad (IV-6)$$

Here, ρ_0 is constant. This assumption is called as the hypothesis of a priori probability. Like the case of classical statistical mechanics, this assumption is derived as a new postulate. And this validity is recognized by the important point that the experience agrees well to the conclusion derived from this assumption.

Density matrix: The state of the mechanical system at a certain time t is decided with the probability amplitude $\Psi(q,t)$ in quantum mechanics. The mean values of various physical quantities are calculated with $\int \Psi^*(q,t_0) F(q,p,t_0) \Psi(q,t_0) dq^3$.

Here, q indicates the position coordinate q_1, \dots, q_f and the spin coordinate ω exactly. But generally q is understood as a significance of only the position coordinate like the concept that is described at the paragraph relating to Pauli's principle. Then, it is better to consider the spin in only the case that the number of eigenstate becomes the subject. And the time-like change of Ψ is decided by Schrödinger's equation, $\mathbb{H}\Psi + \frac{\hbar}{2\pi i} \frac{\partial \Psi}{\partial t} = 0$. Therefore, in quantum mechanics, the change of state of the mechanical system is possible to be pursued exactly in principle at least in analogy with the case of classical mechanics. However, the method of statistical mechanics must be applied to treat the assembly that the exact change of the state cannot be pursued by one reason. It is one reason that the determination is not exact. Namely, the assembly in the ensemble is distributed widely to the various possible states as the assembly corresponds to the uncertain circumstances obtained with these determinations. Moreover, the ensemble is composed with an aggregation of the assembly that the composition is same to the assembly in question. To study the mean property and behavior of the assembly in the ensemble is this object.

The circumstance of the ensemble in classical mechanics is indicated by distribution density ρ of the representative point in phase space like the description at the paragraph²⁾ relating to distribution density, the density matrix $\rho_{k,l}$ defined by the following condition in quantum mechanics plays a similar role to distribution density in classical mechanics.

As the consideration is indicated at the paragraph relating to eigenvalue,³⁾ in quantum mechanics, the state is described variously by the selection of any physical quantity as one eigenvalue. In statistical mechanics, the case that energy is selected as eigenvalue becomes mainly the point in question. So, to have the generality, it is assumed that arbitrary physical quantity F is selected as eigenvalue. If probability amplitude $\Psi(q,t)$ is developed by the following eq. (IV-7) with the usage of eigenvalue $u_k(q)$ of F , density matrix $\rho_{k,l}$ is defined with the following eq. (IV-8).

$$\Psi(q,t) = \sum_k a_k(t) u_k(q) \quad (IV-7)$$

$$\rho_{k,l} = \frac{1}{N} \sum_{\alpha=1}^N a_l^{(\alpha)*}(t) a_k^{(\alpha)}(t) = \overline{a_l^{*(t)} a_k(t)} \quad (IV-8)$$

Namely, $\rho_{k,l}$ is arithmetic mean value of $a_l^{(\alpha)*}(t) a_k^{(\alpha)}(t)$ against the component $\alpha = 1, 2, \dots, N$ of the ensemble. Here, $a_k^{(\alpha)}(t)$ indicates $a_k(t)$ of component α .

Probability W_k that a certain assembly is at characteristic state corresponding to eigenvalue F_k is given by the following eq. (IV-9) according to $W(F_k,t) = |a_k(t)|^2$ ⁵⁾.

$$W_k = a_k^{*(t)} a_k(t) \quad (IV-9)$$

Then, the diagonal element $\rho_{k,k}$ of matrix $\rho_{k,l}$ defined above is the probability that a certain assembly selected from the ensemble at random exists at state k .

As $\Psi(q,t)$ is normalized in 1 and $u_k(q)$ is normalized orthogonal function, the following relation indicated with the following eq. (IV-10) is valid against each assembly in the ensemble.

$$\begin{aligned} \int \Psi^* \Psi dq &= \int (\sum_l a_l^* u_l \sum_k a_k u_k) dq \\ &= \sum_{k,l} a_l^* a_k \int u_l^* u_k dq = \sum_k a_k^* a_k = 1 \end{aligned} \quad (IV-10)$$

Consequently, the following eq. (IV-11) is valid with regard to the quantity $\rho_{k,k}$ of matrix $\rho_{k,l}$ defined

$$\sum_k \rho_{k,k} = \sum_k \overline{W_k} = \sum_k \overline{a_k^* a_k} = 1 \quad (IV-11)$$

The probability that a certain assembly selected at random from the ensemble exists at an arbitrary state is 1. This result that the probability is 1 corresponds to $I = \int \dots \int \rho dq_1 \dots dp_f^2$ in classical statistical mechanics.

And the mean value regarding the ensemble of physical quantity $\rho_{k,k}$ against the assembly can be given by this $\rho_{k,k}$. If lots of determinations are averaged, the value of F against a certain assembly is given by

$$\sum_k a_k^* a_k F_k \quad \text{according to} \quad \int \Psi^*(q,t) F^n \Psi(q,t) dq = \sum_k a_k^*(t) a_k(t) (F_k)^n \quad (3)$$

Therefore, the mean value \bar{F} of this quantity against the ensemble is expressed by the following eq. (IV-12).

$$\bar{F} = \frac{\sum_k a_k^* a_k F_k}{\sum_k a_k^* a_k} = \sum_k \rho_{k,k} F_k \quad (IV-12)$$

This equation corresponds to $\bar{F} = \int \dots \int F \rho dq_1 \dots dq_f^2$ in classical statistical mechanics.

H-theorem in quantum statistical mechanics: H-theorem in quantum statistical mechanics is proved by the usage of hypothesis of a priori probability as follows: At first, a distinction between fine-grained density and coarse-grained density must be considered in detail. As the diagonal element $\rho_{k,k} = a_k^* a_k$ of density matrix $\rho_{k,l}$ gives the probability that the assembly selected at random from the ensemble exists at state k , it is called as fine-grained density. On the other hand, the case of existence of limit in accuracy of determination comes into question in statistical mechanics. So, it is assumed as follows: the contiguous g pieces of state l, \dots, k, \dots, g that has well similar property for it cannot be distinguished each other. Then, coarse-grained density is defined by the following eq. (IV-13).

$$P_k = \frac{\sum_{k=1}^g \rho_{k,k}}{g} \quad (IV-13)$$

As this definition clarifies, P_k is arithmetic mean value of the probability that the assembly in the ensemble exists at one of the contiguous g pieces of state. And as the probability exists at any state of all state is 1, the following relation is valid as shown in the following eq. (IV-14).

$$\sum_k P_k = 1 \quad (IV-14)$$

The quantity H against the ensemble according to the quantity P_k is defined by the following eq. (IV-15).

$$H = \sum_k P_k \log P_k \quad (IV-15)$$

Here, the summation is made about all state k . P_k is same against the contiguous g pieces of state k , consequently $\log P_k$ is same to them. And as it is expressed as $g P_k = \sum_k \rho_{k,k}$ according to eq. (IV-13), also H is expressed by the following eq. (IV-16).

$$H = \sum_k \rho_{k,k} \log P_k \quad (IV-16)$$

As taking various things into consideration in classical statistical mechanics, when the quantity F of the objective assembly is determined approximately at the time t_0 and the representative ensemble of the assembly is expressed, the component of the ensemble is distributed homogeneously over the contiguous g pieces of state of F_k according to hypothesis of a priori probability. Namely, the following relation is valid as shown in the following eq. (IV-17).

$$\rho_{k,k}(t_0) = P_k(t_0) \quad (IV-17)$$

In consequence, if H at the initial time t_0 is expressed by $H(t_0)$, and if H at the late time t is expressed by $H(t)$, the following relation is obtained as shown in the following eq. (IV-18).

$$H(t) - H(t_0) = \sum_k \rho_{k,k}(t_0) \log \rho_{k,k}(t_0) - \sum_l \rho_{l,l}(t) \log P_l(t) \quad (IV-18)$$

Then, Klein's relation equation⁵⁾ obtained from the general solution of Schrödinger's equation against the isolated system is expressed as the following eq. (IV-19).

$$\sum_k \rho_{k,k}(t_0) \log \rho_{k,k}(t_0) \geq \sum_l \rho_{l,l}(t) \log \rho_{l,l}(t) \quad (IV-19)$$

When eq. (IV-19) is substituted in eq. (IV-18), the following relation is obtained as shown in the following eq. (IV-20).

$$H(t_0) - H(t) \geq \sum_l \left\{ \rho_{l,l}(t) \log \rho_{l,l}(t) - \rho_{l,l}(t) \log P_l(t) \right\} \quad (IV-20)$$

$$\sum_k E_k \delta P_k = 0 \quad (IV-25)$$

And the following relation shown in the following eq. (IV-21) is obtained from eq. (IV-11) and eq. (IV-14).

$$H(t_0) - H(t) \geq \sum_l \left\{ \rho_{l,l}(t) \log \rho_{l,l}(t) - \rho_{l,l}(t) \log P_l(t) - \rho_{l,l}(t) + P_l(t) \right\} \quad (IV-21)$$

Then, as the following relation shown in the following eq. (IV-22) is proved at the paragraph of H-theorem of Gibbs³⁾ in classical statistical mechanics,

$$\rho \log \rho - \rho \log P - \rho + P \geq 0 \quad (IV-22)$$

the following relation is obtained as shown in the following eq. (IV-23).

$$H(t_0) - H(t) \geq 0 \quad (IV-23)$$

That is to say, the quantity H decreases with time and finally it becomes minimum value. In this case, the relation, $\rho_{k,k} = P_k$, is obtained from eq. (IV-23). From eq. (IV-19), $\rho_{k,k}$ does not change with time and the assembly exists at statistical equilibrium.

Even if the real assembly exists at "equilibrium state", the energy is lost or obtained by collision between the chemical species and its surroundings. Therefore, there are two kinds of consideration. The first consideration is general consideration that the total energy is exactly constant. The second consideration that the statistical mean value E of energy of the representative ensemble is regarded as being constant may be more natural than the first consideration. And, if the condition that H in this case becomes minimum is considered, the following relation may be valid as follows. Now, if the energy is selected as eigenvalue, the following relation is valid as shown in the following eq. (IV-24).

$$\sum_k P_k E_k = \bar{E} = \text{constant} \quad (IV-24)$$

In consequence, the variations equation is valid as shown in the following eq. (IV-25).

also, the following eq. (IV-26) is valid from eq. (IV-14).

$$\sum_k P_k = 1 \quad (IV-26)$$

Consequently, the following eq. (IV-27) is valid.

$$\sum_k \delta P_k = 0 \quad (IV-27)$$

Moreover, as H , $H = \sum_k P_k \log P_k$, is minimum, the following eq. (IV-28) is valid.

$$\delta H = \sum_k (\log P_k + 1) \delta P_k = 0 \quad (IV-28)$$

These three variations equations are combined by the method of undermined multipliers of Lagrange, then the following relation is obtained as shown in the following eq. (IV-29).

$$\sum_k (\log P_k - \frac{\varphi}{\theta} + \frac{1}{\theta} E_k) \delta P_k = 0 \quad (IV-29)$$

Here, $-\frac{\varphi}{\theta}$ and $\frac{1}{\theta}$ are undetermined multipliers. In this variations equation, as δP_k is entirely arbitrary, the coefficient must be zero. Namely, against each characteristic state k the following relation is valid as shown in the following eq. (IV-30).

$$\log P_k - \frac{\varphi}{\theta} + \frac{1}{\theta} E_k = 0 \quad (IV-30)$$

That is to say, the following relation is valid as shown in the following eq. (IV-31).

$$P_k = e^{\frac{\varphi - E_k}{\theta}} \quad (IV-31)$$

So, the canonical ensemble is given. Thus, the canonical ensemble can express the assembly that \bar{E} is constant. Also, the canonical ensemble can indicate that the assembly exists at statistical equilibrium.

Statistical equilibrium: Liouville's theorem in quantum mechanics; Like the description of paragraph relating to density matrix, the exact circumstance of the ensemble is described by density matrix $\rho_{k,l}$ in quantum statistical mechanics. Then, it is considered that $\rho_{k,l}$

occurs any change with time.

At first, time differential of $a_l(t)$ is given by generalized Schrödinger's equation, $\frac{\partial a_l(t)}{\partial t} = -\frac{2\pi i}{h} \sum_k a_k(t) H_{l,k}$ ³⁾ Namely, the following relation is valid as shown in the following eq. (IV-32).

$$\frac{\partial a_l}{\partial t} = -\frac{2\pi i}{h} \sum_n a_n(t) H_{l,n} \quad (IV-32)$$

Therefore, the following relation is derived as follows;

$$\begin{aligned} \frac{\partial \rho_{k,l}}{\partial t} &= \frac{\partial}{\partial t} \overline{a_l^* a_k} = \overline{a_l^*} \frac{\partial a_k}{\partial t} + a_k \frac{\partial \overline{a_l^*}}{\partial t} \\ &= -\frac{2\pi i}{h} \sum_n (H_{k,n} \overline{a_l^* a_n} - H_{l,n}^* \overline{a_n^* a_k}) \\ &= -\frac{2\pi i}{h} \sum_n (H_{k,n} \rho_{n,l} - \rho_{k,n} H_{n,l}^*) \end{aligned} \quad (IV-33)$$

Here, the last equation is obtained from $H_{l,k} = H_{k,l}^*$ ³⁾. This equation is called as Liouville theorem in quantum mechanics. There is the assembly represented by the ensemble that distributes to various quantum states, as $\rho_{k,l}$ does not change with time. It is said that the assembly exists at statistical equilibrium. If $\rho_{k,l}$ is the function that is the exchangeable quantity – constant of motion – to Hamiltonian operator, $\rho_{k,l}$ is possible to exchange to H operator itself. ⁴⁾ In consequence, it does not change with time as the development can be understood from eq. (IV-33). The case that $\rho_{k,l}$ is the function of energy is especially interested to statistical mechanics among others. If energy is selected as eigenvalue, the description of $\rho_{k,l}$ becomes simplest in the above described case. Then, such two examples are tried to show as follows;

(1) Microcanonical ensemble: In this ensemble, the component distributes homogeneously to characteristic state of energy that is between energy range E and energy range $E + \delta E$. Moreover, the component does not distribute to other range. That is to say, the following relations are shown in the following eq. (IV-34) and eq. (IV-35) respectively.

$$\rho_{k,l} = \rho_0 \delta_{k,l} \quad (IV-34)$$

Here, in the case that E_k exists between energy range E and energy range $E + \delta E$.

Next,

$$\rho_{k,l} = 0 \quad (IV-35)$$

Here, in the case that E_k exists in the other energy range.

(2) Canonical ensemble: In this ensemble, $\rho_{k,l}$ is given by the following eq. (IV-36).

$$\rho_{k,l} = e^{-\frac{\varphi - E_k}{\theta}} \delta_{k,l} \quad (IV-36)$$

Therefore, the following relation is derived as follows;

$$\rho_{k,k} = e^{-\frac{\varphi - E_k}{\theta}} \quad (IV-37)$$

And the following relation is derived from eq. (IV-11) as shown in the following eq. (IV-38).

$$\sum_k \rho_{k,k} = \sum_k e^{-\frac{\varphi - E_k}{\theta}} = 1 \quad (IV-38)$$

Consequently, the relation between parameter of distribution φ and parameter distribution θ is shown in the following eq. (IV-39).

$$e^{-\frac{\varphi}{\theta}} = \sum_k e^{-\frac{E_k}{\theta}} \quad (IV-39)$$

Then, canonical ensemble is just appropriate to represent the assembly existed at a constant temperature. And canonical ensemble is important especially to consider the relation between statistical mechanics and thermodynamics.

Pauli's principle: Spin: Uhlenbeck and Goudsmit ⁶⁾ introduced position, momentum and a new physical quantity, spin, into electron for the explanation of the multiple property (multiplicity) that is determined in atomic spectrum of alkali metal. As the example of the phenomenon of multiplicity, two determinations are shown as follows; Namely, 1) two D lines of natrium (Na) appears. 2) anomalous Zeeman effect appears when they are placed in magnetic field.

The spin could not be found in classical mechanics and is characteristic angular momentum and magnetic efficiency. The multiplicity of atomic spectrum is given as magnetic interaction between spin of electron and orbital momentum. Successively, it is found that spin exists in other elementary particle, positron, and

neutron.

The following assumption is necessary to explain the experimental result. Namely, spin possesses a parallel component s_x, s_y, s_z , to each axis x, y, z , and each characteristic angular momentum is which of $+\frac{1}{2}h/2\pi$ or $-\frac{1}{2}h/2\pi$. Pauli⁷⁾ inducted operator S_x, S_y, S_z , that posseses the same property to angular momentum of classical quantity against s_x, s_y, s_z . The different point from angular momentum is the point that eigenvalue of these spin variables is only $\pm\frac{1}{2}$. For example, $s_x = \frac{1}{2}$ means that a parallel characteristic angular momentum to axis x is $\frac{1}{2}h/2\pi$.

The operator S_x, S_y, S_z is unexchangeable each other, but is changeable to operator of position. Therefore, one component $-s_z$ is selected generally – and position can be determined together. Consequently, Ψ of elementary particle is regarded as $\Psi(x, y, z, \omega, t)$. The $\Psi(x, y, z, \omega, t)$ is the function of position x, y, z , that is continuous variable and is the function of spin coordinate ω at the same time, and the operation of S_z to Ψ is given by the following relation as shown in the following eq. (IV-39) and eq. (IV-40) respectively.

$$S_z\Psi(x, y, z, \omega = +\frac{1}{2}, t) = +\frac{1}{2}\Psi(x, y, z, \omega = +\frac{1}{2}, t) \quad \text{(IV-39)}$$

$$S_z\Psi(x, y, z, \omega = -\frac{1}{2}, t) = -\frac{1}{2}\Psi(x, y, z, \omega = -\frac{1}{2}, t) \quad \text{(IV-40)}$$

In the generality of cases, as Hamilton function is little affected by the magnetic interaction of spin and orbital momentum, the concept and the development of consideration at the paragraphs relating to quantum mechanics²⁾ and eigenvalue, characteristic value, are valid without modification. However, as s_z possesses two eigenvalues of $+\frac{1}{2}$ or $-\frac{1}{2}$, it is one specific result that number of eigenfunction doubles.

After Pauli assumed that electron cannot exist only one else at the same quantum state that includes the spin, also, he can explain the periodic law of element with limitation of arrangement of electron in atom. This assumption is called as Pauli's principle. At late time, this assumption is extended further. So, a lot of fact can be found as the following description. The elementary particle – electron, positron, neutron –

that the spin is $\frac{1}{2}$ cannot exist until only one at the same quantum state. Also, the chemical species that is composed with odd number of elementary particle cannot exist until only one at the same quantum state. However, photon, meson, and chemical species that is composed with even number of elementary particle can exist until even many times at one state against the former elementary particles.

Discussion and Conclusion

Hypothesis of a priori probability: The hypothesis of a priori probability is introduced to modern quantum statistical mechanics similary to classical statistical mechanics as one postulate. The recognition of validity of introduction is placed on the point that the conclusion derived agrees well to the experience. The result produced from the experience is most valuable, because the result is the established fact. However, it must be considered that there is its level at its experience. The concept and value of hypothesis of a priori probability in classical statistical mechanics are compared with the concept and value of hypothesis of a priori probability in modern quantum statistical mechanics.

Density matrix: The circumstance of the ensemble is represented by distribution density of the representative point in the phase space in classical mechanics. Density matrix in quantum mechanics fills the similar role of distribution density in classical mechanics.

The concept of the ensemble in classical mechanics is compared with the concept of the ensemble in quantum mechanics. Also, as the ensemble is composed with the assembly, the summation of the behavior of assembly represents the behavior of ensemble. Moreover, as the assembly is composed with the representative point, the summation of the behavior of representative point represents the behavior of assembly.

H – theorem: H – theorem considered in classical statistical mechanics is considered similarly in quantum statistical mechanics. H – theorem in quantum mechanics is considered on the base of hypothesis of a priori probability. The probability that the assembly exists at one state at random is given by the diagonal element of density matrix. Namely, it is called as coarse-grained density. Generally, one problem in statistical

mechanics is the case of limitation of accuracy of determination. The coarse-grained density is arithmetic mean value of the probability that the assembly in the ensemble exists at one state of the contiguous states. As the probability that exists at any state of all state is normalized, the quantity H against the ensemble is defined. The concept is developed similarly in classical statistical mechanics. So, Klein relation equation is derived from the general solution of Schrödinger equation against the isolated system.

As the explanation in classical statistical mechanics, the quantity H decreases with time. And it becomes minimum at last. So, density matrix is unchangeable with time. And the assembly exists at statistical equilibrium.

However, the real assembly that exists at equilibrium state lost or obtained the energy as the chemical species collides with the surroundings. So, there are two kinds of understanding as follows; the first one: the statistical mean value of energy of the representative ensemble is constant. The second one: the total energy is exactly constant. In comparison of the both understanding, the regarding as the second one is more natural than the first one. Then, consider the condition that the quantity H becomes minimum. So, energy is selected as eigenvalue. And, according to the method of undetermined multipliers of Lagrange, after three variations equations are combined, the coarse-grained density against each characteristic state is obtained. Namely, the ensemble is given as a canonical ensemble. Thus, canonical ensemble represents the assembly that exists at statistical equilibrium under the constant mean energy.

Statistical equilibrium: the treatment of the representative point in classical statistical mechanics is compared with the treatment of the representative point in quantum statistical mechanics. The concept of the distribution density in classical statistical mechanics is compared with the concept of the density matrix in quantum statistical mechanics.

The exact circumstance of the ensemble is indicated by density matrix. So, Liouville's theorem is classical statistical mechanics. The statistical equilibrium of the assembly is considered in the both mechanics. Then, microcanonical ensemble and canonical ensemble are explained on the back ground of consideration about

the relation between both statistical mechanics and thermodynamics.

Pauli's principle: A new physical quantity that cannot be found in classical mechanics is introduced to modern quantum mechanics. The spin that is characteristic angular momentum and magnetic efficiency is considered as a new physical quantity. And the spin is proved in positron, proton, and neutron, but it has a characteristic angular momentum of $+\frac{1}{2}h/2\pi$ or $-\frac{1}{2}h/2\pi$ and has the parallel component with axis. The validity of spin is held by the assumptions of characteristic angular momentum and parallel component with axis.

Some new phenomena are discovered in the field of physics. However, the result appeared in the experimental condition that can be changed mainly by artificial method becomes the objective problem. Namely, the experimental result is classified from the result of natural phenomenon, and is studied successively. But, some problems that could not be treated by classical mechanics appeared with the progress of study year by year. So, to solve the problem, the method of quantum mechanics is applied with new concept.

Pauli inducted this operator that possesses similar property to classical quantity against parallel component to axis. The specific point that spin variable of eigenvalue is only $\pm\frac{1}{2}$ is different from angular momentum. This operator is unexchangeable each other, but is exchangeable to the operator of position. So, Ψ of elementary particle is regarded as the function of both position of continuous variable and spin coordinate. Generally, Hamilton function does not be affected almost by magnetic interaction of both spin and orbital momentum. As one component of spin s_z possesses two eigenvalues, $+\frac{1}{2}$ or $-\frac{1}{2}$, eigenfunction doubles.

Pauli assumed that only one electron exists at the same quantum state. This assumption is applied to the electron, proton, neutron, or the chemical species composed with odd number of elementary particle.

Summary

The concept in classical statistical mechanics is compared and considered with the concept in quantum statistical mechanics.

Hypothesis of a priori probability: In statistical

mechanics, by using the representative ensemble that is the same composition to the assembly in question, its mean behavior and property are studied. And the component of ensemble has to be distributed corresponding to unsatisfactory knowledge. The hypothesis of a priori probability is necessary to be deduced as a postulate, and it in classical statistical mechanics is considered in comparison with quantum statistical mechanics. The validity of introduction of the assumption, hypothesis, is proved by the agreement between the conclusion derived and the experience.

Density matrix: In quantum mechanics, the state of mechanical system at a certain time is decided by probability amplitude, and can be pursued at least like classical mechanics. Density matrix in quantum mechanics plays a similar role to distribution density in classical mechanics. The concept in quantum statistical mechanics corresponds well to the concept in classical statistical mechanics.

H – Theorem: H – theorem in quantum statistical mechanics is proved with the hypothesis of a priori probability. Fine-grained density and coarse-grained density are considered separately. And, the component of ensemble is distributed homogeneously to the state decided by the hypothesis. Canonical ensemble expresses assembly that statistical mean value of energy is constant under existence of statistical equilibrium.

Statistical equilibrium: The exact circumstance in quantum statistical mechanics is described with density matrix. The time-like change of density matrix is considered. And Liouville theorem is derived. The case that the density matrix is a function of energy is interested in statistical mechanics. Microcanonical ensemble and canonical ensemble are considered. So, canonical ensemble is satisfactory for represent the assembly existed at constant temperature, and it is important to consider the relation between statistical mechanics and thermodynamics.

Pauli's principle: Uhlenbeck and Goudsmit deduced position, momentum, and new physical quantity (spin) to electron. Spin cannot be found in classical mechanics. Spin is found in positron, proton, and neutron. Spin possesses three components that characteristic angular momentum is $+\frac{1}{2}h/2\pi$ or $-\frac{1}{2}h/2\pi$. Pauli assumed that only one electron exists at the same quantum state.

This principle is developed to electron, proton, neutron, chemical species composed with odd number of elementary particle, and photon, meson, chemical species composed with even number of elementary particle.

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化学反応の理論的取扱

第4報 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, 本報では量子力学の一部(紙面の都合上)に関し報告する。前報同様に古典力学, 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とともにもそれらを基にし, 次の項に関し合せて記した。(1)先験的確率の仮定, (2)密度マトリックス, (3)H定理, (4)統計的平衡, (5)Pauli の原則。

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