

# Second quantization representation for classical many-particle system

Masao Doi

Department of Physics, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo, 158 Japan

Received 11 February 1976, in final form 5 April 1976

**Abstract.** The second quantization method is applied to classical many-particle systems. Statistical quantities such as free energy and time correlation functions are expressed in terms of creation and annihilation operators. The method is especially useful for the system in which the number of the composite molecules changes with time, e.g. the system including chemical reaction.

## 1. Introduction

The second quantization method is a very convenient way of treating quantum many-body problems. Almost all quantum many-body theories are written in this representation (Abrikosov *et al* 1963). The method, however, is not limited to quantum systems. In fact, creation and annihilation operators  $\psi^\dagger(\mathbf{r})$  and  $\psi(\mathbf{r})$  can be introduced independently of the quantum conditions; they are operationally defined by the following commutation relations:

$$[\psi(\mathbf{r}), \psi^\dagger(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}'), \quad [\psi(\mathbf{r}), \psi(\mathbf{r}')] = [\psi^\dagger(\mathbf{r}), \psi^\dagger(\mathbf{r}')] = 0, \quad (1)$$

together with the definition of the vacuum state  $|0\rangle$ ,

$$\psi(\mathbf{r})|0\rangle = 0 \quad \langle 0|\psi^\dagger(\mathbf{r}) = 0. \quad (2)$$

Planck's constant  $\hbar$  does not appear in these expressions. Therefore it is possible to introduce these operators into classical many-particle systems. The purpose of this paper is to develop such a formulation.

The present formulation differs from the theory recently developed by Martin *et al* (1973, see also Phythian 1975, 1976). They start from the differential equation for the operators under consideration, but we start from the time evolution equation for the probability distribution function. The present formulation resembles more closely the standard operator formalism of quantum field theory (de Boer 1965). To clarify this point, we first give a rough outline of our method.

Consider a system consisting of  $N$  identical molecules. Let  $q_i$  be the set of coordinates specifying the state of each molecule:  $q_i$  may be the position and momentum coordinates and, if necessary, other coordinates describing the internal degrees of

freedom. Let us consider the problem: given the time evolution equation for the probability distribution function  $f^{(N)}(q_1, q_2, \dots, q_N; t) = f^{(N)}(q^N; t)$ ,

$$\frac{\partial}{\partial t} f^{(N)}(q^N; t) + \mathcal{G}^{(N)} f^{(N)}(q^N; t) = 0, \quad (3)$$

together with the initial condition  $f^{(N)}(q^N; 0)$ , calculate the mean value of some physical quantity  $A(q^N)$  at time  $t$ :

$$\bar{A}(t) = \int dq^N A(q^N) f^{(N)}(q^N; t); \quad dq^N = dq_1 dq_2 \dots dq_N. \quad (4)$$

We shall show that  $\bar{A}(t)$  is expressed in terms of the creation and annihilation operators  $\psi^\dagger(q)$  and  $\psi(q)$  as

$$\bar{A}(t) = \langle \text{sum} | \tilde{A}[\psi^\dagger, \psi] \exp(-\tilde{\mathcal{G}}[\psi^\dagger, \psi]t) | F(t=0) \rangle, \quad (5)$$

where  $\tilde{A}[\psi^\dagger, \psi]$  and  $\tilde{\mathcal{G}}[\psi^\dagger, \psi]$  are the 'quantum' operators which are constructed from  $A$  and  $\mathcal{G}^{(N)}$  just as in quantum field theory,  $|F(t=0)\rangle$  is a 'quantum' state determined by the initial distribution function  $f^{(N)}(q^N; 0)$ , and  $\langle \text{sum} |$  is given by

$$\langle \text{sum} | = \langle 0 | \exp\left(\int dq \psi(q)\right). \quad (6)$$

In general, the distribution function  $f^{(N)}(q^N; t)$  corresponds to a quantum state, physical quantities to quantum operators, and the operation of taking the average is equivalent to that of taking the scalar product with the state  $\langle \text{sum} |$ .

From the practical viewpoint, the second quantization representation may not be a very useful one for the usual classical systems, though some of the formal discussions are simplified. The difficulty in calculating equation (5) is almost the same as equation (4). However, there are cases where the second quantization representation is clearly advantageous. A typical example is the system including chemical reaction. In that system, the number of the composite molecules changes with time owing to the reaction. The time evolution operator includes the terms describing the transition between states containing different numbers of molecules. Therefore, for the complete statistical description, the set of distribution functions  $f^{(N)}, f^{(N-1)}, \dots$  must be considered, and analyses must be made in the Fock space. For this system, a serious difficulty arises in the conventional representation: to define the distribution function  $f^{(N)}(q^N; t)$ , we must label all molecules existing in the system; however, the procedure of labelling becomes complicated if the molecules are created or destroyed in the course of time. (As a matter of fact, this difficulty can be removed by introducing a new definition of the distribution function (see § 2), but even in that case the time evolution equation is still very complicated (see equation (51)).)

The second quantization method removes these difficulties. It is the method most suitable for treating the Fock space, and it does not require the labelling of molecules.

Actually, the present work is motivated by the problem of chemical reaction. The chemical reaction is a prototype of those problems for which the composite elements change with time through birth and death processes, or fusion and fission processes. Therefore the method developed here may be applied to a rather wider class of problems. In this paper, however, we do not discuss these applications, but restrict ourselves to the general scheme of formulation. An actual calculation and discussion of the chemical reaction problem is given in a separate paper (Doi 1976).

## 2. Specification of the states

First we clarify the meaning of 'state' used in this paper. We consider a system consisting of  $N$  identical molecules. In the conventional description, all the molecules are numbered as  $1, 2, \dots, N$ , and the state  $(q_1, q_2, \dots, q_N) = q^N$  is defined as the state for which the  $i$ th molecule is located at  $q_i$  ( $i = 1, 2, \dots, N$ ). Following this definition the states  $(q_1, q_2, \dots, q_N)$  and  $(q_2, q_1, \dots, q_N)$  are different. The conventional distribution function  $f^{(N)}(q^N; t)$  is normalized as

$$\int dq^N f^{(N)}(q^N; t) = 1. \quad (7)$$

However, if the molecules are identical, we need not distinguish the states  $(q_1, q_2, \dots, q_N)$  and  $(q_2, q_1, \dots, q_N)$  etc, because they are physically equivalent. In this paper we regard them as the same states. More generally, we define the system to be in a state  $(q_1, q_2, \dots, q_N) = q^N$  if the system consists of  $N$  molecules, and if these molecules are located at  $q_1, q_2, \dots, q_N$ . Let  $F^{(N)}(q^N; t)$  be the probability of finding the system in a state  $q^N$  of this definition.  $F^{(N)}(q^N; t)$  is related to  $f^{(N)}(q^N; t)$  as

$$F^{(N)}(q^N; t) = \sum_{\substack{\text{all} \\ \text{permutations} \\ \text{of } q_i}} f^{(N)}(q_1, \dots, q_N; t) \quad (8)$$

where the summation is taken over all permutations of the arguments of  $f^{(N)}(q^N; t)$ . Clearly  $F^{(N)}(q^N; t)$  is symmetric with respect to its arguments.

The normalization of  $F^{(N)}(q^N; t)$  is different from that of  $f^{(N)}(q^N; t)$ . If  $F^{(N)}(q^N; t)$  is integrated over all possible values of  $q_1, q_2, \dots, q_N$ , the same state  $(q_1, q_2, \dots, q_N)$ ,  $(q_2, q_1, \dots, q_N)$  etc is counted  $N!$  times. Such overcounting is avoided if the integration is taken under the condition  $q_1 \leq q_2 \leq \dots \leq q_N$ . (If  $q_i$  stands for the set of variables  $(q_{i1}, q_{i2}, \dots)$ , the inequality should be understood as  $q_{11} \leq q_{21} \leq \dots \leq q_{N1}$ .) The normalization of  $F^{(N)}(q^N; t)$  is thus

$$\int_{q_1 \leq q_2 \leq \dots \leq q_N} dq^N F^{(N)}(q^N; t) = 1. \quad (9)$$

We shall denote the integral  $\int dq^N$  under the condition  $q_1 \leq q_2 \leq \dots \leq q_N$  as  $\int dQ^N$ . Evidently the following identity:

$$\int dQ^N \dots \equiv \int_{q_1 \leq q_2 \leq \dots \leq q_N} dq^N \dots = \frac{1}{N!} \int dq^N \dots \quad (10)$$

holds if the integrand is a symmetric function of  $q_i$ . The normalization condition (9) is also derived from equations (7), (8) and (10).

If the number of molecules is not fixed, we must consider a set of probability distribution functions  $\{F^{(0)}(t), F^{(1)}(q^1; t), F^{(2)}(q^2; t), \dots\} = F(t)$ . These functions are normalized as

$$\sum_{N=0}^{\infty} \int dQ^N F^{(N)}(q^N; t) = 1. \quad (11)$$

Equation (9) is a special case of this equation.

### 3. Second quantization representation

To the distribution function  $F(t)$ , we assign a 'quantum' state  $|F(t)\rangle$  as

$$|F(t)\rangle = \sum_{N=0}^{\infty} \int dQ^N F^{(N)}(q^N; t) \psi^\dagger(q_1) \psi^\dagger(q_2) \dots \psi^\dagger(q_N) |0\rangle, \quad (12)$$

where  $|0\rangle$  is the vacuum state:

$$\psi(q)|0\rangle = 0, \quad \langle 0|\psi^\dagger(q) = 0, \quad (13)$$

and  $\psi^\dagger(q)$  and  $\psi(q)$  are creation and annihilation operators which satisfy the commutation relations

$$[\psi(q), \psi^\dagger(q')] = \delta(q - q'), \quad [\psi(q), \psi(q')] = [\psi^\dagger(q), \psi^\dagger(q')] = 0. \quad (14)$$

For simplicity, we use the abbreviation

$$\begin{aligned} |q^N\rangle &\equiv |q_1, q_2, \dots, q_N\rangle \equiv \psi^\dagger(q_1) \psi^\dagger(q_2) \dots \psi^\dagger(q_N) |0\rangle, \\ \langle q^N| &\equiv \langle 0| \psi(q_1) \dots \psi(q_N). \end{aligned} \quad (15)$$

The following identities can be readily shown from equations (13) and (14):

$$\begin{aligned} \langle q|q'\rangle &= \delta(q - q') \\ \langle q^N|q'^{N'}\rangle &= \delta_{NN'} \sum_{\substack{\text{all} \\ \text{permutations} \\ \text{of } q_i}} \prod_{i=1}^N (q_i - q'_i). \end{aligned} \quad (16)$$

Then from equations (12) and (16)

$$F^{(N)}(q^N; t) = \langle q^N|F(t)\rangle. \quad (17)$$

Equations (12) and (17) indicate that there is a unique correspondence between a set of functions  $F = \{F^{(0)}, F^{(1)}, \dots\}$  and the quantum state  $|F\rangle$ . Note that  $F$  need not be a distribution function but may be a general set of functions provided its components are symmetric functions.

Next we consider a linear operator  $A$  which transforms  $F = \{F^{(0)}, F^{(1)}, \dots\}$  to  $F_A = \{F_A^{(0)}, F_A^{(1)}, \dots\}$ :

$$F_A = AF. \quad (18)$$

We assign a quantum operator  $\tilde{A}$  to  $A$  in such a way that  $|F_A\rangle$  is equal to  $\tilde{A}|F\rangle$  or, equivalently, that

$$F_A^{(N)}(q^N) = \langle q^N|\tilde{A}|F\rangle \quad (19)$$

for any  $|F\rangle$ . For the pertinent system of identical molecules, most operators are written in the following form:

$$F_A^{(N)}(q^N) = A^{(N)}(q^N) F^{(N)}(q^N), \quad (20)$$

with

$$A^{(N)}(q^N) = \sum_{i=1}^N A_1(q_i) + \sum_{1 \leq i < j \leq N} A_2(q_i, q_j) + \dots, \quad (21)$$

where  $A_1(q_i)$  (or  $A_2(q_i, q_j)$ ) is a linear operator depending only on  $q_i$  (or  $q_i$  and  $q_j$ ).

Examples of such operators are: the Liouville operator  $\mathcal{L}$ ,

$$\mathcal{L}^{(N)} = \sum_{i=1}^N \frac{p_i}{m} \frac{\partial}{\partial r_i} - \sum_{1 \leq i < j \leq N} \frac{\partial u(r_i - r_j)}{\partial r_i} \left( \frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) \quad (22)$$

(where  $m$  is mass,  $p_i, r_i$  are momentum and position coordinates respectively and  $u(r_i - r_j)$  is the interaction potential); and the number density operators  $n(r), n(r, r')$ ,

$$\begin{aligned} n(r) &= \sum_{i=1}^N \delta(r - r_i), \\ n(r, r') &= \sum_{1 \leq i \neq j \leq N} \delta(r - r_i) \delta(r' - r_j). \end{aligned} \quad (23)$$

For this type of operator,  $\tilde{A}$  is found to be

$$\begin{aligned} \tilde{A} &= \tilde{A}_1 + \tilde{A}_2 + \dots, \\ \tilde{A}_1 &= \int dq \psi^\dagger(q) A_1(q) \psi(q), \\ \tilde{A}_2 &= \frac{1}{2} \int dq dq' \psi^\dagger(q) \psi^\dagger(q') A_2(q, q') \psi(q) \psi(q'), \\ &\vdots \end{aligned} \quad (24)$$

These expressions are just the same as those in quantum field theory. Equation (24) is readily verified by use of equations (13) and (14), for example,

$$\begin{aligned} \tilde{A}_1 |F\rangle &= \sum_{N=0}^{\infty} \int dQ^N F^{(N)}(q^N) \int dq \psi^\dagger(q) A_1(q) \psi(q) \psi^\dagger(q_1) \dots \psi^\dagger(q_N) |0\rangle \\ &= \sum_{N=0}^{\infty} \int dQ^N F^{(N)}(q^N) \int dq \psi^\dagger(q) A_1(q) \\ &\quad \times \sum_{i=1}^N \delta(q - q_i) \psi^\dagger(q_1) \dots \psi^\dagger(q_{i-1}) \psi^\dagger(q_{i+1}) \dots \psi^\dagger(q_N) |0\rangle \\ &= \sum_{N=0}^{\infty} \int dQ^N \left( \sum_{i=1}^N A_1(q_i) F^{(N)}(q^N) \right) \psi^\dagger(q_1) \dots \psi^\dagger(q_N) |0\rangle \\ &= |F_{A_1}\rangle. \end{aligned} \quad (25)$$

In particular, the density operators are written as

$$\begin{aligned} \tilde{n}(r) &= \psi^\dagger(r) \psi(r) \\ \tilde{n}(r, r') &= \psi^\dagger(r) \psi^\dagger(r') \psi(r) \psi(r'). \end{aligned} \quad (26)$$

If the system includes chemical reaction, we must treat operators connecting the states with different numbers of composite molecules. Such operators will be discussed in § 5.

Next we introduce states  $|\alpha\rangle$  and  $\langle\alpha|$  defined by

$$|\alpha\rangle = \exp\left(\alpha \int dq \psi^\dagger(q)\right) |0\rangle, \quad \langle\alpha| = \langle 0| \exp\left(\alpha \int dq \psi(q)\right), \quad (27)$$

where  $\alpha$  is a real number. These states will appear frequently in the following

discussions. The state  $|\alpha\rangle$  is a coherent state introduced by Glauber (1963). An important property of  $|\alpha\rangle$  is that it is an eigenstate of the operator  $\psi(q)$ :

$$\psi(q)|\alpha\rangle = \alpha|\alpha\rangle, \quad \langle\alpha|\psi^\dagger(q) = \alpha\langle\alpha|. \tag{28}$$

These relations are justified by use of equations (13) and (14).

The state  $|\alpha = 1\rangle$  is particularly important. Consider the scalar product

$$\langle\alpha = 1|F\rangle = \langle 0|\exp\left(\int dq \psi(q)\right)|F\rangle. \tag{29}$$

Expanding  $\exp(\int dq \psi(q))$  and using equation (17), we have

$$\langle\alpha = 1|F\rangle = \sum_{N=0}^{\infty} \frac{1}{N!} \int dq^N \langle q^N|F\rangle = \sum_{N=0}^{\infty} \int dQ^N F^{(N)}(q^N). \tag{30}$$

Thus the operation of taking the scalar product between  $\langle\alpha = 1|$  and  $|F\rangle$  is equivalent to the operation of summing up all the states, i.e.

$$\langle\alpha = 1|\dots\rangle \Leftrightarrow \sum \int dQ^N \dots \tag{31}$$

For this reason, we may write  $\langle\alpha = 1|$  as  $\langle\text{sum}|$ . As a special case of equation (28), we have

$$\langle\text{sum}|\psi^\dagger(q) = \langle\text{sum}|. \tag{32}$$

If  $F(t)$  denotes the distribution function, the normalization condition (11) is simply written as

$$\langle\text{sum}|F(t)\rangle = 1. \tag{33}$$

The mean value of some physical quantity  $A$  is expressed by use of  $\langle\text{sum}|$ . As is understood in the example of the density operator, any physical quantity can be regarded as an operator in the sense of equation (18). Thus the mean value is given by

$$\bar{A}(t) = \sum_{N=0}^{\infty} \int dQ^N A^{(N)}(q^N) F^{(N)}(q^N; t) = \langle\text{sum}|\bar{A}|F(t)\rangle. \tag{34}$$

Let  $\tilde{\mathcal{G}}$  be the quantum operator associated with the time evolution operator  $\mathcal{G}$ . From the equation

$$\frac{\partial}{\partial t}|F(t)\rangle + \tilde{\mathcal{G}}|F(t)\rangle = 0 \tag{35}$$

$|F(t)\rangle$  is solved as

$$|F(t)\rangle = \exp(-\tilde{\mathcal{G}}t)|F(t=0)\rangle, \tag{36}$$

then equation (34) is rewritten as

$$\bar{A}(t) = \langle\text{sum}|\bar{A} \exp(-\tilde{\mathcal{G}}t)|F(t=0)\rangle. \tag{37}$$

In particular, the equilibrium time correlation function is written as

$$\overline{A(t)B(0)} = \langle\text{sum}|\bar{A} \exp(-\tilde{\mathcal{G}}t)\bar{B}|eq\rangle, \tag{38}$$

where  $|eq\rangle$  denotes the ‘quantum’ state corresponding to the equilibrium distribution function. Examples of  $|eq\rangle$  will be given in the next section.

Equations (37) and (38) are the final results of our formal discussion. Operators  $\tilde{A}$ ,  $\tilde{B}$  and  $\tilde{\mathcal{G}}$  are constructed from equation (24), and the states  $|F(t=0)\rangle$  and  $|eq\rangle$  are from equation (12). Thus the statistical averages are calculated by manipulations of quantum operators  $\psi^\dagger(q)$  and  $\psi(q)$ .

We can easily generalize the above discussion to the case when the system includes several kinds of molecules. Consider a system consisting of two types of molecules A and B. The distribution function of this system has the form  $F^{(N,M)}(q_{A1}, \dots, q_{AN}, q_{B1}, \dots, q_{BM}) = F^{(N,M)}(q_A^N, q_B^M)$ . The second quantization representation is constructed in terms of the operators  $\psi_A^\dagger(q)$ ,  $\psi_A(q)$ ,  $\psi_B^\dagger(q)$  and  $\psi_B(q)$  in the almost same manner as described above. An example will be given in § 6.

#### 4. Example 1: classical dynamical system

As an example of the above formulation, let us consider a many-particle system obeying classical dynamics. The time evolution operator of this system is a Liouville operator (22). The associated quantum operator is immediately obtained from equation (24):

$$\mathcal{L} = \mathcal{L}_{\text{free}} + \mathcal{L}_{\text{int}}$$

where

$$\begin{aligned} \tilde{\mathcal{L}}_{\text{free}} &= \int dr dp \frac{p}{m} \psi^\dagger(r, p) \frac{\partial \psi(r, p)}{\partial r}, \\ \tilde{\mathcal{L}}_{\text{int}} &= -\frac{1}{2} \int dr dp dr' dp' \psi^\dagger(r, p) \psi^\dagger(r', p') \frac{\partial u(r-r')}{\partial r} \left( \frac{\partial \psi(r, p)}{\partial p} \psi(r', p') - \frac{\partial \psi(r', p')}{\partial p'} \psi(r, p) \right) \\ &= -\int dr dp dr' dp' \psi^\dagger(r, p) \psi^\dagger(r', p') \frac{\partial u(r-r')}{\partial r} \frac{\partial \psi(r, p)}{\partial p} \psi(r', p'). \end{aligned} \quad (39)$$

Next we discuss the second quantization representation of the equilibrium state. First we consider the canonical ensemble of the  $N$ -particle system. The equilibrium distribution function for this ensemble is

$$F_{\text{eq}, N}((rp)^N) = \frac{1}{Z_N} \exp(-\beta \mathcal{H}^{(N)}) \quad (40)$$

with

$$\mathcal{H}^{(N)} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{1 \leq i < j \leq N} u(r_i - r_j); \quad \beta = \frac{1}{k_B T}, \quad (41)$$

where  $Z_N$  is the normalization constant determined by equation (9):

$$Z_N = \frac{1}{N!} \int dr^N dp^N \exp(-\beta \mathcal{H}^{(N)}). \quad (42)$$

This indicates that  $Z_N$  is equal to the partition function except for the factor  $(2\pi\hbar)^{-3N}$ . The corresponding quantum state is

$$|eq, N\rangle = \frac{1}{Z_N N!} \int dr^N dp^N \exp(-\beta \mathcal{H}^{(N)}) |(rp)^N\rangle. \quad (43)$$

This equation is rewritten into a more compact form: by using the relation

$$\exp(-\beta\mathcal{H}^{(N)})|(rp)^N\rangle = \exp(-\beta\tilde{\mathcal{H}})|(rp)^N\rangle \quad (44)$$

with

$$\begin{aligned} \tilde{\mathcal{H}} = & \int dr dp \frac{p^2}{2m} \psi^\dagger(r, p) \psi(r, p) \\ & + \frac{1}{2} \int dr dp dr' dp' u(r-r') \psi^\dagger(r, p) \psi^\dagger(r', p') \psi(r, p) \psi(r', p'), \end{aligned}$$

we have

$$\begin{aligned} |\text{eq}, N\rangle &= \frac{1}{Z_N N!} \exp(-\beta\tilde{\mathcal{H}}) \int dr^N dp^N \psi^\dagger(r_1, p_1) \dots \psi^\dagger(r_N, p_N) |0\rangle \\ &= \frac{1}{Z_N N!} \exp(-\beta\tilde{\mathcal{H}}) \left( \int dr dp \psi^\dagger(r, p) \right)^N |0\rangle. \end{aligned} \quad (45)$$

For many purposes, the grand canonical ensemble is more convenient. The distribution function for this ensemble is

$$F_{\text{eq}\lambda}^{(N)}((rp)^N) = \frac{\lambda^N}{Z_\lambda} \exp(-\beta\mathcal{H}^{(N)}) \quad (N = 0, 1, \dots), \quad (46)$$

where  $\lambda = \exp(\mu/k_B T)$  ( $\mu$  is the chemical potential) is the fugacity and  $Z_\lambda$  is the grand partition function. The associated quantum state is

$$\begin{aligned} |\text{eq}, \lambda\rangle &= \frac{1}{Z_\lambda} \sum_{N=0}^{\infty} \frac{\lambda^N}{N!} \int dr^N dp^N \exp(-\beta\mathcal{H}^{(N)}) |(rp)^N\rangle \\ &= \frac{1}{Z_\lambda} \sum_{N=0}^{\infty} \frac{\lambda^N}{N!} \exp(-\beta\tilde{\mathcal{H}}) \left( \int dr dp \psi^\dagger(r, p) \right)^N |0\rangle \\ &= \frac{1}{Z_\lambda} \exp(-\beta\tilde{\mathcal{H}}) \exp\left(\lambda \int dr dp \psi^\dagger(r, p)\right) |0\rangle = Z_\lambda^{-1} \exp(-\beta\tilde{\mathcal{H}}) |\lambda\rangle. \end{aligned} \quad (47)$$

Here we have written  $\exp(\lambda \int dr dp \psi^\dagger(r, p)) |0\rangle$  as  $|\lambda\rangle$  following the notation (27).

From the normalization condition (33), the expression for the grand partition function is obtained as

$$Z_\lambda = \langle \lambda = 1 | \exp(-\beta\tilde{\mathcal{H}}) | \lambda \rangle. \quad (48)$$

The expression for the equilibrium time correlation function is written compactly as

$$\frac{A(t)B(0)}{A(t)B(0)} = \frac{\langle \lambda = 1 | \tilde{A} \exp(-\tilde{\mathcal{L}}t) \tilde{B} \exp(-\beta\tilde{\mathcal{H}}) | \lambda \rangle}{\langle \lambda = 1 | \exp(-\beta\tilde{\mathcal{H}}) | \lambda \rangle} \quad (49)$$

Although these formal expressions have simple forms, actual calculations are, of course, very difficult. To calculate these expressions, we must have recourse to the perturbation technique or to some decoupling approximation. We can reproduce the conventional formulae starting from these expressions, but we shall not discuss it here.



## 5. Chemical reaction

Let us now consider systems including a reaction process. From the viewpoint of quantum mechanics, chemical reaction is a complicated inelastic collision process, and its general treatment does not seem well established. Therefore, here we take a simple stochastic treatment for the reaction process: we assume that reaction takes place instantaneously with some transition probability and that the process is described by an appropriate Markoffian master equation.

Let us consider the reaction system,



We introduce an intrinsic reaction rate  $R(q_A, q'_A \rightarrow q_B)$  defined as:  $R(q_A, q'_A \rightarrow q_B) dt$  is the probability that a pair of A molecules located at  $q_A$  and  $q'_A$  react in a time interval  $dt$ , producing B molecules at  $q_B$ .

For this system, the time evolution equation for the distribution function  $F^{(N,M)}(q_A^N, q_B^M, t)$  becomes:

$$\begin{aligned} & \frac{\partial}{\partial t} F^{(N,M)}(q_A^N, q_B^M, t) + \mathcal{G}_0^{(N,M)} F^{(N,M)}(q_A^N, q_B^M, t) \\ &= - \sum_{1 \leq i < j \leq N} \int dq_B R(q_{Ai}, q_{Aj} \rightarrow q_B) F^{(N,M)}(q_A^N, q_B^M, t) \\ & \quad + \frac{1}{2} \sum_{i=1}^M \int dq_A dq'_A dq_{Bi} R(q_A, q'_A \rightarrow q_{Bi}) \\ & \quad \times F^{(N+2, M-1)}(q_A^N q_A q'_A, q_B^M / q_{Bi}, t). \end{aligned} \quad (51)$$

Here  $\mathcal{G}_0^{(N,M)}$  is the time evolution operator in the absence of chemical reaction:  $\mathcal{G}_0^{(N,M)}$  may be a Liouville operator, or the diffusion operator (see the example of the next section). The right-hand side of equation (51) represents the balance of the probability due to chemical reaction: the first term represents the transition from the state  $(q_A^N, q_B^M)$  to  $(q_A^N / q_{Ai} q_{Aj}, q_B^M / q_B)$  ( $q_A^N / q_{Ai} q_{Aj}$  stands for the state that the molecules at  $q_{Ai}$  and  $q_{Aj}$  are removed from the state  $q_A^N$ , and  $q_B^M / q_B$  stands for that the molecule at  $q_B$  is added to the state  $q_B^M$ , i.e.,  $(q_A^N / q_{Ai} q_{Aj}) = (q_{A1}, q_{A2}, \dots, q_{Ai-1}, q_{Ai+1}, \dots, q_{Aj-1}, q_{Aj+1}, \dots, q_{AN})$  and  $(q_B^M / q_B) = (q_{B1}, q_{B2}, \dots, q_{BM}, q_B)$ ). The second term represents the transition from  $(q_A^N q_A q'_A, q_B^M / q_{Bi})$  to  $(q_A^N, q_B^M)$ . In the second term, the factor 1/2 is needed to compensate the double counting of the state  $(q_A^N q_A q'_A) = (q'_A q_A q_A)$ .

The corresponding quantum operator for equation (51) is

$$\tilde{\mathcal{G}} = \tilde{\mathcal{G}}_0 + \tilde{\mathcal{G}}_r. \quad (52)$$

The operator  $\tilde{\mathcal{G}}_0$  is constructed in the manner described previously. The reaction part  $\tilde{\mathcal{G}}_r$  is given by

$$\tilde{\mathcal{G}}_r = \tilde{\mathcal{G}}_{r1} + \tilde{\mathcal{G}}_{r2} \quad (53)$$

$$\tilde{\mathcal{G}}_{r1} = \frac{1}{2} \int dq_A dq'_A dq_B R(q_A, q'_A \rightarrow q_B) \psi_A^\dagger(q_A) \psi_A^\dagger(q'_A) \psi_A(q_A) \psi_A(q'_A) \quad (54)$$

$$\tilde{\mathcal{G}}_{r2} = -\frac{1}{2} \int dq_A dq'_A dq_B R(q_A, q'_A \rightarrow q_B) \psi_B^\dagger(q_B) \psi_A(q_A) \psi_A(q'_A). \quad (55)$$

The expression (54) is readily verified because the first term of the right-hand side of equation (51) has the form of  $A_2$  in equation (21). To verify equation (55), we use the relation

$$\langle q_A^N, q_B^M | \psi_B^\dagger(q_B) \psi_A(q_A) \psi_A(q'_A) \rangle = \sum_{i=1}^M \langle q_A^N q_A q'_A, q_B^M / q_{B_i} | \delta(q_B - q_{B_i}) \rangle. \quad (56)$$

Thus

$$\langle q_A^N, q_B^M | \tilde{\mathcal{G}}_{r2} | F \rangle = \frac{1}{2} \sum_{i=1}^M \int dq_A dq'_A dq_{B_i} R(q_A, q'_A \rightarrow q_{B_i}) F^{(N+2, M-1)}(q_A^N q_A q'_A, q_B^M / q_{B_i}; t). \quad (57)$$

The simple forms of equations (53)–(55) may be compared with equation (51) in the conventional representation. This simplicity is precisely the advantage of the second quantization representation.

As is understood from the above example, the reaction operator  $\tilde{\mathcal{G}}_r$  consists of two parts: the operator  $\tilde{\mathcal{G}}_{r1}$  does not change the number of composite molecules, but the operator  $\tilde{\mathcal{G}}_{r2}$  does change, destroying reactant molecules and creating product molecules.

At first sight, it may seem that only the operator  $\tilde{\mathcal{G}}_{r2}$  is needed to describe the reaction process; however this is not true. The operator  $\tilde{\mathcal{G}}_{r1} dt$  represents the probability that the system does not make a reactive transition in a time interval  $dt$ . These two operators are necessary to insure the normalization of  $F(t)$ . To see this, we show

$$\frac{\partial}{\partial t} \langle \text{sum} | F(t) \rangle = - \langle \text{sum} | \tilde{\mathcal{G}} | F(t) \rangle = 0. \quad (58)$$

Noting  $\langle \text{sum} | \tilde{\mathcal{G}}_0 | F(t) \rangle = 0$  and using the relation (32), we have

$$\begin{aligned} \frac{\partial}{\partial t} \langle \text{sum} | F(t) \rangle &= - \langle \text{sum} | \tilde{\mathcal{G}}_r | F(t) \rangle \\ &= - \int dq_A dq'_A dq_B R(q_A, q'_A \rightarrow q_B) \langle \text{sum} | \psi_A(q_A) \psi_A(q'_A) \\ &\quad - \psi_A(q_A) \psi_A(q'_A) | F(t) \rangle = 0. \end{aligned} \quad (59)$$

Thus the normalization of  $|F(t)\rangle$  is assured. Note that if  $\tilde{\mathcal{G}}_{r1}$  is excluded, equation (58) does not hold.

In a similar manner, we can construct the reaction operator for the general type of reaction. The results may be almost self-evident from the above discussions. Examples are listed below:

(i) For the reaction between different kinds of molecules,  $A + B \rightarrow C$ :

$$\begin{aligned} \tilde{\mathcal{G}}_r &= \int dq_A dq_B dq_C R(q_A, q_B \rightarrow q_C) \\ &\quad \times \{ \psi_A^\dagger(q_A) \psi_B^\dagger(q_B) \psi_A(q_A) \psi_B(q_B) - \psi_A(q_A) \psi_B(q_B) \psi_C^\dagger(q_C) \}. \end{aligned} \quad (60)$$

Note that the factor 1/2 does not appear in this case.

(ii) For the unimolecular reaction,  $A \rightarrow B$ :

$$\tilde{\mathcal{G}}_r = \int dq_A dq_B R(q_A \rightarrow q_B) \{ \psi_A^\dagger(q_A) \psi_A(q_A) - \psi_B^\dagger(q_B) \psi_A(q_A) \}. \quad (61)$$

(iii) For the decomposition reaction,  $A \rightarrow B + C$ :

$$\tilde{\mathcal{G}}_t = \int dq_A dq_B dq_C R(q_A \rightarrow q_B, q_C) \{ \psi_A^\dagger(q_A) \psi_A(q_A) - \psi_A(q_A) \psi_B^\dagger(q_B) \psi_C^\dagger(q_C) \}. \quad (62)$$

If the system includes many types of reaction processes concurrently, we must sum up the pertinent reaction operators.

For the system including only irreversible reaction, a simplification is possible. In this system, if the product molecules do not affect the motion of the reactant molecules, the time evolution equation is closed within the equation for the distribution function of the reactant molecules. For example, in the reaction  $A + A \rightarrow B$ , we need not consider the distribution function  $F^{(N,M)}(q_A^N, q_B^M; t)$  but need only  $F^{(N)}(q_A^N; t)$  provided we are interested only in A molecules, and provided the interactions between A and B are neglected. In that case, the reaction operator (53)–(55) is reduced to

$$\tilde{\mathcal{G}}_t = \frac{1}{2} \int dq_A dq'_A R(q_A, q'_A) \{ \psi_A^\dagger(q_A) \psi_A^\dagger(q'_A) \psi_A(q_A) \psi_A(q'_A) - \psi_A(q_A) \psi_A(q'_A) \}, \quad (63)$$

where

$$R(q_A, q'_A) = \int dq_B R(q_A, q'_A \rightarrow q_B) \quad (64)$$

is the reaction rate with which A molecules located at  $q_A$  and  $q'_A$  react producing B molecules at some unspecified position.

## 6. Example 2: diffusion controlled reaction in liquid media

As an example, we consider a Brownian particle system undergoing  $A + A \rightarrow B$  type irreversible reaction. We assume that the Brownian motions of the molecules are independent of each other. Thus we may discuss only the distribution function of A molecules (therefore suffix A is dropped).

In the absence of reaction, the distribution function of the A molecules obeys the diffusion equation,

$$\frac{\partial}{\partial t} F^{(N)}(r^N; t) = -\tilde{\mathcal{G}}_0^{(N)} F^{(N)}(r^N; t) \equiv D \sum_{i=1}^N \frac{\partial^2}{\partial r_i^2} F^{(N)}(r^N; t), \quad (65)$$

where  $D$  is the diffusion constant and  $r$  is the position of the A molecule. The corresponding diffusion operator becomes

$$\tilde{\mathcal{G}}_0 = -D \int dr \psi^\dagger(r) \nabla^2 \psi(r). \quad (66)$$

The reaction operator (63) is written as

$$\tilde{\mathcal{G}}_t = \frac{1}{2} \int dr dr' R(r-r') \{ \psi^\dagger(r) \psi^\dagger(r') \psi(r) \psi(r') - \psi(r) \psi(r') \}. \quad (67)$$

We now consider the probability  $P_N(t)$  that the system includes  $N$  A molecules at time  $t$ . By definition,

$$P_N(t) = \int dR^N F(r^N; t) = \frac{1}{N!} \int dr^N \langle r^N | F(t) \rangle. \quad (68)$$

The moment generating function of  $P_N(t)$  is thus given by

$$P(\alpha, t) \equiv \sum_{N=0}^{\infty} \alpha^N P_N(t) = \sum_{N=0}^{\infty} \frac{\alpha^N}{N!} \left\langle 0 \left| \left( \int dr \psi(r) \right)^N \right| F(t) \right\rangle = \langle \alpha | F(t) \rangle \quad (69)$$

with

$$\langle \alpha | = \langle 0 | \exp \left( \alpha \int dr \psi(r) \right). \quad (70)$$

Suppose that initially A molecules are uniformly distributed in a volume  $V$ , then the initial distribution function is

$$F^{(N)}(r^N; t=0) = \frac{N!}{V^N} P_N(t=0). \quad (71)$$

If  $P_N(t=0)$  is the Poisson distribution function with mean value  $cV$ , i.e.

$$P_N(t=0) = \frac{\exp(-cV)}{N!} (cV)^N, \quad (72)$$

the initial state becomes

$$|F(t=0)\rangle = e^{-cV} \sum_{N=0}^{\infty} \frac{c^N}{N!} \left( \int dr \psi^\dagger(r) \right)^N |0\rangle = e^{-cV} |c\rangle \quad (73)$$

with

$$|c\rangle = \exp \left( c \int dr \psi^\dagger(r) \right) |0\rangle. \quad (74)$$

From equations (69) and (73),  $P(\alpha, t)$  is compactly written as

$$P(\alpha, t) = \langle \alpha | \exp(-(\tilde{\mathcal{G}}_0 + \tilde{\mathcal{G}}_t)t) |c\rangle e^{-cV}. \quad (75)$$

This equation is the starting point of our analysis of diffusion-controlled chemical reaction which will be reported in a separate paper (Doi 1976). Note that the evaluation of equation (75) involves a difficulty of many-body problems because  $\tilde{\mathcal{G}}_t$  contains a term such as  $\psi^\dagger(r)\psi^\dagger(r')\psi(r')\psi(r)$ .

## 8. Conclusion

It is shown that classical many-particle systems are conveniently described by creation and annihilation operators. Since the starting point of this formulation is the general time evolution equation for the distribution function, the system need not be a dynamical system, but may be one described by some statistical master equations. This representation is shown to be particularly useful for the system including chemical reaction.

Though the present discussion is limited to the derivation of the formal expressions for the quantities which we are interested in, it can be shown that these expressions are convenient starting points for the perturbation analysis. An example of such an analysis is given in the following paper (Doi 1976).

## References

- Abrikosov A A, Gorkov L P and Dzyaloshinski I E 1963 *Methods of Quantum Field Theory in Statistical Physics* (Englewood Cliffs, NJ: Prentice Hall)
- de Boer J 1965 *Studies in Statistical Mechanics* vol 3, eds J de Boer and G E Uhlenbeck (Amsterdam: North-Holland) pp 213–75
- Doi M 1976 *J. Phys. A: Math. Gen.* **9** 1479–95
- Glauber R J 1963 *Phys. Rev.* **131** 2766–88
- Martin P C, Siggia E D and Rose H A 1973 *Phys. Rev. A* **8** 423–37
- Phythian R 1975 *J. Phys. A: Math. Gen.* **8** 1423–32
- 1976 *J. Phys. A: Math. Gen.* **9** 269–81