

# H-theorem in the Boltzmann approximation for bimolecular chemical reactions

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(Submitted 9 June 1994)

Zh. Eksp. Teor. Fiz. **106**, 753–766 (September 1994)

The dynamic method of proof, developed by the present author in previous work, is extended to the case of chemical reactions of the form  $A+B \rightleftharpoons C+D$  occurring in gases of moderate density. The reacting molecules can contain any number of atoms. The internal states of the molecules are regarded as quantum-mechanical, while the states of the centers of mass are semiclassical. It is assumed that the same conditions ( $v^{1/3} \Delta P \gg \hbar$ ,  $r_{\text{int}}^{1/2} v^{1/6} \Delta P \gg \hbar$ , where  $v = V/N$ ) hold as in R. L. Stratonovich, Zh. Eksp. Teor. Fiz. **101**, 838 (1992) [Sov. Phys. JETP **74**, 447 (1992)].

## I. INTRODUCTION

In previous works<sup>1,2</sup> an  $H$ -theorem was proved in the Boltzmann approximation for association and spontaneous dissociation reactions of the form  $A+B \rightleftharpoons C$ ,  $A+B+C \rightleftharpoons D$ . It is natural to generalize the analytical technique developed there to reactions of another type, the simplest of which are bimolecular reactions of the form  $A+B \rightleftharpoons C+D$ . It goes without saying that the same method may be used to treat more complicated reactions as well.

The  $H$ -theorem for bimolecular reactions was previously proved in a number of papers,<sup>3–6</sup> but in our opinion the theories presented there cannot be regarded as an exhaustive treatment of the problem. Thus, Polak and Khachoyan<sup>5</sup> used a semiphenomenological method, in which they employed phenomenological concepts such as the reaction cross section. It would be desirable to have a purely dynamical theory, like the Boltzmann theory, wholly free of phenomenological elements. Kolesnichenko<sup>6</sup> treated a more complicated theory than that of Refs. 3–5, but implicitly assumed that the operator distribution functions describing the molecules before they enter into the reaction and the functions describing the molecules after the reaction can be diagonalized simultaneously. It is only by virtue of this assumption that a generalized Boltzmann equation can be written down, not for the operator distribution functions but for  $c$ -functions of the molecular momentum and internal quantum numbers. In contrast with Ref. 6, we will deal with operators rather than with  $c$ -function distributions.

The distribution of the molecules A, B, C, and D will be described by the operators  $f_j(P_j)$ ,  $j=1, \dots, 4$ , which depend on the numerical (not operator) momentum  $P_j$  of the molecular center of mass. This is possible because the states of the center of mass are assumed to be semiclassical. By virtue of the condition  $v^{1/3} \Delta P \gg \hbar$  for  $v = V/N$  we can neglect quantum degeneracy of the gas made up of these molecules. We also assume that the interaction radius  $r_{\text{int}}$  of the molecules is much shorter than the mean free path, i.e., that the gas is of moderate density.

We note also that in the kinetic equations (5.3)–(5.6) used below, the simple collision processes  $A+B \rightleftharpoons A=B$ ,  $C+D \rightleftharpoons C+D$  are indistinguishable from chemical transformation processes. Indeed, this distinction cannot be made in

the case of internal quantum variables. In the classical case, however, each term on the right-hand side of the equations can be broken up into two parts: one corresponding to encounters without reactions and one corresponding to reactions.

Strictly speaking, the right-hand sides of these equations should also contain collision integrals for A with A, A with C, A with D, B with B, B with D, etc. However, we have not done this in order not to complicate the formulas and to concentrate attention on the terms corresponding to the reactions.

## 2. NOTATION FOR THE INTERNAL AND EXTERNAL VARIABLES OF THE MOLECULES

Assume that the A molecule consists of  $k_1$  atoms. Some of them, say, the first  $k'_1$  atoms out of the  $k_1$ , are transformed into C in the reaction  $A+B \rightarrow C+D$ . Then the other  $k''_1 = k_1 - k'_1$  atoms are transformed into D. Similarly,  $k'_2$  atoms of the B molecule are transformed into C, and  $k''_2 = k_2 - k'_2$  atoms into D. We have the sets

$$\{\mathbf{q}_1^{(1)}, \dots, \mathbf{q}_{k'_1}^{(1)}, \mathbf{q}_{k'_1+1}^{(1)}, \dots, \mathbf{q}_{k_1}^{(1)}\}, \{\mathbf{q}_1^{(2)}, \dots, \mathbf{q}_{k'_2}^{(2)}, \mathbf{q}_{k'_2+1}^{(2)}, \dots, \mathbf{q}_{k_2}^{(2)}\}$$

of atomic radius vectors for A and B respectively. Here the radius vectors of the atoms transformed into C are written first. It is easy to see that the radius vectors making up C and D can be written in the form

$$\{\mathbf{q}_1^{(3)}, \dots, \mathbf{q}_{k_3}^{(3)}\} \equiv \{\mathbf{q}_1^{(1)}, \dots, \mathbf{q}_{k'_1}^{(1)}, \mathbf{q}_1^{(2)}, \dots, \mathbf{q}_{k'_2}^{(2)}\},$$

$$\{\mathbf{q}_1^{(4)}, \dots, \mathbf{q}_{k_4}^{(4)}\} \equiv \{\mathbf{q}_{k'_1+1}^{(1)}, \dots, \mathbf{q}_{k_1}^{(1)}, \mathbf{q}_{k'_2+1}^{(2)}, \dots, \mathbf{q}_{k_2}^{(2)}\}, \quad (1)$$

i.e.,  $\mathbf{q}_\alpha^{(3)} \equiv \mathbf{q}_\alpha^{(1)}$ ,  $\alpha=1, \dots, k'_1$ ;  $\mathbf{q}_{k'_3+\beta}^{(3)} \equiv \mathbf{q}_\beta^{(2)}$ ,  $\beta=1, \dots, k'_2$ , etc. With this notation it is obvious that  $k'_1 + k'_2 = k_3$ ,  $k''_1 + k''_2 = k_4$ . Thus, the total number  $k_1 + k_2 = k_3 + k_4$  of atoms taking part in  $A+B \rightleftharpoons C+D$  reactions can be divided up into four sets ("submolecules"), such that these reactions can be regarded as exchanges of the submolecules (see Fig. 1). It is convenient to introduce the radius vectors of the submolecule centers of mass:

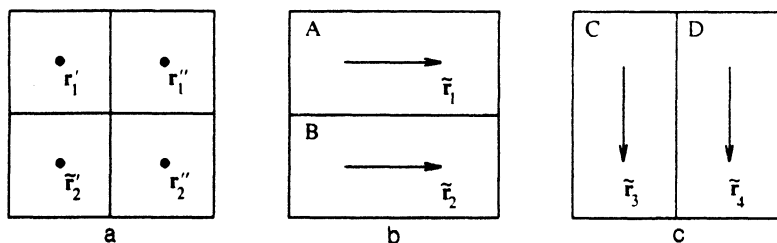


FIG. 1. Schematic representation of the molecules in terms of "submolecules." a) The four submolecules and their centers of mass; b) the A and B molecules and the vectors  $\tilde{r}_1, \tilde{r}_2$ ; c) the C and D molecules and the vectors  $\tilde{r}_3, \tilde{r}_4$ .

$$\mathbf{r}'_1 \equiv \mathbf{r}'_3 = \frac{1}{M'_1} \sum_{\alpha=1}^{k'_1} m_{\alpha}^{(1)} \mathbf{q}_{\alpha}^{(1)}, \quad \mathbf{r}''_1 \equiv \mathbf{r}''_4 = \frac{1}{M''_1} \sum_{\alpha=k'_1+1}^{k_1} m_{\alpha}^{(1)} \mathbf{q}_{\alpha}^{(1)}, \quad (2.1)$$

$$\mathbf{r}'_2 \equiv \mathbf{r}'_3 = \frac{1}{M'_2} \sum_{\alpha=1}^{k'_2} m_{\alpha}^{(2)} \mathbf{q}_{\alpha}^{(2)}, \quad \mathbf{r}''_2 \equiv \mathbf{r}''_4 = \frac{1}{M''_2} \sum_{\alpha=k'_2+1}^{k_2} m_{\alpha}^{(2)} \mathbf{q}_{\alpha}^{(2)}.$$

Here we have written  $M'_i = \sum_{\alpha=1}^{k'_i} m_{\alpha}^{(i)}$ ,  $M''_i = \sum_{\alpha=k'_i+1}^{k_i} m_{\alpha}^{(i)}$ .

These radius vectors can be used in an obvious way to express the radius vectors of the centers of mass of the molecules, i.e., the external coordinates of the molecules:

$$\begin{aligned} \mathbf{r}_1 &= (M'_1 \mathbf{r}'_1 + M''_1 \mathbf{r}''_1) / M_1, & \mathbf{r}_2 &= (M'_2 \mathbf{r}'_2 + M''_2 \mathbf{r}''_2) / M_2, \\ \mathbf{r}_3 &= (M'_1 \mathbf{r}'_1 + M'_2 \mathbf{r}'_2) / M_3, & \mathbf{r}_4 &= (M''_1 \mathbf{r}''_1 + M''_2 \mathbf{r}''_2) / M_4, \end{aligned} \quad (2.2)$$

where

$$\begin{aligned} M_i &= M'_i + M''_i, \\ (M'_3 &= M'_1, \quad M'_3 = M'_2, \quad M'_4 = M''_1, \quad M'_4 = M''_2). \end{aligned}$$

Moreover, we introduce the differences

$$\begin{aligned} \tilde{\mathbf{r}}_1 &= \mathbf{r}''_1 - \mathbf{r}'_1, & \tilde{\mathbf{r}}_2 &= \mathbf{r}''_2 - \mathbf{r}'_2, & \tilde{\mathbf{r}}_3 &= \mathbf{r}'_2 - \mathbf{r}'_1, \\ \tilde{\mathbf{r}}_4 &= \mathbf{r}''_2 - \mathbf{r}''_1 = \tilde{\mathbf{r}}_2 + \tilde{\mathbf{r}}_3 - \tilde{\mathbf{r}}_1. \end{aligned} \quad (2.3)$$

The internal coordinates of the submolecules are the components of the set of vectors

$$\begin{aligned} \mathbf{q}'_{i\sigma} &= \mathbf{q}_{\sigma}^{(i)} - \mathbf{q}_1^{(i)}, & \sigma &= 2, \dots, k'_i, \\ \mathbf{q}''_{i\tau} &= \mathbf{q}_{\tau}^{(i)} - \mathbf{q}_{k'_i+1}^{(i)}, & \tau &= k'_i+2, \dots, k_i \end{aligned} \quad (2.4)$$

for  $i=1, \dots, 4$ . We will write

$$\mathbf{q}'_i = (\mathbf{q}'_{i\sigma}, \sigma=2, \dots, k'_i), \quad \mathbf{q}''_i = (\mathbf{q}''_{i\tau}, \tau=k'_i+1, \dots, k_i). \quad (2.5)$$

Then  $(\tilde{\mathbf{r}}_1, q'_1, q''_1)$  is the complete set of internal coordinates of an A molecule and  $(\tilde{\mathbf{r}}_2, q'_2, q''_2)$  is the analogous set for the B molecule. Likewise,  $(\tilde{\mathbf{r}}_3, q'_3, q''_3)$  and  $(\tilde{\mathbf{r}}_4, q'_4, q''_4)$  are the internal coordinates of C and D molecules respectively. Combining the external coordinates (2.2) with these sets we find the complete set of all the coordinates of a particular molecule.

The relations (2.1)–(2.4) specify transformations from the initial variables to the new variables  $(\mathbf{r}_i, \tilde{\mathbf{r}}_i, q'_i, q''_i)$ ,  $i=1, \dots, 4$ . These transformations induce transformations of the momenta. Let  $\mathbf{P}'_1, \mathbf{P}'_1, \mathbf{P}'_2, \mathbf{P}'_2$  be the momenta of the submolecule conjugate to the coordinates (2.1) and  $p'_1, p''_1, p'_2, p''_2$  those conjugate to (2.5). It is not difficult to show that

the variables conjugate to the external coordinates (2.2) will be the momenta  $\mathbf{P}_i = \mathbf{P}'_i + \mathbf{P}''_i$  (where  $\mathbf{P}'_3 = \mathbf{P}'_1, \mathbf{P}''_3 = \mathbf{P}''_2, \mathbf{P}'_4 = \mathbf{P}''_1, \mathbf{P}''_4 = \mathbf{P}''_2$ ) of the centers of mass of the molecules, while the momenta

$$\tilde{\mathbf{P}}_i = \mu'_i \mathbf{P}'_i - \mu''_i \mathbf{P}''_i, \quad i=1, \dots, 4,$$

will be conjugate to the vectors (2.3); here we have written  $\mu'_i = M'_i / M_i$ ,  $\mu''_i = M''_i / M_i$ . In what follows we will also write  $\mathbf{P}_1 + \mathbf{P}_2 = \mathbf{P}_3 + \mathbf{P}_4 = \mathbf{P}_5$ ,  $M_1 + M_2 = M_3 + M_4 = M_5$ . In Ref. 1 it was noted that these coordinate transformations (along with the momentum transformations) have a Hamiltonian equal to unity. The new variables are thus equivalent to the old ones. For brevity we also write  $\tilde{q}_i = (q'_i, q''_i)$ , and likewise for  $\tilde{p}_i$ ,  $i=1, \dots, 4$ .

In the classical version of the theory, the condition of spatial homogeneity implies that we can look for distribution functions  $f_j(\mathbf{P}_j, \tilde{\mathbf{r}}_j, \tilde{\mathbf{P}}_j, \tilde{q}_j, \tilde{p}_j) = f_j(\mathbf{P}_j, \xi_j)$ ,  $j=1, \dots, 4$  for the A, B, C, and D molecules respectively. Here  $\xi_j$  is the set of internal dynamical variables of a molecule. For internal quantum states, instead of these functions we must treat operators  $\hat{f}_j(P_j)$  which are functions of  $P_j$ . In the coordinate representation they have matrix elements  $f_j(\mathbf{P}_j, \tilde{\mathbf{r}}_j, \tilde{q}_j, \tilde{r}'_j, \tilde{q}'_j) = \langle \tilde{\mathbf{r}}_j, \tilde{q}_j | \hat{f}_j(\mathbf{P}_j) | \tilde{\mathbf{r}}'_j, \tilde{q}'_j \rangle$ .

### 3. THE SHORT-LIVED INTERACTION STATE: THE STATE IN WHICH ALL $k_1 + k_2$ ATOM INTERACT

When

$$\tilde{r}_1 \sim r_{\text{int}}, \dots, \tilde{r}_4 \sim r_{\text{int}}, \quad (3.1)$$

where  $r_{\text{int}}$  is the interaction radius and  $\tilde{r}_j = |\tilde{\mathbf{r}}_j|$ , all the atoms that make up A, B and C, D interact simultaneously. Then none of the four molecules retains its individuality. We specify some value  $r_0$  satisfying  $r_{\text{int}} \ll r_0 \ll v^{1/3}$  (Where  $v = V/N$ ), e.g.,

$$r_0 = r_{\text{int}}^{1/2} v^{1/6}. \quad (3.2)$$

With some loss of generality we assume that only under the condition  $\tilde{r}_1 + \tilde{r}_2 + \tilde{r}_3 + \tilde{r}_4 \geq 2r_0$  does the pair of A and B molecules or the pair of C and D molecules exist. Then the interaction region is determined by the inequality

$$\tilde{r}_1 + \tilde{r}_2 + \tilde{r}_3 + \tilde{r}_4 < 2r_0. \quad (3.3)$$

Using the extended region (3.3) instead of the actual interaction region (3.1) makes no essential difference, since  $r_0 \ll v^{1/3}$ .

The transition state can be regarded as the short-lived state of a "fifth molecule" whose center of mass is located at  $\mathbf{r}_5 = (M_1 \mathbf{r}_1 + M_2 \mathbf{r}_2) / M_5$ . We introduce the 9-component vector

$$\zeta = (\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_3, \bar{\mathbf{r}}_2). \quad (3.4)$$

Its components, together with those of the vector  $r_5$ , are equivalent to the components of the set of vectors (2.1). The momentum  $P_5$  of the center of mass of the A+B combination is conjugate to  $r_5$ , and

$$\pi = (\bar{\mathbf{P}}_1, \bar{\mathbf{P}}_3, \bar{\mathbf{P}}_2) = (\mathbf{P}'_1 - \mu''_1 \mathbf{P}_5, \mu_1 \mathbf{P}_2 - \mu_2 \mathbf{P}_1, \mathbf{P}''_2 - \mu''_2 \mathbf{P}_5), \quad (3.5)$$

(where  $\mu_1 = M_1/M_5$ ,  $\mu_2 = 1 - \mu_1$ ) is the set of momenta conjugate to (3.4). Below (in Sec. 4) we will pass from the variables (3.5) to the equivalent variables  $(\bar{\mathbf{r}}_1, \mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1, \bar{\mathbf{r}}_2)$  and to the variables  $(\mathbf{r}_{43}, \bar{\mathbf{r}}_3, \bar{\mathbf{r}}_4)$ .

Condition (3.3) determines the region  $V_5$  in the space of the coordinates  $\zeta$ . Let  $L$  be the surface of this region. On  $L$  and outside it a molecular pair exists. It is natural to assume that this is the pair consisting of A and B if  $\bar{r}_1 + \bar{r}_2 < \bar{r}_3 + \bar{r}_4$  holds, and the pair consisting of C and D if  $\bar{r}_1 + \bar{r}_2 > \bar{r}_3 + \bar{r}_4$ . Thus  $L$  is broken up into two parts, which we denote  $L_{AB}$  and  $L_{CD}$ . Of course, A and D exist on the portion  $L_{AB}^0$  where  $r_3 \sim r_{\text{int}}, r_4 \sim r_{\text{int}}$ .

Next we consider the equation

$$\bar{r}_1 + \bar{r}_2 + \bar{r}_3 + \bar{r}_4 = 2r_0. \quad (3.6)$$

for the hypersurface  $L$ . Eliminating  $\mathbf{r}'_1$  and then  $\mathbf{r}'_1$  from the first equations of the system consisting of (2.2) and (2.3), we find

$$\mathbf{r}'_1 = \mathbf{r}_1 - \mu''_1 \bar{\mathbf{r}}_1, \quad \mathbf{r}'_1 = \mathbf{r}_1 + \mu'_1 \bar{\mathbf{r}}_1. \quad (3.7)$$

Similarly we find

$$\mathbf{r}'_2 = \mathbf{r}_1 + \mathbf{r}_{21} - \mu''_2 \bar{\mathbf{r}}_2, \quad \mathbf{r}'_2 = \mathbf{r}_1 + \mathbf{r}_{21} + \mu'_2 \bar{\mathbf{r}}_2. \quad (3.8)$$

Substituting (3.7) and (3.8) into the right-hand sides of Eqs. (2.3) we can easily find

$$\mathbf{r}_3 = \mathbf{r}_{21} + \mu'_1 \bar{\mathbf{r}}_1 - \mu''_2 \bar{\mathbf{r}}_2, \quad \bar{\mathbf{r}}_4 = \mathbf{r}_{21} - \mu'_1 \bar{\mathbf{r}}_1 + \mu'_2 \bar{\mathbf{r}}_2. \quad (3.9)$$

After substituting (3.9) into Eq. (3.6) we have

$$2r_{21} \left[ 1 + O\left(\frac{\bar{r}_1 + \bar{r}_2}{r_{21}}\right) \right] = 2r_0. \quad (3.10)$$

Consequently, the portion  $L_{AB}^0$  where  $\bar{r}_1 \sim r_{\text{int}} \ll r_0$ ,  $\bar{r}_2 \sim r_{\text{int}} \ll r_0$  and where at the same time  $r_{21} \sim r_0$  [as can be seen from (3.10)] approximately coincides with the portion  $K_{21}^0$  of the sphere  $K_{21}$  defined by the equation  $r_{21} = r_0$  (the other variables are arbitrary). Similarly it can be shown that the portion  $L_{BC}^0$  in which the B and C molecules actually exist essentially coincide (by virtue of the inequality  $r_{\text{int}} \ll r_0$ ) with the corresponding portion  $K_{43}^0$  of the sphere  $K_{43}$  defined by the equation  $r_{43} = r_0$ , where the other variables are arbitrary.

In the nonquantum version, the ensemble of "fifth molecules" is described in  $V_5$  and on  $L$  by the distribution function

$$f_5(\mathbf{P}_5, \zeta, \pi, \bar{q}_1, \bar{q}_2, \bar{p}_1, \bar{p}_2) = f_5(\mathbf{P}_5, \xi_5). \quad (3.11)$$

This object can be regarded as closely approaching A and B molecules, and we can consider the joint distribution function  $f_{21}(P_5, \xi_{21})$ , where  $\xi_{21} = (\mathbf{r}_{21}, \mathbf{P}_{21}, \xi_1, \xi_2)$ ,  $\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1$ ,  $\mathbf{P}_{21} = (M_1 \mathbf{P}_2 - M_2 \mathbf{P}_1)/M_5$ . It can also be regarded as closely

approaching C and D molecules, and we can treat  $f_{43}(P_5, \xi_{43})$ , where  $\xi_{43} = (\mathbf{r}_{43}, \mathbf{P}_{43}, \xi_3, \xi_4)$ ,  $\mathbf{r}_{43} = \mathbf{r}_4 - \mathbf{r}_3$ ,  $\mathbf{P}_{43} = (M_3 \mathbf{P}_4 - M_4 \mathbf{P}_3)/M_5$ .

The function (3.11) satisfies the Liouville equation

$$\dot{f}_5 = L_5 f_5 = -\nabla_5[\dot{\xi}_5(\xi_5) f_5], \quad (3.12)$$

where  $\nabla_5$  represents the gradient with respect to  $\xi_5$ . The functions  $f_{21}$  and  $f_{43}$  satisfy analogous equations. In view of the inequality  $r_0 \ll v^{1/3}$ , the average time for the particles to pass through the region  $V_5$  is much less than the time required to traverse the average distance  $v^{1/3}$  between molecules. A fortiori, it is much less than the average time between two successive encounters by a single particle ( $\lambda \gg v^{1/3}$ ). The average time to traverse the region  $V$  is therefore much less than the time constants which characterize the rate at which the functions  $f_j$ ,  $j=1, \dots, 5$  change. In other words, they cannot change in this short time. Consequently, the derivative  $\dot{f}_5$  in (3.12) is very small, and in place of (3.12) we can use the equation

$$\nabla_5(\dot{\xi}_5 f_5) = 0. \quad (3.13)$$

It is equivalent to the approximation in which the region  $V_5$  is traversed instantaneously. The integral of  $\nabla_5(\dot{\xi}_5 f_5)$  over the region where  $\zeta \in V_5$ , with the other arguments of  $f_5$  arbitrary, can be transformed into an integral over the surface of this region.

#### 4. PRELIMINARY FORMULAS IN THE QUANTUM CASE

The quantum generalization of Eq. (3.13) is  $[\hat{H}_5, \hat{f}_5] = 0$ , where  $\hat{H}_5$  is the joint Hamiltonian of all four submolecules. For generality it is convenient to consider the operator  $\hat{G} = g(f_5)$ , where  $g$  is some numerical function. It satisfies the analogous equation

$$[\hat{H}_5, \hat{G}] = 0. \quad (4.1)$$

Below we will consider two special cases of the operator  $\hat{G}$ :  $\hat{G} = \hat{f}_5$  and  $\hat{G} = k \hat{f}_5 \ln(\text{const} \cdot \hat{f}_5)$ . Using the coordinates and momenta introduced in Sec. 2 we can write the combined Hamiltonian in a natural way as

$$\hat{H}_5 = \hat{T}_0 + \hat{H}'_1 + \hat{H}''_1 + \hat{H}'_2 + \hat{H}''_2 + \hat{\Phi}. \quad (4.2)$$

Here

$$\hat{T}_0 = \frac{|\hat{\mathbf{P}}'_1|^2}{(2M'_1)} + \frac{|\hat{\mathbf{P}}''_1|^2}{(2M''_1)} + \frac{|\hat{\mathbf{P}}'_2|^2}{(2M'_2)} + \frac{|\hat{\mathbf{P}}''_2|^2}{(2M''_2)} \quad (4.3)$$

is the kinetic energy of the centers of mass of the submolecules,  $\hat{H}'_1, \dots, \hat{H}''_2$  are the energies of the four submolecules expressed in terms of their internal variables, and  $\hat{\Phi}$  is the interaction potential energy of the submolecules. Calculations reveal that the kinetic energy (4.3) can be expressed in terms of  $\hat{P}_5$  and the components (3.5) as follows:

$$\hat{T}_0 = \hat{T}'_0 + \hat{T}''_0, \quad 2\hat{T}'_0 = \hat{P}_5^2/M_5, \\ 2\hat{T}''_0 = \frac{|\hat{\mathbf{P}}_1 + \hat{\mathbf{P}}_3|^2}{M'_1} + \frac{\hat{P}_1^2}{M''_1} + \frac{|\hat{\mathbf{P}}_3 - \hat{\mathbf{P}}_2|^2}{M'_2} + \frac{\hat{P}_2^2}{M''_2} \quad (4.4)$$

or more concisely  $2\hat{T}'_0 = M_{\alpha\beta}^{-1} \hat{\pi}_\alpha \hat{\pi}_\beta$ . Here summation is implied over repeated indices.

Writing  $\text{Tr}_{\text{in}}$  for the trace with respect to the internal variables of the submolecules, we have from (4.1)

$$\text{Tr}_{\text{in}}[\hat{H}_5, \hat{G}] = 0.$$

The operator on the left-hand side here is taken in the  $\hat{\zeta}$  representation [the variables (3.4) are related to the external variables of the submolecules]. Then we set  $\zeta' = \zeta$ , i.e., we take the diagonal elements of the matrix. Substituting (4.2) and (4.4) in the resulting equation

$$\text{Tr}_{\text{in}}[\hat{H}_5, \hat{G}]|_{\zeta'=\zeta} = 0, \quad (4.5)$$

we can easily show that the terms with  $\hat{H}_1', \dots, \hat{H}_2''$  drop out when  $\text{Tr}_{\text{in}}$  is evaluated and the term with the potential energy  $\Phi$ , which depends only on the coordinates, drops out by virtue of the relation  $\zeta' = \zeta$ . Then the commutator with  $\hat{T}_0'$  vanishes by virtue of the spatial homogeneity. Consequently, from (4.5) we have

$$\text{Tr}_{\text{in}}[\hat{T}_0'', \hat{G}]|_{\zeta'=\zeta} = 0.$$

Integrating the expression on the left-hand side over the region  $V_5$  of the 9-dimensional space defined by the inequality (3.3) and using Eq. (A1.3) of Appendix 1, we can represent this integral in the form of an integral over the hypersurface  $L$  of region  $V_5$ :

$$-\frac{i\hbar}{2} \int_L dL l_\alpha \text{Tr}_{\text{in}} \left[ \frac{d\hat{\zeta}_\alpha}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta} = 0$$

or, since  $L = L_{\text{AB}} + L_{\text{CD}}$ ,

$$J_{\text{AB}} + J_{\text{CD}} = 0, \quad (4.6)$$

where

$$J_{\text{AB}} = \int_{L_{\text{AB}}} dL l_\alpha \text{Tr}_{\text{in}} \left[ \frac{d\hat{\zeta}_\alpha}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta}, \quad (4.7)$$

$$J_{\text{CD}} = \int_{L_{\text{CD}}} dL l_\alpha \text{Tr}_{\text{in}} \left[ \frac{d\hat{\zeta}_\alpha}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta}. \quad (4.8)$$

Here  $e$  is a unit vector in the direction of the external normal to  $L$ .

We start by setting  $\hat{G} = f_5$ . It is easy to see that in  $L_{\text{AB}}$ , i.e., when the A and B molecules are present, the submolecules that enter into A and into B are generally close to one another. This means that the function  $\chi(\zeta) = \text{Tr}_{\text{in}} f_5|_{\zeta'=\zeta}$  is significantly different from zero only for  $|r_1'' - r_1'| \sim r_{\text{int}}$  and  $|r_2'' - r_2'| \sim r_{\text{int}}$  (i.e., for  $\tilde{r}_1, \tilde{r}_2 \sim r_{\text{int}}$ ), while outside the portion  $L_{\text{AB}}^0$  it is essentially equal to zero. The same applies to the case  $\hat{G} = k f_5 \ln(\text{const } f_5)$ . Hence the integral (4.7) can be replaced by

$$J_{\text{AB}}^0 = \int_{L_{\text{AB}}^0} dL l_\alpha \text{Tr}_{\text{in}} \left[ \frac{d\hat{\zeta}_\alpha}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta}.$$

But, as shown in Sec. 3, the segment  $L_{\text{AB}}^0$  essentially coincides with the portion  $K_{21}^0$  of the sphere  $K_{21}$  (by virtue of the inequality  $r_0 \gg r_{\text{int}}$ ). This sphere is defined by  $r_{21} = r_0$  with arbitrary  $\tilde{r}_1, \tilde{r}_2$ . The variables  $\tilde{r}_1, r_{21}, \tilde{r}_2$  are equivalent to the variables  $\tilde{r}_1, \tilde{r}_3, \tilde{r}_2$  [see the first inequality of (3.9)]. By virtue of this identity we have

$$\begin{aligned} J_{\text{AB}} &\approx \int d\tilde{r}_1 d\tilde{r}_2 \int_{K_{21}^0} dK_{21} \mathbf{n}_{21} \text{Tr}_{\text{in}} \left[ \frac{d\hat{r}_{21}}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta} \\ &\approx \int d\tilde{r}_1 d\tilde{r}_2 \int_{K_{21}} dK_{21} \mathbf{n}_{21} \text{Tr}_{\text{in}} \left[ \frac{d\hat{r}_{21}}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta}. \end{aligned} \quad (4.9)$$

Here  $n_{21}$  is the unit vector in the direction of the exterior normal to  $K_{21}$ .

In a similar manner we can show that the integral (4.8) can be replaced by

$$J_{\text{CD}}^0 \approx \int d\tilde{r}_3 d\tilde{r}_4 \int_{K_{43}} dK_{43} \mathbf{n}_{43} \text{Tr}_{\text{in}} \left[ \frac{d\hat{r}_{43}}{dt}, \hat{G} \right]_+ \Big|_{\zeta'=\zeta}. \quad (4.10)$$

The relation  $\zeta' = \zeta$  here is equivalent to  $\tilde{r}_3' = \tilde{r}_3, \tilde{r}_4' = \tilde{r}_4, \tilde{r}_{43}' = \tilde{r}_{43}$ . But the relations  $\tilde{r}_3' = \tilde{r}_3, \tilde{r}_4' = \tilde{r}_4$  imply that diagonal elements are specified, while the last integration with respect to  $\tilde{r}_3$  and  $\tilde{r}_4$  represent traces taken with respect to these variables. Consequently

$$\int d\tilde{r}_3 d\tilde{r}_4 \text{Tr}_{\text{in}} \hat{M} \Big|_{\zeta'=\zeta} = \text{Tr}_3 \text{Tr}_4 \hat{M},$$

where  $\text{Tr}_3$  ( $\text{Tr}_4$ ) is the trace with respect to the internal variables of the C(D) molecule. It is likewise convenient to introduce the traces  $\text{Tr}_1$  and  $\text{Tr}_2$  with respect to the internal variables of the A and B molecules. By virtue of (4.9) and (4.10) we can use this notation to convert (4.6) to

$$\begin{aligned} &\text{Tr}_1 \text{Tr}_2 \int_{K_{21}} dK_{21} \mathbf{n}_{21} \left[ \frac{d\hat{r}_{21}}{dt}, \hat{G} \right]_+ \Big|_{r_{21}'=r_{21}} \\ &+ \text{Tr}_3 \text{Tr}_4 \int_{K_{43}} dK_{43} \mathbf{n}_{43} \left[ \frac{d\hat{r}_{43}}{dt}, \hat{G} \right]_+ \Big|_{r_{43}'=r_{43}} = 0. \end{aligned} \quad (4.11)$$

The Wigner transformation with respect to some of the variables can be used to introduce the remaining operators that depend on numerical (not operator) arguments  $\mathbf{r}_{21}, \mathbf{P}_{21}$  or  $\mathbf{r}_{43}, \mathbf{P}_{43}$ :

$$\begin{aligned} \mathscr{W}_{21}[\hat{G}]_{\mathbf{r}_{21}, \mathbf{P}_{21}} &= \frac{1}{(2\pi\hbar)^3} \int \exp\left(-\frac{i}{\hbar} \mathbf{P}_{21} \mathbf{u}\right) \\ &\times G_{21}\left(\mathbf{r}_{21} + \frac{\mathbf{u}}{2}, \mathbf{r}_{21} - \frac{\mathbf{u}}{2}\right) d\mathbf{u}, \\ \mathscr{W}_{43}[\hat{G}]_{\mathbf{r}_{43}, \mathbf{P}_{43}} &= \frac{1}{(2\pi\hbar)^3} \int \exp\left(-\frac{i}{\hbar} \mathbf{P}_{43} \mathbf{u}\right) \\ &\times G_{43}\left(\mathbf{r}_{43} + \frac{\mathbf{u}}{2}, \mathbf{r}_{43} - \frac{\mathbf{u}}{2}\right) d\mathbf{u}, \end{aligned} \quad (4.12)$$

where

$$G_{ij}(\mathbf{r}'_{ij}, \mathbf{r}''_{ij}) = \langle \mathbf{r}'_{ij} | \hat{G} | \mathbf{r}''_{ij} \rangle.$$

By means of these operators we can write Eq. (4.11) as

$$\begin{aligned} & \text{Tr}_1 \text{Tr}_2 \int d\mathbf{P}_{21} \int_{K_{21}^-} dK_{21}(\mathbf{v}_{21})_n \mathscr{W}_{21}[\hat{G}] \\ & + \text{Tr}_3 \text{Tr}_4 \int d\mathbf{P}_{43} \int_{K_{43}^-} dK_{43}(\mathbf{v}_{43})_n \mathscr{W}_{43}[\hat{G}] = 0, \end{aligned} \quad (4.13)$$

where

$$\begin{aligned} (\mathbf{v}_{21})_n &= \frac{\mathbf{P}_{21} \mathbf{n}_{21}}{M_{21}}, \quad (\mathbf{v}_{43})_n = \frac{\mathbf{P}_{43} \mathbf{n}_{43}}{M_{43}}, \\ M_{21} &= \frac{M_1 M_2}{M_5}, \quad M_{43} = \frac{M_3 M_4}{M_5}. \end{aligned}$$

When  $r_{\text{int}}^{1/2} v^{1/6} \Delta P \gg \hbar$ , we have  $r_0 \Delta P \gg \hbar$  for the case (3.2). By virtue of the latter inequality the state of the A+B (or C+D) complex in the region  $r_0/2 < |\zeta| < 3r_0/2$  is quasiclassical with respect to  $r_{21}$  (or  $r_{43}$ ). Consequently, as shown in Ref. 2, the following approximate expressions hold:

$$\begin{aligned} \mathscr{W}_{21}g(\hat{f}_5) &\approx g(\mathscr{W}_{21}[\hat{f}_5]), \quad \mathscr{W}_{43}g(\hat{f}_5) \\ &\approx g(\mathscr{W}_{43}[\hat{f}_5]). \end{aligned}$$

Using them, and also dividing the sphere  $K_{21}$  into the hemisphere  $K_{21}^+$  where  $(\mathbf{v}_{21})_n > 0$  and the hemisphere  $K_{21}^-$  where  $(\mathbf{v}_{21})_n < 0$ , and analogously the sphere  $K_{43}$  into  $K_{43}^+$  and  $K_{43}^-$ , depending on the sign of  $(\mathbf{v}_{43})_n$ , we find from (4.13)

$$\begin{aligned} & \text{Tr}_1 \text{Tr}_2 \int d\mathbf{P}_{21} \left\{ \int_{K_{21}^-} dK_{21} + \int_{K_{21}^+} dK_{21} \right\} \\ & \times (\mathbf{v}_{21})_n g(\hat{F}_{21}(\mathbf{P}_5, \mathbf{r}_{21}, \mathbf{P}_{21})) \\ & + \text{Tr}_3 \text{Tr}_4 \int d\mathbf{P}_{43} \left\{ \int_{K_{43}^-} dK_{43} + \int_{K_{43}^+} dK_{43} \right\} \\ & \times (\mathbf{v}_{43})_n g(\hat{F}_{43}(\mathbf{P}_5, \mathbf{r}_{43}, \mathbf{P}_{43})) = 0. \end{aligned} \quad (4.14)$$

Here we have written

$$\begin{aligned} \hat{F}_{21}(\mathbf{P}_5, \mathbf{r}_{21}, \mathbf{P}_{21}) &= \mathscr{W}_{21}[\hat{f}_{21}(\mathbf{P}_5)], \\ \hat{F}_{43}(\mathbf{P}_5, \mathbf{r}_{43}, \mathbf{P}_{43}) &= \mathscr{W}_{43}[\hat{f}_{43}(\mathbf{P}_5)]. \end{aligned}$$

In (4.14) we carry out additionally integration with respect to  $\mathbf{P}_5$ . Furthermore, we replace the integration with respect to  $\mathbf{P}_5$  and  $\mathbf{P}_{21}$  by integration with respect to  $\mathbf{P}_1$  and  $\mathbf{P}_2$ , and we transform from the integration variables  $\mathbf{P}_5$  and  $\mathbf{P}_{43}$  to  $\mathbf{P}_3$  and  $\mathbf{P}_4$ . On the incoming (for the A and B molecules) hemisphere  $K_{21}^-$  these molecules still do not interact with one another. Consequently, their states are independent:

$$\begin{aligned} \hat{F}_{21}(\mathbf{P}_1 + \mathbf{P}_2, \mathbf{r}_{21}, \mu_1 \mathbf{P}_2 - \mu_2 \mathbf{P}_1) &= \hat{f}_1(\mathbf{P}_1) \hat{f}_2(\mathbf{P}_2) \\ \text{for } \mathbf{r}_{21} \in K_{21}^-. \end{aligned} \quad (4.15)$$

Similarly, on the incoming hemisphere  $K_{43}^-$  of the C and D molecules, we have

$$\hat{F}_{43}(\mathbf{P}_3 + \mathbf{P}_4, \mathbf{r}_{43}, \mu_3 \mathbf{P}_4 - \mu_4 \mathbf{P}_3) = \hat{f}_3(\mathbf{P}_3) \hat{f}_4(\mathbf{P}_4). \quad (4.16)$$

Since  $\hat{f}_1(\mathbf{P}_1)$ ,  $\hat{f}_2(\mathbf{P}_2)$  are independent of  $\mathbf{r}_{21}$  we have

$$\begin{aligned} & \int_{K_{21}^-} dK_{21}(\mathbf{v}_{21})_n g(\hat{f}_1 \hat{f}_2) \\ & = g(\hat{f}_1 \hat{f}_2) \int_{K_{21}^-} dK_{21}(\mathbf{v}_{21})_n = -\pi r_0^2 g(\hat{f}_1 \hat{f}_2) \\ & = -g(\hat{f}_1 \hat{f}_2) \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n. \end{aligned}$$

Similarly, by virtue of (4.16) the integral over  $K_{43}^-$  can be converted into an integral over  $K_{43}^+$ , taken with the opposite sign. Using this, we find from (4.14) after substituting (4.15) and (4.16)

$$\begin{aligned} & \text{Tr}_1 \text{Tr}_2 \int d\mathbf{P}_1 d\mathbf{P}_2 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n [g(\hat{F}_{21}(\mathbf{P}_1 \\ & + \mathbf{P}_2, \mathbf{r}_{21}, \mu_1 \mathbf{P}_2 - \mu_2 \mathbf{P}_1)) - g(\hat{f}_1(\mathbf{P}_1) \hat{f}_2(\mathbf{P}_2))] \\ & + \text{Tr}_3 \text{Tr}_4 \int d\mathbf{P}_3 d\mathbf{P}_4 \int_{K_{43}^+} dK_{43}(\mathbf{v}_{43})_n [g(\hat{F}_{43}(\mathbf{P}_3 \\ & + \mathbf{P}_4, \mathbf{r}_{43}, \mu_3 \mathbf{P}_4 - \mu_4 \mathbf{P}_3)) - g(\hat{f}_3(\mathbf{P}_3) \hat{f}_4(\mathbf{P}_4))] = 0. \end{aligned} \quad (4.17)$$

## 5. KINETIC EQUATIONS FOR BIMOLECULAR REACTIONS AND THE H-THEOREM

We first set  $g(f) = f$  in Eq. (4.17). Clearly, the first term

$$\text{Tr}_1 \text{Tr}_2 \int d\mathbf{P}_1 d\mathbf{P}_2 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n [\hat{F}_{21} - \hat{f}_1 \hat{f}_2] \quad (5.1)$$

on the left-hand side of the relation thus obtained is equal to the number of pairs of A and B molecules per unit volume which appear as a result of the reaction  $C+D \rightarrow A+B$  and disappear because they enter into the reaction  $A+B \rightarrow C+D$ . Likewise, the second term

$$\text{Tr}_3 \text{Tr}_4 \int d\mathbf{P}_3 d\mathbf{P}_4 \int_{K_{43}^+} dK_{43}(\mathbf{v}_{43})_n [\hat{F}_{43} - \hat{f}_3 \hat{f}_4] \quad (5.2)$$

is equal to the number of pairs of C and D molecules which appear due to the second of these reactions minus the number of pairs that disappear due to the first reaction. The sum of these two terms vanishes, since the total number of molecules does not change as a result of the reactions. In order to find the derivative  $\hat{f}_1(\mathbf{P}_1)$  it is enough to take the trace  $\text{Tr}_1$  and integrate with respect to  $\mathbf{P}_1$  in (5.1):

$$\begin{aligned} \hat{f}_1(\mathbf{P}_1) &= \text{Tr}_2 \int d\mathbf{P}_2 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n [\hat{F}_{21}(\mathbf{P}_1 \\ & + \mathbf{P}_2, \mathbf{r}_{21}, \mu_1 \mathbf{P}_2 - \mu_2 \mathbf{P}_1) - \hat{f}_1(\mathbf{P}_1) \hat{f}_2(\mathbf{P}_2)] \\ & - \frac{i}{\hbar} [\hat{H}_1, \hat{f}_1(\mathbf{P}_1)]. \end{aligned} \quad (5.3)$$

Similarly, from (5.1) and (5.2) we find

$$\begin{aligned} \hat{f}_2(\mathbf{P}_2) = & \text{Tr}_1 \int d\mathbf{P}_1 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n [\hat{F}_{21} - \hat{f}_1 \hat{f}_2] \\ & - \frac{i}{\hbar} [\hat{H}_2, \hat{f}_2] \end{aligned} \quad (5.4)$$

$$\begin{aligned} \hat{f}_3(\mathbf{P}_3) = & \text{Tr}_4 \int d\mathbf{P}_4 \int_{K_{43}^+} dK_{43}(\mathbf{v}_{43})_n [\hat{F}_{43}(\mathbf{P}_3) \\ & + \mathbf{P}_4, r_{43}, \mu_3 \mathbf{P}_4 - \mu_4 \mathbf{P}_3] - \hat{f}_3(\mathbf{P}_3) \hat{f}_4(\mathbf{P}_4) \\ & - \frac{i}{\hbar} [\hat{H}_3, \hat{f}_3(\mathbf{P}_3)], \end{aligned} \quad (5.5)$$

$$\begin{aligned} \hat{f}_4(\mathbf{P}_4) = & \text{Tr}_3 \int d\mathbf{P}_3 \int_{K_{43}^+} dK_{43}(\mathbf{v}_{43})_n [\hat{F}_{43} - \hat{f}_3 \hat{f}_4] \\ & - \frac{i}{\hbar} [\hat{H}_4, \hat{f}_4]. \end{aligned} \quad (5.6)$$

We determine the entropy density of the different types of molecules using the same formula

$$s_j = -k \text{Tr}_j \int d\mathbf{P}_j \hat{f}_j(\mathbf{P}_j) \{ \ln[\gamma_j \hat{f}_j(\mathbf{P}_j)] - 1 \},$$

$$j = 1, \dots, 4,$$

as in Ref. 2. Here we have written  $\gamma_j = (2\pi\hbar)^3 \delta_j / G_j$ . Differentiating this expression with respect to time, summing over  $j$ , and taking into account (5.3)–(5.6), we find

$$\begin{aligned} \dot{s} = & \sum_{j=1}^4 \dot{s}_j = -k \text{Tr}_1 \text{Tr}_2 \int d\mathbf{P}_1 d\mathbf{P}_2 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n \\ & \times [\hat{F}_{21} - \hat{f}_1 \hat{f}_2] \ln(\gamma_1 \gamma_2 \hat{f}_1 \hat{f}_2) \\ & - k \text{Tr}_3 \text{Tr}_4 \int d\mathbf{P}_3 d\mathbf{P}_4 \int_{K_{43}^+} dK_{43}(\mathbf{v}_{43})_n \\ & \times [\hat{F}_{43} - \hat{f}_3 \hat{f}_4] \ln(\gamma_3 \gamma_4 \hat{f}_3 \hat{f}_4). \end{aligned}$$

To the expression on the right-hand side we add the expression on the left-hand side of Eq. (4.17) for the case  $g(f) = kf[\ln(\gamma_1 \gamma_2 f) - 1]$ . Since we have  $\gamma_3 \gamma_4 = \gamma_1 \gamma_2$ , after some simplification we are left with

$$\begin{aligned} \dot{s} = & k \text{Tr}_1 \text{Tr}_2 \int d\mathbf{P}_1 d\mathbf{P}_2 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n \\ & \times [\hat{F}_{21} \ln(\gamma_1 \gamma_2 \hat{F}_{21}) - \hat{F}_{21} + \hat{f}_1 \hat{f}_2 - \hat{F}_{21} \ln(\gamma_1 \gamma_2 f_1 f_2)] \\ & + k \text{Tr}_3 \text{Tr}_4 \int d\mathbf{P}_3 d\mathbf{P}_4 \int_{K_{43}^+} dK_{43}(\mathbf{v}_{43})_n \\ & \times [\hat{F}_{43} \ln(\gamma_3 \gamma_4 \hat{F}_{43}) - \hat{F}_{43} + \hat{f}_3 \hat{f}_4 - \hat{F}_{43} \ln(\gamma_3 \gamma_4 f_3 f_4)]. \end{aligned} \quad (5.7)$$

Using the notation  $\gamma_1 \gamma_2 \hat{F}_{21} = \hat{M}$ ,  $\gamma_1 \gamma_2 \hat{f}_1 \hat{f}_2 = \hat{N}$  we can write the first term on the right-hand side of (5.7) as

$$\begin{aligned} \frac{k}{\gamma_1 \gamma_2} \int d\mathbf{P}_1 d\mathbf{P}_2 \int_{K_{21}^+} dK_{21}(\mathbf{v}_{21})_n \text{Tr}_1 \text{Tr}_2 [\hat{M} \ln \hat{M} - \hat{M} \\ + \hat{N} - \hat{M} \ln \hat{N}]. \end{aligned} \quad (5.8)$$

In Ref. 2 it was shown that

$$\text{Tr}(\hat{M} \ln \hat{M} - \hat{M} + \hat{N} - \hat{M} \ln \hat{N}) \geq 0$$

for arbitrary nonnegative definite operators  $\hat{M}$  and  $\hat{N}$ . In Appendix 2 it is shown that the operator  $\hat{F}_{21}$  is nonnegative definite (or rather, is essentially identical with such an operator). Also taking into account the fact that  $(\mathbf{v}_{21})_n \geq 0$  on  $K_{21}^+$ , we can convince ourselves that expression (5.8) is nonnegative. By the same means we can show the nonnegativity of the second term on the right-hand side of (5.7). Thus the inequality  $\dot{s} \geq 0$  is proven.

Exactly the same method of proof is also applicable to more complicated reactions, e.g.,  $A+B+C \rightleftharpoons D+E$ . In this case there are six submolecules, which can combine in various ways with one another.

## APPENDIX 1. DERIVATION OF AN AUXILIARY FORMULA

Assume that the kinetic energy has the form

$$\hat{T}_0'' = \frac{1}{2} M_{\alpha\beta}^{-1} \hat{\pi}_\alpha \hat{\pi}_\beta. \quad (A1.1)$$

Consider the commutator  $[\hat{T}_0'', \hat{G}]$ . Since  $M_{\alpha\beta}^{-1} = M_{\beta\alpha}^{-1}$  holds, we have

$$\sum_{\alpha\beta} M_{\alpha\beta}^{-1} [\hat{\pi}_\alpha \hat{\pi}_\beta, \hat{G}] = \sum_{\alpha\beta} M_{\alpha\beta}^{-1} [\hat{\pi}_\alpha, \hat{\pi}_\beta, \hat{G} + \hat{G} \hat{\pi}_\beta].$$

Hence by virtue of (A1.1)

$$[\hat{T}_0'', \hat{G}] = \frac{1}{2} \sum_{\alpha} [\hat{\pi}_\alpha, \hat{R}_\alpha \hat{G} + \hat{G} \hat{R}_\alpha], \quad (A1.2)$$

where  $\hat{R}_\alpha = \sum_{\beta} M_{\alpha\beta}^{-1} \hat{\pi}_\beta$ . By virtue of the relation  $[\hat{\pi}_\gamma, \hat{\zeta}_\alpha] = -i\hbar \delta_{\gamma\alpha}$  we have

$$\hat{R}_\alpha = \frac{i}{\hbar} [\hat{T}_0'', \hat{\zeta}_\alpha].$$

Since  $\zeta_\alpha$  commutes with all terms on the right-hand side of the relation (4.2) (where  $T_0 = T_0' + T_0''$ ) except  $T_0''$ , we have

$$\frac{i}{\hbar} [\hat{T}_0'', \hat{\zeta}_\alpha] = \frac{i}{\hbar} [\hat{H}_5, \hat{\zeta}_\alpha] = \frac{d\hat{\zeta}_\alpha}{dt},$$

i.e.,  $\hat{R}_\alpha = d\hat{\zeta}_\alpha/dt$ . Using the  $\hat{\zeta}$  representation, in which  $\hat{\pi}_\alpha = -i\hbar \partial/\partial \zeta_\alpha$ , we can easily show that for any operator  $\hat{M}$  the expression

$$[\hat{\pi}_\alpha, \hat{M}]|_{\zeta'=\zeta} = -i\hbar \left\{ \left( \frac{\partial}{\partial \zeta_\alpha} + \frac{\partial}{\partial \zeta'_\alpha} \right) M_{\zeta\zeta'} \right\}_{\zeta'=\zeta}$$

is equivalent to  $-i\hbar \partial M_{\zeta\zeta'}/\partial \zeta$ . Hence from (A1.2) we find

$$[\hat{T}_0'', \hat{G}]|_{\zeta'=\zeta} = -\frac{i\hbar}{2} \frac{\partial}{\partial \zeta} \left\{ \left[ \frac{d\hat{\zeta}_\alpha}{dt}, \hat{G} \right] \right\}_{\zeta'=\zeta}.$$

Integrating this relation over some region  $V$  and using Gauss's theorem we have

$$\int_V d\xi [\hat{T}_0'', \hat{G}]|_{\xi'=\xi} = -\frac{i\hbar}{2} \int_L dL l_\alpha \left[ \frac{d\hat{\xi}_\alpha}{dt}, \hat{G} \right]_+ \Big|_{\xi'=\xi} \quad (\text{A1.3})$$

Here  $L$  is a surface enclosing the region  $V$  and  $l$  is the unit vector in the direction of the exterior normal to  $L$ .

## APPENDIX 2. NONNEGATIVE DEFINITENESS OF THE OPERATOR $\hat{F}_{21}$

We introduce the auxiliary density matrix  $\hat{\rho}_0(\mathbf{r}, \mathbf{P})$ , which corresponds to the Wigner distribution

$$\mathcal{W}_{21}[\hat{\rho}_0(\mathbf{r}, \mathbf{P})]_{r_{21}, P_{21}} = (2\pi\sigma_r^2\sigma_P^2)^{-3/2} \exp\left[-\frac{1}{2\sigma_r^2}|\mathbf{r}_{21} - \mathbf{r}|^2 - \frac{1}{2\sigma_P^2}|\mathbf{P}_{21} - \mathbf{P}|^2\right]. \quad (\text{A2.1})$$

This function defines  $\hat{\rho}_0(\mathbf{r}, \mathbf{P})$  for  $\sigma_r, \sigma_P \geq \hbar/2$ . We assume

$$\sigma_r, \sigma_P = \hbar/2. \quad (\text{A2.2})$$

Then the state  $\rho_0$  is pure, i.e.,

$$\rho_0(\mathbf{r}, \mathbf{P}) = |\mathbf{r}, \mathbf{P}\rangle\langle\mathbf{r}, \mathbf{P}|. \quad (\text{A2.3})$$

Using (A2.3) we introduce the operator function

$$\begin{aligned} \hat{D}(\mathbf{r}, \mathbf{P}) &= (2\pi\hbar)^{-3} \text{Tr}_0 \hat{\rho}_0(\mathbf{r}, \mathbf{P}) \hat{f}_{21} \\ &= (2\pi\hbar)^{-3} \langle\mathbf{r}, \mathbf{P}|\hat{f}_{21}|\mathbf{r}, \mathbf{P}\rangle, \end{aligned} \quad (\text{A2.4})$$

where  $\text{Tr}_0$  is a partial trace, which does not involve the internal variables of the A and B molecules. It is evident that the operator (A2.4) is nonnegative definite, i.e.,  $\varphi^+ \hat{D} \varphi \geq 0$  for any function  $\varphi$ . In fact, setting  $\chi = |\mathbf{r}, \mathbf{P}\rangle \otimes \varphi$  we have  $\chi^+ \hat{f}_{21} \chi = \varphi^+ \hat{D} \varphi / (2\pi\hbar)^3 \geq 0$  by virtue of the nonnegative definiteness of the operator  $\hat{f}_{21}$ .

Let us compare the operator function (A2.4) with  $F_{21}(r_{21}, P_{21}) \equiv \mathcal{W}_{21}[\hat{f}_{21}]$ . These operator functions are of the same type, i.e., they act in the same Hilbert space and depend on the same arguments if we set  $\mathbf{r}_{21} = \mathbf{r}$ ,  $\mathbf{P}_{21} = \mathbf{P}$ . We will show that the difference between (A2.4) and  $F_{21}(\mathbf{r}, \mathbf{P})$  is small.

Taking into account the explicit form (4.12) of the Wigner transformation we can show without difficulty that for arbitrary operators  $\hat{L}$  and  $\hat{M}$  we have

$$\text{Tr}_0 \hat{L} \hat{M} = (2\pi\hbar)^3 \int \mathcal{W}_{21}[\hat{L}] \mathcal{W}_{21}[\hat{M}] dr_{21} dP_{21}.$$

Hence by virtue of (A2.1) we find from the relation  $(2\pi\hbar)^3 \hat{D} = \text{Tr}_0 \hat{\rho}_0 \hat{f}_{21}$

$$\begin{aligned} \hat{D}(\mathbf{r}, \mathbf{P}) &= (2\pi\sigma_r^2\sigma_P^2)^{-3/2} \int \exp\left[-\frac{1}{2\sigma_r^2}|\mathbf{r} - \mathbf{r}_{21}|^2 - \frac{1}{2\sigma_P^2}|\mathbf{P} - \mathbf{P}_{21}|^2\right] \hat{F}_{21}(\mathbf{r}_{21}, \mathbf{P}_{21}) d\mathbf{r}_{21} d\mathbf{P}_{21}. \end{aligned} \quad (\text{A2.5})$$

Using the freedom to choose the quantities  $\sigma_r, \sigma_P$  within the constraint (A2.2), we can set

$$\sigma_r^2 = r_0 \left(\frac{\hbar}{2r_0\Delta P}\right)^{1/2}, \quad \sigma_P = \Delta P \left(\frac{\hbar}{2r_0\Delta P}\right)^{1/2}.$$

Then, on the one hand, (A2.2) will hold, while on the other hand, by virtue of  $r_0\Delta P \ll \hbar$  we have

$$\sigma_r \ll r_0, \quad \sigma_P \ll \Delta P. \quad (\text{A2.6})$$

The integral on the right-hand side of (A2.5) is nothing but a smoothing integral. In view of (A2.6) this smoothing deforms the function  $\hat{F}_{21}(r_{21}, P_{21})$  very slightly in the region which is semiclassical with respect to  $r_{21}$  and  $P_{21}$ . In fact, (A2.5) can be written

$$\begin{aligned} \hat{D}(\mathbf{r}, \mathbf{P}) &= (2\pi\sigma_r^2\sigma_P^2)^{-3/2} \int \exp\left(-\frac{|\xi|^2}{2\sigma_r^2} - \frac{|\eta|^2}{2\sigma_P^2}\right) \\ &\quad \times \hat{F}_{21}(\mathbf{r} - \xi, \mathbf{P} - \eta) d\xi d\eta. \end{aligned}$$

Expanding  $\hat{F}_{21}$  in a Taylor series with respect to  $\xi$  and  $\eta$  and performing the integration, we find

$$\hat{D}(\mathbf{r}, \mathbf{P}) = \hat{F}_{21}(\mathbf{r}, \mathbf{P}) + \frac{1}{2} (\sigma_r^2 \nabla_r^2 + \sigma_P^2 \nabla_P^2) \hat{F}_{21}(\mathbf{r}, \mathbf{P}) + \dots$$

Since we can estimate  $r_0/2 \leq r_{21} \leq 3r_0/2$  in the semiclassical region  $\|\nabla_r^2 \hat{F}_{21}\| \sim \|\hat{F}_{21}\|/r_0^2$ ,  $\|\nabla_P^2 \hat{F}_{21}\| \sim \|\hat{F}_{21}\|/(\Delta P)^2$ , the difference between  $\hat{D}(\mathbf{r}, \mathbf{P})$  and  $\hat{F}_{21}(\mathbf{r}, \mathbf{P})$  is small in view of (A2.6). Here  $\|\dots\|$  denotes the norm of the operator.

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Translated by David L. Book