

## Quantum theory of the "classical" intermolecular interaction potential

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The "classical" potential of intermolecular interaction, defining the motion of centers of mass of interacting molecules and taking into account a mutual dependence on internal and external motions of molecules, has been determined on the basis of the quantum theory. A semiclassical representation has been introduced into the quantum theory of interacting molecules and this allows us to obtain the self-consistent semiclassical approximation, to find its applicability limits, and to take into account the quantum and fluctuation corrections to the semiclassical approximations.

### I. INTRODUCTION

The use of the "classical" intermolecular interaction potential and the semiclassical approximation results in significant simplification of calculations in statistical physics of interacting molecules and its applications.<sup>1-3</sup>

In the present paper the determination of the classical intermolecular potential has been obtained using the method of transition from the quantum theory of the interacting subsystem to the semiclassical one. This method was developed in quantum electrodynamics<sup>4</sup> and then it was applied in statistical physics of interacting molecules.<sup>5</sup>

The method of the transition to the semiclassical theory enables one to determine the applicability limits of the classical potential in the quantum theory of the intermolecular interaction, to obtain the self-consistent Hamilton equations, describing the intermolecular interaction in semiclassical approximation and to find the applicability limits of the semiclassical approximation. The possibility to use the semiclassical approximation equations for calculation of the quantum averages is also discussed.

In Sec. II the classical momentum and coordinate operators are introduced, and their use in the quantum theory is discussed. Section III is devoted to the proceeding to the classical limit of the quantum theory on the basis of the classical momentum and coordinate operators. In Sec. IV the classical intermolecular potential is defined and the self-consistent Hamilton equations are derived from the quantum theory. These are the equations of the semiclassical theory. The semiclassical representation of the quantum theory is introduced and a possibility of its using to improve the semiclassical theory is discussed. In Sec. V the statistical physics of the interacting molecules, namely, the problem of statistical description of the external degrees of freedom of

molecules is formulated on the basis of the semiclassical representation. The generalized Fokker-Planck equation for the distribution function of the molecular momenta and coordinates is obtained. This equation takes into account the quantum and fluctuations corrections to the semiclassical approximation description. In Sec. VI we discuss briefly the possibility of the use of the suggested approach for solving definite problems of the intermolecular interaction. The possibility of taking into account the influence of the strong electromagnetic field on the intermolecular interaction is pointed out.

### II. OPERATORS OF CLASSICAL MOMENTUM AND COORDINATE

The quantum-mechanical operators of the momentum  $\hat{p}$  and the coordinate  $\hat{q}$  can be represented in the following form:

$$\begin{aligned}\hat{p} &= i \left( \frac{\hbar m \omega}{2} \right)^{1/2} (\hat{a}^\dagger - \hat{a}), \\ \hat{q} &= \left( \frac{\hbar}{2m\omega} \right)^{1/2} (\hat{a}^\dagger + \hat{a}), \\ \omega &= \frac{\langle 0 | H | 0 \rangle}{\hbar}.\end{aligned}\tag{1}$$

Here  $\hat{a}^\dagger$  and  $\hat{a}$  are the creation and annihilation operators, obeying the condition  $[\hat{a}, \hat{a}^\dagger] = 1$ ,  $m$  is the mass of a quantum particle,  $|0\rangle$  is the vacuum state, and  $H$  is the Hamiltonian of the particle. In the case of the harmonic oscillator  $\omega$  is the angular frequency and Eq. (1) gives us well-known definitions.<sup>6</sup> The operators  $\hat{p}$ ,  $\hat{q}$ ,  $\hat{a}^\dagger$ , and  $\hat{a}$  are defined in the Hilbert space  $\mathcal{H}$ .

For proceeding to the classical limit of the quantum theory one should use the extended Hilbert space  $\mathcal{W} = \mathcal{H} \otimes \mathcal{H}$ , where  $\otimes$  is the direct product sign. In the space  $\mathcal{W}$  the operators  $\hat{p}$  and  $\hat{q}$  are written as

$$\hat{p}_{\mathcal{W}} = \hat{p} \otimes I, \quad \hat{q}_{\mathcal{W}} = \hat{q} \otimes I,\tag{2}$$

where  $I$  is the unit operator in  $\mathcal{K}$ . Now we can introduce in the space  $\mathcal{W}$  the commutation operators  $p_0$  and  $q_0$ , which are connected with the classical description of the particle

$$\begin{aligned} p_0 &= \hat{p} \otimes I - I \otimes \hat{p}, \\ q_0 &= \hat{q} \otimes I + I \otimes \hat{q}, \\ [p_0, q_0] &= 0. \end{aligned} \quad (3)$$

The eigenstates  $|\Psi_a\rangle$  of the operators  $p_0$  and  $q_0$  can easily be found<sup>4,5</sup> and the system of eigenstates is complete and orthonormal:

$$p_0 |\Psi_a\rangle = p |\Psi_a\rangle, \quad q_0 |\Psi_a\rangle = q |\Psi_a\rangle, \quad (4)$$

$$p = \langle a | \hat{p} | a \rangle = (2\hbar m \omega)^{1/2} \text{Im} a, \quad (5)$$

$$q = \langle a | \hat{q} | a \rangle = \left(\frac{2\hbar}{m\omega}\right)^{1/2} \text{Re} a,$$

$$|\Psi_a\rangle = \pi^{-5/2} e^{-|a|^2/2} \int e^{\bar{\alpha}\beta + a\bar{\alpha} - \bar{\alpha}\beta} |\alpha\rangle_l \otimes |\beta\rangle_r e^{-(|\alpha|^2 + |\beta|^2)/2} d^2\alpha d^2\beta, \quad (6)$$

$$\langle \Psi_a | \Psi_b \rangle = \delta(\text{Re} a - \text{Re} b) \delta(\text{Im} a - \text{Im} b), \quad (7)$$

$$\int |\Psi_a\rangle \langle \Psi_a| da = I \otimes I, \quad da = d \text{Re} a d \text{Im} a. \quad (8)$$

Here  $|\alpha\rangle$ ,  $|\beta\rangle$ ,  $|a\rangle$  are the coherent states and  $|\alpha\rangle_l$  and  $|\beta\rangle_r$  indicate that the state  $|\alpha\rangle$  is from the left-hand  $\mathcal{K}$  and the state  $|\beta\rangle$  is from the right-hand  $\mathcal{K}$  in  $\mathcal{W} = \mathcal{K} \otimes \mathcal{K}$ . The facts that the eigenvalues of the operators  $p_0$  and  $q_0$  are the means with respect to the coherent state  $|a\rangle$ , and the existence of complete orthonormal set of eigenstates  $|\Psi_a\rangle$  allows to interpret the operators  $p_0$  and  $q_0$  as the operators of the classical momentum and coordinate. Now we show that it is possible to use the operators in the extended Hilbert space  $\mathcal{W}$  for solving a quantum problem. For this purpose we determine the state in  $\mathcal{W}$  as

$$R = \rho \otimes |0\rangle_r \langle 0|_r, \quad (9)$$

where  $\rho$  is the density matrix (the state) in  $\mathcal{K}$  and

$|0\rangle_r$  is the vacuum state from the right-hand  $\mathcal{K}$  in  $\mathcal{W}$ . If  $f(\hat{p}, \hat{q})$  is an operator in  $\mathcal{K}$ , then the transformation to  $\mathcal{W}$  according to the rule  $f_{\mathcal{W}} = f(p_{\mathcal{W}}, q_{\mathcal{W}})$  and Eqs. (2) and (9) gives the obvious relation

$$\text{Tr}_{\mathcal{K}} \rho f(\hat{p}, \hat{q}) = \text{Tr}_{\mathcal{W}} R f(p_{\mathcal{W}}, q_{\mathcal{W}}). \quad (10)$$

It should be noted that a similar approach was used to describe the simultaneous measurement of the momentum and coordinate of the quantum harmonic oscillator with the minimum uncertainty.<sup>7</sup> The Hilbert space extension for studying the connection between the classical and the quantum mechanics was also used by Sudarshan and co-workers.<sup>8</sup>

For description of the transition from the quantum theory to the classical one we represent the operators  $p_{\mathcal{W}}$  and  $q_{\mathcal{W}}$  in the form

$$p_{\mathcal{W}} = p_0 + \Delta p, \quad q_{\mathcal{W}} = q_0 + \Delta q, \quad (11)$$

where the operators  $\Delta p$  and  $\Delta q$  are determined by Eqs. (2) and (3) and obey the following commutation relations:

$$[p_0, \Delta p] = [q_0, \Delta q] = 0, \quad (12)$$

$$[q_0, \Delta p] = [\Delta q, p_0] = [\Delta p, \Delta q] = i\hbar. \quad (13)$$

It should be noted that the above commutation relations as well as the existence of the operators  $p_0$  and  $q_0$  and their properties allow the calculations to be made without using an explicit form of the eigenstates  $|\Psi_a\rangle$ .

Now we insert Eq. (11) into  $f(p_{\mathcal{W}}, q_{\mathcal{W}})$  and expand  $f$  into the power series over  $\Delta p$  and  $\Delta q$ :

$$\begin{aligned} f(p_{\mathcal{W}}, q_{\mathcal{W}}) &= f(p_0, q_0) + \frac{\partial f(p_0, q_0)}{\partial p_0} \Delta p \\ &+ \frac{\partial f(p_0, q_0)}{\partial q_0} \Delta q + \dots \end{aligned} \quad (14)$$

Here the derivatives  $\partial f / \partial p_0$  and  $\partial f / \partial q_0$  are defined due to the commutativity of  $p_0$  and  $q_0$ . Substituting Eq. (14) into Eq. (10) and averaging it, we obtain

$$\begin{aligned} \langle f \rangle &= \text{Tr}_{\mathcal{W}} R \left( f(p_0, q_0) + \frac{\partial^2 f(p_0, q_0)}{\partial p_0^2} \langle 0 |_r (\Delta p)^2 | 0 \rangle_r + \frac{\partial^2 f(p_0, q_0)}{\partial q_0^2} \langle 0 |_r (\Delta q)^2 | 0 \rangle_r + \dots \right) \\ &= \int dp dq R(p, q) \left( f(p, q) + \frac{\partial^2 f(p, q)}{\partial p^2} \langle 0 |_r (\Delta p)^2 | 0 \rangle_r + \frac{\partial^2 f(p, q)}{\partial q^2} \langle 0 |_r (\Delta q)^2 | 0 \rangle_r + \dots \right), \end{aligned} \quad (15)$$

$$R(p, q) \equiv \langle \Psi_a | R | \Psi_a \rangle.$$

While deriving Eq. (15) we use the following relationship for the averaging in the space  $\mathcal{W}$ . If the operator is of the form  $A \otimes B$ , its average value in accordance with the definition of the state in  $\mathcal{W}$  can be written as

$$\langle A \otimes B \rangle = \text{Tr}_{\mathcal{W}} R A \otimes B = \text{Tr}_{\mathcal{K}} \rho A \langle 0 |_r B | 0 \rangle_r. \quad (16)$$

In the right-hand side of Eq. (15) we rewrite the trace operation using the properties of the states  $|\Psi_a\rangle$ , i.e., Eqs. (7) and (8).

Taking into account the definitions of  $\Delta p$  and  $\Delta q$ , resulting from Eqs. (11), (1), and (2), and the definition of  $\omega$  from Eq. (1), it is not difficult to show that

$$\begin{aligned} \langle 0 | (\Delta p)^2 | 0 \rangle &= \hbar m \omega / 2 = O(\hbar^2 / \lambda^2), \\ \langle 0 | (\Delta q)^2 | 0 \rangle &= \hbar / 2m \omega = O(\lambda^2), \end{aligned} \quad (17)$$

where  $\lambda$  is the de Broglie wavelength in the state  $|0\rangle$ , i.e., the operators  $\Delta p$  and  $\Delta q$  describe the quantum fluctuations.<sup>6</sup> It should be noted that the same definition of the average, Eq. (15), can easily be obtained in the coherent-state representation, using the procedures of antinormal ordering.<sup>9,10</sup> This fact can easily be understood if we take into account the following relation:

$$\langle \Psi_a | R | \Psi_a \rangle = R(p, q) = \langle a | \rho | a \rangle,$$

which results from the property  $\langle 0 | {}_r \Psi_a \rangle = |a\rangle$ . Here, as above,  $|a\rangle$  is the coherent state and  $|0\rangle_r$  is the vacuum state from the right-hand  $\mathcal{X}$  in  $\mathcal{W}$ . It should be noted that the properties of  $R(p, q)$  allow one to interpret it as the ordinary positively definite distribution function in the phase space. It is known<sup>6</sup> that the classical limit of the quantum value is obtained by neglecting the noncommutativity of the operators  $\hat{p}$  and  $\hat{q}$ , when the first term in the right-hand side of Eq. (15) is sufficient for calculating the average value.

Now we see that using the operators of the classical momentum and coordinate defined in the Hilbert space  $\mathcal{W}$ , and restricting ourselves to  $f(p_0, q_0)$ , we obtain from Eq. (15) the usual definition of the average value in the classical theory.

### III. CLASSICAL LIMIT OF QUANTUM THEORY

Now we discuss the use of the operators of the classical momentum and coordinate for proceeding to the classical limit of the quantum theory. Consider, for this purpose, the time evolution of the particle. Let  $H(\hat{p}, \hat{q})$  be the Hamiltonian of the particle and  $S$  be the evolution operator, obeying the Schrödinger equation

$$i\hbar \frac{\partial S}{\partial t} = HS, \quad S(t_0) = 1. \quad (18)$$

Let us make a transition to the space  $\mathcal{w}$ . In this case

$$H_{\mathcal{w}} = H(p_{\mathcal{w}}, q_{\mathcal{w}}), \quad S_{\mathcal{w}} = S \otimes I, \quad i\hbar \frac{\partial S_{\mathcal{w}}}{\partial t} = H_{\mathcal{w}} S_{\mathcal{w}}. \quad (19)$$

In order to determine the operators  $p_{\mathcal{w}}$  and  $q_{\mathcal{w}}$  in the Heisenberg representation it is necessary, according to Eq. (10), to determine time evolution of the operators  $p_0$ ,  $q_0$ ,  $\Delta p$ , and  $\Delta q$ . Using Eqs. (2), (3), (11), and (19), we obtain

$$S_{\mathcal{w}}^{-1} \Delta p S_{\mathcal{w}} = \Delta p, \quad S_{\mathcal{w}}^{-1} \Delta q S_{\mathcal{w}} = \Delta q, \quad (20)$$

$$\begin{aligned} S_{\mathcal{w}}^{-1} p_0 S_{\mathcal{w}} &\equiv p_H(t) = p_0 + \frac{i}{\hbar} \int_{t_0}^t S_{\mathcal{w}}^{-1}(\tau) [H_{\mathcal{w}}, p_0] S_{\mathcal{w}}(\tau) d\tau \\ &= p_0 - \int_{t_0}^t \frac{\partial H(p_S(\tau), q_S(\tau))}{\partial q_S(\tau)} d\tau - \sum_{n=1} \int_{t_0}^t \frac{\partial^{n+1} H(p_S, q_S)}{\partial q_S^{n+1}} d\tau \frac{(\Delta q)^n}{n!}, \end{aligned} \quad (21)$$

$$S_{\mathcal{w}}^{-1} q_0 S_{\mathcal{w}} \equiv q_H(t) = q_0 + \int_{t_0}^t \frac{\partial H(p_S(\tau), q_S(\tau))}{\partial p_S(\tau)} d\tau + \sum_{n=1} \int_{t_0}^t \frac{\partial^{n+1} H(p_S, q_S)}{\partial p_S^{n+1}} d\tau \frac{(\Delta p)^n}{n!}. \quad (22)$$

Here  $\partial H / \partial p_S \equiv S_{\mathcal{w}}^{-1} [\partial H(p_0, q_0) / \partial p_0] S_{\mathcal{w}}$ , whose eigenvalues will be the derivatives if  $p_S = p_S(p_0, q_0)$ ;  $q_S = q_S(p_0, q_0)$ . This is valid if one can restrict oneself by the two first terms in Eqs. (21) and (22) only. Introducing the designation

$$p_H = p_0 - \int_{t_0}^t \frac{\partial H(p_H(\tau), q_H(\tau))}{\partial q_H(\tau)} d\tau, \quad q_H = q_0 + \int_{t_0}^t \frac{\partial H(p_H(\tau), q_H(\tau))}{\partial p_H(\tau)} d\tau, \quad (23)$$

we can rewrite Eqs. (21) and (22) as

$$p_S = p_H + \delta p_H, \quad q_S = q_H + \delta q_H. \quad (24)$$

Here  $\delta p_H$  and  $\delta q_H$  denote the differences between  $p_S$  and  $p_H$  and  $q_S$  and  $q_H$ , respectively. Now we can write the average value of a certain operator  $f(\hat{p}, \hat{q})$  as follows:

$$\begin{aligned}
\langle f \rangle_t &= \text{Tr} R f(p_s + \Delta p, q_s + \Delta q) = \text{Tr} R \left( f(p_s, q_s) + \frac{\partial f(p_s, q_s)}{\partial p_s} \Delta p + \frac{\partial f(p_s, q_s)}{\partial q_s} \Delta q + \dots \right) \\
&= \text{Tr} R \left( f(p_H, q_H) + \frac{\partial f(p_H, q_H)}{\partial q_H} \delta q_H + \frac{\partial f(p_H, q_H)}{\partial p_H} \Delta p + \dots \right). \quad (25)
\end{aligned}$$

Taking into account Eqs. (21)–(24) and (17) and converting in Eq. (25) to the integration over  $p$  and  $q$ , we can easily find the conditions, which, if fulfilled, allow us to truncate Eq. (25) by the first term. So we have

$$\frac{\partial^2 \mathcal{U}}{\partial q^2} \lambda \ll \frac{\partial \mathcal{U}}{\partial q}, \quad p \gg \hbar/\lambda. \quad (26)$$

Here  $\mathcal{U}$  is the potential energy and  $p$  is the particle momentum. When the conditions (26) are fulfilled, we can rewrite the average value (25) in the form

$$\langle f \rangle_t = \int R(p, q) f(p(t), q(t)) dp dq. \quad (27)$$

Here

$$\begin{aligned}
p(t) \delta(a-b) &\equiv \langle \Psi_a | \hat{p}_H(t) | \Psi_b \rangle, \\
q(t) \delta(a-b) &\equiv \langle \Psi_a | q_H(t) | \Psi_b \rangle,
\end{aligned}$$

where  $p$  and  $q$  are given by Eqs. (23). Differentiation of Eq. (22) with respect to  $t$  and the above definition lead to the equation for  $p(t)$  and  $q(t)$ :

$$\begin{aligned}
\dot{p}(t) &= - \frac{\partial H(p(t), q(t))}{\partial q(t)}, \quad p(0) = p \\
\dot{q}_H(t) &= \frac{\partial H(p(t), q(t))}{\partial p(t)}, \quad q(0) = q. \quad (28)
\end{aligned}$$

One can see that Eqs. (28) are the usual Hamilton equations and the definition of the average value is identical to that in the classical theory. As a matter of fact, the conditions (26) which lead to the definition (27) determine the applicability limits of a classical approximation in the quantum mechanics.<sup>6</sup> It is clear, that  $p$  and  $q$  are the canonical conjugate variables of the classical mechanics. The above analysis shows the way in which the use of the classical momentum and coordinate operators enables one to solve the problem of proceeding to the classical limit in the quantum theory.

It should be noted that we can truncate the expansion of the Hamiltonian  $H(p_w, q_w)$  by the terms

$$H(p_0, q_0) + \frac{\partial H(p_0, q_0)}{\partial p_0} \Delta p + \frac{\partial H(p_0, q_0)}{\partial q_0} \Delta q$$

and obtain the same results, since the rest terms of the expansion give rise to the appearance of the

values negligible in the classical limit.

Now we can briefly formulate the main rules of using the classical momentum and coordinate operators to proceed to the classical limit in the quantum theory as follows.

(1) One has to convert the initial state  $\rho$  and the operators  $\hat{p}$  and  $\hat{q}$  into the extended Hilbert space in accordance with Eqs. (2) and (9); one should expand, using Eq. (11), all the operators  $f(p_w, q_w)$  corresponding to the physical values and the Hamiltonian of the problem  $H(p_w, q_w)$  over the powers of  $\Delta p$  and  $\Delta q$  and then to restrict oneself to  $f=f(p_0, q_0)$  and

$$H_w = H(p_0, q_0) + \frac{\partial H(p_0, q_0)}{\partial p_0} \Delta p + \frac{\partial H(p_0, q_0)}{\partial q_0} \Delta q.$$

(2) One has to find the operators  $p_0$  and  $q_0$  in the Heisenberg representation with the Hamiltonian  $H_w$  and to calculate the average values of  $f$  in the Heisenberg representation in accordance with the definition (10), using, for the trace calculation the states  $|\Psi_a\rangle$  and their properties, Eqs. (4)–(8). As a result we obtain Eqs. (27) and (28).

It should be noted that the above analysis is of methodical significance only, and it has been presented here just to illustrate the use of the classical momentum and coordinate operators. But in the case of interacting subsystems, one of which can be described by the classical mechanics, the application of the method of classical values operators leads to interesting physical results and allows significant simplification of the quantum problem of interacting subsystems.

#### IV. THE CLASSICAL INTERMOLECULAR POTENTIAL

The Hamiltonian of the quantum intermolecular interaction problem can be written in the form<sup>6</sup>

$$H = H_1(x) + H_2(\hat{p}) + H_{12}(\hat{q}, x). \quad (29)$$

Here  $H_1(x)$  is the Hamiltonian of internal molecular motions and  $x$  denotes the set of variables of the internal degrees of freedom,  $H_2(\hat{p})$  is the kinetic energy operator of the centers of mass of the molecules,  $H_{12}$  describes the intermolecular interactions, and  $\hat{p}$  and  $\hat{q}$  denote the sets of momenta and coordinates of the centers of mass of the molecules. The initial state of the system at the time moment  $t_0$  is determined by the density

matrix  $\rho = \rho_0 T$ , where  $\rho_0$  is the initial density matrix for the external degrees of freedom and  $T$  is the initial density matrix for the internal ones. Further we shall suppose that the applicability conditions of classical description of motions of the centers of mass of the molecules are fulfilled.

In order to proceed to the classical limit over the external degrees of freedom we use the results of the above sections and extend the Hilbert space of the external degrees of freedom. The initial density matrix of the system is written now as  $R = \rho \otimes |0\rangle_r \langle 0|_r$  and the operators  $\hat{p}_w, \hat{q}_w$  are used in the Hamiltonian (29) instead of the operators  $\hat{p}$  and  $\hat{q}$ . From the solution of the

Schrödinger equation with the transformed Hamiltonian (29) one can note that, as earlier, the operators  $\Delta p$  and  $\Delta q$  do not depend on time and in the classical limit their contribution to the average value can be neglected. In order to find time evolution of the operators  $p_0$  and  $q_0$  in the classical limit it is sufficient to take into account only the terms of the transformed Hamiltonian (29) expansion involving the first power  $\Delta p$  and  $\Delta q$ .

Now the quantum problem can be formulated using the following relations: The Schrödinger equation

$$i\hbar \frac{\partial U}{\partial t} = \left( H_1(x) + H_{12}(q_0, x) + \frac{\partial H_{12}(q_0, x)}{\partial q_0} \Delta q + H_2(p_0) + \frac{\partial H_2(p_0)}{\partial p_0} \Delta p \right) U, \quad U(t_0) = 1. \quad (30)$$

The definition of the average values

$$\langle f \rangle_t = \text{Tr} R U^{-1}(t) f(p_0, q_0, x) U(t). \quad (31)$$

It can easily be understood that to define the classical potential of the intermolecular interaction it is necessary to transit from the quantum theory of the interacting subsystems to a semiclassical one. For this purpose we represent the evolution operator  $U$ , obeying Eq. (30) in the following form:

$$U = Q Q_1, \quad (32)$$

where the unitary operator  $Q$  satisfies the equation

$$i\hbar \frac{\partial Q}{\partial t} = \left( \frac{\partial H_2(p_0)}{\partial p_0} \Delta p + \frac{\partial \Phi(q_0 | \varphi(p_0, q_0, t))}{\partial q_0} \Delta q + \frac{1}{2} \left[ \Delta q, \frac{\partial \Phi(q_0 | \varphi)}{\partial q_0} \right] \right) Q, \quad Q(t_0) = 1. \quad (33)$$

Here the operator  $\Phi(q_0 | \varphi)$  is not yet defined and the designation  $\partial \Phi(q_0 | \varphi) / \partial q_0$  means that  $\Phi$  is differentiated only with respect to  $q_0$  written to the left of the line. The need for taking into account two kinds of the dependence of  $\Phi$  on  $q_0$  will become obvious later, when we define  $\Phi$ .

Using Eq. (33), we can easily find that the operator  $Q$  converts the operators  $p_0$  and  $q_0$  into the solutions of the operator Hamilton equations and does not change the operator  $x$  as follows:

$$Q^{-1} p_0 Q = p_H, \quad \dot{p}_H = - \frac{\partial \Phi(q_H | Q^{-1} \varphi Q)}{\partial q_H}, \quad p_H(0) = p_0 \quad (34)$$

$$Q^{-1} q_0 Q = q_H, \quad \dot{q}_H = \frac{\partial H_2(p_H)}{\partial p_H}, \quad q_H(0) = q_0.$$

Equations (34) written for the eigenvalues of  $\dot{p}_H$  and  $\dot{q}_H$  are the Hamilton equations, describing the classical motion of the centers of mass of molecules in a certain potential  $\Phi(q_H | Q^{-1} \varphi Q)$ . The equation for the operator  $Q_1$  can be obtained if we take into account Eqs. (30) and (32)–(34) as follows:

$$i\hbar \frac{\partial Q_1}{\partial t} = \left\{ H_1(x) + H_2(p_H) + H_{12}(q_H, x) + \left( \frac{\partial H_{12}(q_H, x)}{\partial q_H} - \frac{\partial \Phi(q_H | Q^{-1} \varphi Q)}{\partial q_H} \right) Q^{-1} \Delta q Q - \frac{1}{2} Q^{-1} \left[ \Delta q, \frac{\partial \Phi(q_0 | \varphi)}{\partial q_0} \right] Q \right\} Q_1. \quad (35)$$

It can easily be seen that three first terms in the right-hand side of Eq. (35) are the Hamiltonian of the quantum subsystem (the internal degrees of the molecules) interacting with the classical subsystem (the centers of mass of the molecules motion in the potential  $\Phi$ ). As a consequence, one can separate out from the operator  $Q_1$  the evolution operator  $C$  which describes the time evolution of the states of the internal degrees of freedom interacting with certain classical movement of the molecules.

$$Q_1 = C \Theta, \quad (36)$$

$$i\hbar \frac{\partial C}{\partial t} = [H_1(x) + H_2(p_H) + H_{12}(q_H, x)] C, \quad C(t_0) = 1. \quad (37)$$

It is clear that the operator  $C$  changes only the operators of the quantum subsystem; and the operators  $p_0, q_0, p_H, q_H$  remain unchanged.

Now we see that the operator  $\Omega$ ,

$$\Omega = QC \quad (38)$$

changes both groups of operators. The operators of the classical subsystem are changed according to the Hamilton equations (34), while the operators of the quantum subsystem are changed by evolution operator  $C$ . Equations (34) and (37) give us the mathematical foundation of the approximate semiclassical theory and, using Eqs. (32), (36), and (38), one can obtain that the evolution operator of the quantum problem  $U$  can be represented as

$$U = \Omega \Theta. \quad (39)$$

The evolution operator  $\Theta$  takes into account the quantum correction for the equations of semiclassical theory [Eqs. (34) and (37)], and obeys the following equation:

$$i\hbar \frac{\partial \Theta}{\partial t} = \left\{ \left( \frac{\partial H_{12}(q_H | x_C)}{\partial q_H} - \frac{\partial \Phi(q_H | Q^{-1} \varphi Q)}{\partial q_H} \right) \Omega^{-1} \Delta q \Omega - \frac{1}{2} \Omega^{-1} \left[ \Delta q, \frac{\partial \Phi(q_0 | \varphi)}{\partial q_0} \right] \Omega \right\} \Theta, \quad \Theta(t_0) = 1. \quad (40)$$

Now we can determine  $\Phi(q_H | Q^{-1} \varphi Q)$  in such a way that the semiclassical approximation [Eq. (34) and (37)] will be the best possible approximation that can be obtained on the basis of the quantum theory of the interacting subsystems. For this purpose we have to require the Hamiltonian in Eq. (40) to describe the fluctuations only. This gives us

$$\Phi(q_H | Q^{-1} \varphi Q) = \text{Tr}_x T H_{12}(q_H | x_C). \quad (41)$$

It is not difficult to prove that the definition (41) is consistent from the mathematical point of view. This means that the operators  $Q$ ,  $C$  and,  $\Omega$  exist and have all the necessary properties used above.

Substituting Eq. (41) into Eqs. (34) and (37), it can easily be seen that this definition of  $\Phi$  transforms the semiclassical approximation into the selfconsistent one. Instead of Eqs. (34) and (37) we have

$$\Omega^{-1} p_0 \Omega = p_H, \quad \dot{p}_H = - \frac{\partial \langle H_{12}(q_H | x_C) \rangle_x}{\partial q_H}, \quad (42)$$

$$\Omega^{-1} q_0 \Omega = q_H, \quad \dot{q}_H = \frac{\partial H_2(p_H)}{\partial p_H}, \quad (43)$$

$$\Omega^{-1} x \Omega = C^{-1} x C \equiv x_C,$$

$$i\hbar \frac{\partial C}{\partial t} = [H_1(x) + H_{12}(q_H, x) + H_2(p_H)] C. \quad (44)$$

The semiclassical evolution operator  $\Omega$  obeys the equation

$$i\hbar \frac{\partial \Omega}{\partial t} = \left( H_1(x) + H_2(p_0) + \frac{\partial H_2(p_0)}{\partial p_0} \Delta p + H_{12}(q_0, x) + \frac{\partial \langle H_{12}(q_0 | QC^{-1} x C Q^{-1}) \rangle_x}{\partial q_0} \Delta q + \frac{1}{2} \left[ \Delta q, \frac{\partial \langle H_{12}(q_0 | QC^{-1} x C Q^{-1}) \rangle_x}{\partial q_0} \right] \right) \Omega. \quad (45)$$

The set of equations (42)–(44) are the self-consistent Hamilton equations. Equations (42) and (43) give us the molecular trajectories and Eq. (44) describes the time evolution of the internal degrees of freedom of the interacting molecules. Equations (42)–(44) show us how the mutual dependence of internal and external motions can be taken into account. Now it is clear that Eq. (41) defines the classical potential of the intermolecular interaction from the point of view of the quantum theory and that it is this potential which determines the trajectories of the molecules, see Eq. (42).

The form of Eq. (45) shows that it is too difficult to use the semiclassical evolution operator  $\Omega$  for the direct operator calculations of  $d_H$ ,  $q_H$ , and  $x_C$ . But it should be noted that such calculations are not necessary because the semiclassical approximation was introduced into physics for simplifying the calculations. The main results which can be obtained using the existence of the semiclassical evolution operator  $\Omega$  are the definition of the classical potential  $\Phi$ , Eq. (41), and the derivation of the set of self-consistent Hamilton equations (42)–(44). As a matter of fact, these equations are the cal-

culating apparatus of the semiclassical theory.

It is necessary to point out that by Eqs. (39) and (40)–(45) a new representation is introduced to the quantum theory, which can be called the semiclassical representation. In this representation the time dependence of the operators is defined by the operator  $\Omega$ , namely, by the set of Eqs. (42)–(44), and the time dependence of the state is defined by the operator  $\Theta$ . Taking into account Eqs. (41)–(44), one can rewrite Eq. (40) as

$$i\hbar \frac{\partial \Theta}{\partial t} = \left\{ \left( \frac{\partial H_{1,2}(q_H | x_c)}{\partial q_H} - \frac{\partial \langle H_{1,2}(q_H | x_c) \rangle_x}{\partial q_H} \right) \Omega^{-1} \Delta q \Omega - \frac{1}{2} \Omega^{-1} \left[ \Delta q, \frac{\partial \langle H_{1,2}(q_0 | QC^{-1}x CQ^{-1}) \rangle_x}{\partial q_0} \right] \Omega \right\} \Theta. \quad (46)$$

Now we can rewrite the average value, Eq. (31), in the semiclassical representation

$$\langle f \rangle_t = \text{Tr} R(t) f(p_H(t), q_H(t), x_c), \quad (47)$$

$$R(t) \equiv \Theta(t) R \Theta^{-1}(t). \quad (48)$$

The definition (47) gives us a possibility to find the applicability limits of semiclassical theory. When we wrote Eq. (31), we had omitted usual quantum corrections to  $f(p_0, q_0, x)$  which originate from noncommutativity of the operators  $\hat{p}$  and  $\hat{q}$ . The similar corrections were discussed in Secs. II and III. Equation (47) shows us that there is another kind of quantum correction to semiclassical theory which is due to the use of the trajectories or the classical potential instead of the appropriate operator. These corrections yield the time dependence of the density matrix in Eq. (47). The origin and meaning of these corrections are clear from the form of the Hamiltonian in Eq. (46). They are the quantum fluctuations.

It should be mentioned that the scheme for determining the classical potential and the conditions of its applicability to the description of the intermolecular interaction allows one to find the applicability limits of the approximation of given trajectories which is often met in spectroscopy.<sup>11</sup>

In the approximation of the given trajectories the Schrödinger equation is solved for the operator of semiclassical evolution of the internal degrees of freedom:

$$i\hbar \frac{\partial C}{\partial t} = [H_1(x) + H_{1,2}(\tilde{q}, x) + H_2(\tilde{p})] C, \quad (44')$$

where  $\tilde{p}$  and  $\tilde{q}$  are the solutions of the Hamiltonian equations with a certain given potential  $v(\tilde{q})$ . The

Schrödinger equation can be written for the operator  $Q$ , converting  $p_0, q_0$  to  $\tilde{p}, \tilde{q}$ :

$$i\hbar \frac{\partial Q}{\partial t} = \left( \frac{\partial H_2(p_0)}{\partial p_0} \Delta p + \frac{\partial v(q_0)}{\partial q_0} \Delta q \right) Q, \quad (33')$$

and the applicability limits of this approach will be defined by the equation for the operator  $\Theta$

$$i\hbar \frac{\partial \Theta}{\partial t} = \left( \frac{\partial H_{1,2}(\tilde{q} | x_c)}{\partial \tilde{q}} - \frac{\partial v(\tilde{q})}{\partial \tilde{q}} \right) \Omega^{-1} \Delta q \Omega \Theta, \quad (46')$$

where, as previously,  $\Omega = QC$ . It can easily be seen from Eq. (46') that all corrections to the case of the given trajectories can be written in terms of the solutions of Eqs. (44') and (33'). So we have the calculating method, giving us the possibility to solve the intermolecular interaction problem, based on the known solution of the given trajectories approximation. We intend to use this method for taking into account the change of the trajectories and internal states of colliding molecules.

#### V. THE SEMICLASSICAL REPRESENTATION IN THE STATISTICAL PHYSICS OF THE INTERACTING MOLECULES

Let us consider the density matrix  $R(t)$  in the semiclassical representation which is determined by Eqs. (46) and (48). We represent  $R(t)$  in the standard form<sup>12</sup>

$$R(t) = F(t)T + \Delta R, \quad F(t) = \text{Tr}_x R(t), \quad (49)$$

and assume that the time evolution of operators of the quantum subsystem is described quite exactly by the operator  $C$ . So we consider that for calculating the averages it is sufficient to take

$$R(t) = F(t)T. \quad (50)$$

The density-matrix definition in the form of Eq. (50) is equivalent to an assumption that the subsystem of internal degrees of freedom, interacting with the classical subsystem of the external degrees of freedom, is the dissipative subsystem.<sup>12</sup>

Now it is not difficult to obtain from Eqs. (46), (48), and (49) the equation for the density matrix of the external degrees of freedom  $F(t)$  as follows:

$$\frac{\partial F(t)}{\partial t} = \frac{1}{\hbar^2} \text{Tr}_x \int_{t_0}^t [H_\Theta(t), [H_\Theta(\tau), F(\tau)T]] d\tau. \quad (51)$$

Transiting to the matrix elements according to the states  $|\Psi_a\rangle$  and denoting  $\langle \Psi_a | R(t) | \Psi_a \rangle \equiv F(p, q, t)$  and calculating the commutators in Eq. (41), the following equation is obtained:

$$\frac{\partial F(p, q, t)}{\partial t} = \frac{\partial}{\partial p} \int_{t_0}^t \left\langle \left\langle \frac{\partial H_{1,2}(q_H(t) | x_c(t))}{\partial q_H(t)}, \frac{\partial H_{1,2}(q_H(\tau) | x_c(\tau))}{\partial q_H(\tau)} \right\rangle \right\rangle_x \frac{\partial}{\partial p} + \left\langle \left\langle \frac{\partial H_{1,2}(q_H(t) | x_c(t))}{\partial q_H(t)}, \frac{\partial}{\partial p} \frac{\partial H_{1,2}(q_H(\tau) | x_c(\tau))}{\partial q_H(\tau)} \right\rangle \right\rangle_x F(p, q, \tau) d\tau. \quad (52)$$

Here  $\langle\langle A; B \rangle\rangle \equiv \frac{1}{2} \langle AB \rangle + \frac{1}{2} \langle BA \rangle - \langle A \rangle \langle B \rangle$  is the correlator of the intermolecular forces. Deriving Eq. (52), we took into account the fact that the subsystem of external degrees of freedom is classical which allowed us to omit the terms with nondiagonal matrix elements of  $F(t)$  in the right-hand side of Eq. (53).

Equation (52) together with the equations of semiclassical approximation (42)–(44) makes it possible to replace the quantum description of interacting molecules by a simpler, from the calculational point of view, semiclassical one that is based on the use of the classical potential of intermolecular interaction.

It is necessary to add that Eq. (52) is a generalized Fokker-Planck equation, and the absence of usual Liouville term in the right-hand side of Eq. (52) is due to the use of the semiclassical representation. It should be noted that usually in the statistical physics the Fokker-Planck equation is the approximation of the Boltzmann equation.<sup>13</sup> Here we have another case. Equation (52) is that for many-particle distribution function and the irreversibility originates from the influence of the quantum "noise" on the statistical properties of the molecular motion.

## VI. CONCLUSION

The above analysis allowed the determination of the quantum meaning of the "classical" potential for interacting molecules. This gives us the

possibility to calculate the potential, e.g., by solving the set of Eqs. (33) and (35), using the method of successive approximations. This potential can be used in the spectroscopy of intermolecular interactions or in the thermodynamical applications.

The self-consistent Hamilton equations can be used for more precise description of molecular collisions and for improving the method of the given trajectories. The semiclassical representation allows us to find the applicability limits of the semiclassical approximation in any particular case and to improve it, if necessary.

Using the Fokker-Planck equation for the distribution function of momenta and coordinates, one can easily obtain all the usual approximate equations for the one-particle distribution function, in which the influence of internal degrees of freedom will be taken into account in a convenient way. It should be noted that for the molecules whose dimensions satisfy the long-wave approximation, the account of interaction with the external electromagnetic field does not change the interaction Hamiltonian structure. Therefore, it is not difficult to take into account the strong-field effect both on the potential and on the whole problem of the intermolecular interaction.

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