The Statistical Dynamics of a System Consisting of a Classical and a Quantum Subsystem

I. V. Aleksandrov
Institute of Chemical Physics, Academy of Sciences, Moscow

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For a system consisting of a quantum and a classical subsystem, an equation of the Liouville type is obtained starting with the density matrix equation. The validity condition and the transformation properties of this quantum-classical equation as well as the application of the adiabatic approximation and the perturbation theory within the frame of this equation are discussed. Some general expressions are obtained for the probability of the transition between the quasi-equilibrium states of the system.

Special attention is given to the electron-nuclei system, as the general formalism was developed first of all in order to obtain a foundation for the theoretical analysis of elementary processes in liquids. An example is given to demonstrate that the quantum-classical approach in the range of its validity gives the same result as the corresponding quantum solution. It is also shown that both the cases of weak and strong interaction (leading to the transition) can be described by the quantum-classical equation in question.

I. Introduction

The general way to describe the evolution of a quantum system is to solve the equation for the density matrix $\varrho = \varrho(t)$ [1]

$$\dot{\varrho} = (i/\hbar)[\varrho, H] \tag{1}$$

with the initial condition

$$\varrho(0) = \varrho_0 . \tag{2}$$

H is the quantum Hamiltonian. In this paper we discuss the reduction of (1) for a system consisting of a quantum (I) and a classical (II) subsystem. There are many examples of such quantum-classical systems, especially in molecular physics. Indeed, for the molecules it is necessary to consider the electrons according to quantum theory, but the nuclear motion can often be described classically.

It is known how to make use of the classical properties of the subsystem II within the trajectory (half-classical) approximation [2, 3] and for the pure adiabatic [4] evolution. But both approximations do not take the mutual influence of the classical motion and the quantum transitions into account. Therefore they do not permit to discuss some very important chemical processes, such as transitions depending on nonadiabatic effects.

In this paper a general consideration of the quantum-classical system is given; the approximations mentioned above are some limiting cases of our treatment.

II. Quantum — Classical Discription

Let us start with the quantum description of both subsystems I and II. Any interaction known in atomic and molecular physics and, therefore, any reasonable observable Q can be represented by the expression

$$Q = \sum_m F_m \, \phi^{-m} , \tag{3}$$

where the operators ϕ^m and F_m act on the coordinates ξ of the subsystem I and the coordinates q of the subsystem II, respectively. Using a set of basis functions $\psi_a(\xi)$ for the subsystem I, one can consider Q as the matrix of operators acting on q:

$$Q_{aa'} = \sum_m F_m \, \phi_{aa'}^{-m} . \tag{4}$$

The classical interpretation of subsystem II consists of the substitution of the operators F_m (which act on the variables q) by the momentum (p) and coordinate (q) functions: $F_m \to F_m(p, q)$. These functions are already known: we actually obtain the quantum equation (3) on the grounds of the corresponding classical expression, which is a function depending on the moment a and coordinates [1]. Hence we shall consider the matrix of functions instead of the matrix of operators; the numeration

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Reprint requests to Prof. I. V. Aleksandrov, Institute of Chemical Physics, Academy of Sciences, Vorob'evskoe shosse 2b, 117334 Moskau V-334, UDSSR.

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of the lines and columns of this matrix corresponds to the numeration of the quantum states of the subsystem I. For such matrixes we shall use the special notation, $\boldsymbol{Q}=\boldsymbol{Q}(p,q)$:

$$Q_{aa'}=\sum_m F_m(p,q)\,\phi_{aa'}^{-m}\,. \tag{5}$$

The quantum formula for the average value of the observable Q is

$$\bar{Q}=\mathrm{Sp_I}\,\mathrm{Sp_{II}}\,Q\,\varrho\,.$$

$\mathrm{Sp_I}$ and $\mathrm{Sp_{II}}$ mean traces, i.e. diagonal sums over the states of the subsystems I and II, respectively. Evidently, for the quantum-classical description one has

$$\bar{\boldsymbol{Q}}=\mathrm{Sp}\int \mathrm{d}p\,\mathrm{d}q\,\boldsymbol{Q}(p,q)\,\boldsymbol{\rho}(p,q;t)\,, \tag{6}$$

$\mathrm{Sp}\boldsymbol{A}\equiv\mathrm{Sp_I}\boldsymbol{A}$ means the trace of the matrix $\boldsymbol{A}$, $\boldsymbol{\rho}$ is the matrix with the matrix elements $\varrho_{aa'}(p,q;t)$, this matrix presenting the quantum-classical distribution for the combined system. Now we have to obtain some equation of the Liouville type for the $\boldsymbol{\rho}=\boldsymbol{\rho}(p,q;t)$ matrix.

Let the quantum Hamiltonian be

$$H=\hbar\sum_\alpha H_\alpha\Omega_\alpha\,. \tag{7}$$

H_α are the operators of the subsystem II, Ω_α presents the complete set of the operators [5] for the subsystem I. The density matrix $\varrho(t)$ can be written as

$$\varrho(t)=\sum_\alpha P_\alpha(t)\,\Omega_\alpha\,. \tag{8}$$

P_α are the time-dependent operators for the subsystem II.

The operators $P_\alpha(t)$ and H_α may be expanded with the help of the complete set of the operators Y_ω for the subsystem II:

$$P_\alpha(t)=\sum_\omega c_{\alpha\omega}(t)\,Y_\omega\,,\quad H_\alpha=\sum_\omega h_{\alpha\omega}Y_\omega\,, \tag{9}$$

$c_{\alpha\omega}$ and $h_{\alpha\omega}$ are the c-numbers. As far as $[Y_\omega,\Omega_\alpha]=0$ is concerned, one has

$$[Y_\omega\Omega_\alpha,A]=[Y_\omega,[\Omega_\alpha,A]_+]+[\Omega_\alpha,[Y_\omega,A]_+]\,,$$
$$[A,B]_+=I/2(AB+BA)\,.$$

Therefore, by substituting (8) and (9) in (1) one obtains

$$i\sum_\alpha\sum_\omega \dot{c}_{\alpha\omega}Y_\omega\Omega_\alpha =\sum_{\alpha,\alpha'}\sum_{\omega,\omega'}c_{\alpha\omega}h_{\alpha'\omega'}([\Omega_\alpha,\Omega_{\alpha'}]\cdot[Y_\omega,Y_{\omega'}]_+ +[\Omega_\alpha,\Omega_{\alpha'}]_+[Y_\omega,Y_{\omega'}])\,.$$

Or, using again (9), one has

$$\sum_\alpha \dot{P}_\alpha\Omega_\alpha=i\sum_{\alpha,\alpha'}([\Omega_\alpha,\Omega_{\alpha'}][P_\alpha,H_{\alpha'}]_+ +[\Omega_\alpha,\Omega_{\alpha'}]_+[P_\alpha,H_{\alpha'}])\,. \tag{10}$$

In (10) it is easy to make the transition to the classical description of the subsystem II. It is known [1, 6] that the quantum expressions $[P_\alpha(t),H_{\alpha'}]_+$ and $[P_\alpha,H_{\alpha'}]$ correspond to the classical values $P_\alpha(p,q;t)\,H_{\alpha'}(p,q)$ and $-i\hbar\{P_\alpha(p,q;t),H_{\alpha'}(p,q)\}$, respectively ($\{\ldots,\ldots\}$ is the Poisson bracket). Thus, if the subsystem II is the classical one, the equation for the quantum-classical distribution $\boldsymbol{\rho}$ is

$$\dot{\boldsymbol{\rho}}=i[\boldsymbol{\rho},\boldsymbol{H}]+\frac{\hbar}{2}\{\boldsymbol{\rho},\boldsymbol{H}\}-\frac{\hbar}{2}\{\boldsymbol{H},\boldsymbol{\rho}\}\,, \tag{11}$$

where

$$\{\boldsymbol{A},\boldsymbol{B}\}=\sum\left(\frac{\partial\boldsymbol{A}}{\partial p}\frac{\partial\boldsymbol{B}}{\partial q}-\frac{\partial\boldsymbol{A}}{\partial q}\frac{\partial\boldsymbol{B}}{\partial p}\right),$$
$$\boldsymbol{\rho}=\sum_\alpha P_\alpha(p,q;t)\,\Omega_\alpha\,, \tag{12}$$
$$\boldsymbol{H}=\boldsymbol{H}(p,q)=\sum_\alpha H_\alpha(p,q)\,\Omega_\alpha\,,$$

and we took into account that $\{P_\alpha,H_{\alpha'}\}=-\{H_{\alpha'},P_\alpha\}$.

III. General Properties of Equation (11)

It is seen directly that, when the classical subsystem II is absent (i.e in (12) all $H_\alpha(p,q)$ are constant, (11) is the same as the quantum equation (1) with the quantum Hamiltonian $H=H_{\mathrm{I}}$. If the quantum subsystem I is absent (in this case $\boldsymbol{H}(p,q)=H(p,q)\,\boldsymbol{1}$), (11) becomes the well known classical Liouville equation

$$\dot{\varrho}=\{\varrho,\mathscr{H}\}\,. \tag{13}$$

$\mathscr{H}=\hbar H(p,q)$ is the classical Hamiltonian. If both quantum and classical subsystems are present, but do not interact with each other (i.e. $\hbar\boldsymbol{H}(p,q)=\boldsymbol{H}_{\mathrm{I}}+\mathscr{H}\cdot\boldsymbol{1}$) and are independent initially, then the solution of (11) is

$$\boldsymbol{\rho}(p,q;t)=\boldsymbol{\rho}_{\mathrm{I}}(t)\,\varrho(p,q;t)\,.$$

$\boldsymbol{\rho}_{\mathrm{I}}(t)$ is the solution of the quantum equation (1) with $H=H_{\mathrm{I}}$, and $\varrho(p,q;t)$ is the solution of the classical equation (13).

Evidently, (11) is the analogue of the Liouville equation for the system, consisting of the quantum and the classical subsystems.

With the help of the identities

$$\operatorname{Sp} \boldsymbol{A}[\boldsymbol{B}, \boldsymbol{C}] = \operatorname{Sp}[\boldsymbol{A}, \boldsymbol{B}]\, \boldsymbol{C}\,,$$
$$\int \mathrm{d}p\, \mathrm{d}q\, \boldsymbol{A}\{\boldsymbol{B}, \boldsymbol{C}\} = \int \mathrm{d}p\, \mathrm{d}q \{\boldsymbol{A}, \boldsymbol{B}\}\, \boldsymbol{C} \tag{14}$$

it is easy to prove that for the solution of (11) one has

$$\frac{\mathrm{d}}{\mathrm{d}t} \operatorname{Sp} \int \mathrm{d}p\, \mathrm{d}q\, \boldsymbol{\rho}(p, q; t) = 0\,.$$

Therefore it is possible to normalize $\boldsymbol{\rho}$ by the condition

$$\operatorname{Sp} \int \mathrm{d}p\, \mathrm{d}q\, \boldsymbol{\rho}(p, q; t) = 1\,. \tag{15}$$

It is seen from (6) and (15) that the diagonal elements $\varrho_{aa} \equiv \varrho_a(p, q; t)$ present the density of the probability to find the system at the time t in the state ψ_a of the quantum subsystem and at the point (p, q) of the phase space of the classical subsystem. The nondiagonal elements $\varrho_{aa'}$ present the phase relation between the quantum states ψ_a and $\psi_{a'}$.

Using (11) and (14) one can demonstrate that the average value of $\boldsymbol{H}$, calculated by the general expression (6), does not depend on time:

$$\frac{\mathrm{d}}{\mathrm{d}t} \overline{\boldsymbol{H}} = \frac{\mathrm{d}}{\mathrm{d}t} \operatorname{Sp} \int \mathrm{d}p\, \mathrm{d}q\, \boldsymbol{H}(p, q)\, \boldsymbol{\rho}(p, q; t) = 0\,.$$

therefore

$$\overline{\boldsymbol{H}} = \text{const}\,. \tag{16}$$

Obviously (16) means the quantum-classical conservation of the energy. Note that

$$\overline{H}_a = \int \mathrm{d}p\, \mathrm{d}q\, (H)_{aa}\, \boldsymbol{\rho}_a(p, q; t)$$

is not conserved as a result of the possible transitions between the quantum states.

(6) and (11) are some sort of approximation to the corresponding rigorous quantum expressions. The range of validity of this approximation can be established as follows:

The approximate step in the derivation of (11) from (1) is the substitution

$$[P_\alpha(t), H_{\alpha'}]_+ \to P_\alpha(p, q; t)\, H_{\alpha'}(p, q)$$

and

$$[P_\alpha(t), H_{\alpha'}] \to -i\hbar \{P_\alpha(p, q; t), H_{\alpha'}(p, q)\}\,.$$

Both these substitutions are valid within the precision $O(\hbar^2)$ if the condition

$$|P_\alpha H_{\alpha'}| \gg \hbar\, |\{P_\alpha, H_{\alpha'}\}|$$

is fulfilled. This condition may be expressed by two simple unequalities:

$$\Delta q\, p \gg \hbar\,, \quad l \Delta p \gg \hbar\,. \tag{17}$$

p and l are the characteristic momentum and distance for the change of $\boldsymbol{H}$. Δp and Δq are the similar quantities for $\boldsymbol{\rho}$. If the distribution is a quasi-equilibrium, then $\Delta q \cong l$, $\Delta p \cong p$, and (17) reduces to the well known condition for the classical description [4] of the subsystem II:

$$\hbar / p \ll l\,. \tag{18}$$

But generally (18) is not equivalent to (17). For example, if the distribution $\boldsymbol{\rho}$ is of the δ-function type, then the conditions (17) are not valid ($\Delta p = \Delta q = 0$), while the condition (18) may hold.

Thus, the distribution of the variables p, q must be smooth enough. That means that the quantum-classical approximation, expressed by (6) and (11), is valid, if the subsystem II is classical and statistical as well.

Generally the unitary transformation of the form

$$Q' = \exp(-i S/\hbar)\, Q \exp(i S/\hbar) \tag{19}$$

confuses the variables of the subsystem I and II. Therefore generally the transformed subsystem II′ is not the classical one and (11) cannot be used in the new basis.

However, for some special class of S-operators the subsystem II′ remains the classical one. To establish this class let us consider

$$S = \hbar \sum_\alpha R_\alpha \Omega_\alpha\,. \tag{20}$$

We suggest that the R_α operators of subsystem II have the same properties (in the sence of (17) and (18)) as H_α, i.e.

$$|\boldsymbol{\rho} \boldsymbol{S}| \gg \hbar\, |\{\boldsymbol{\rho}, \boldsymbol{S}\}|\,, \quad \boldsymbol{S} = \sum_\alpha R_\alpha(p, q)\, \Omega_\alpha\,. \tag{21}$$

Then (19) itself can be considered in the quantum-classical approximation.

Indeed, according to (19) the expression for Q' can be found from the equation

$$i\hbar\, \partial Q_\lambda / \partial \lambda = [S, Q_\lambda]\,, \quad Q_{\lambda=0} = Q\,,$$
$$Q' = Q_{\lambda=1}\,. \tag{22}$$

With (20) and (21) in mind one can obtain the quantum-classical version of (22) in the same way as (11) was obtained from (1). The corresponding $\boldsymbol{Q}'(p, q)$ value can be obtained with the help of the equation

$$\frac{\partial \boldsymbol{Q}_\lambda}{\partial \lambda} = i[\boldsymbol{Q}_\lambda, \boldsymbol{S}] + \frac{\hbar}{2}\{\boldsymbol{Q}_\lambda, \boldsymbol{S}\} - \frac{\hbar}{2}\{\boldsymbol{S}, \boldsymbol{Q}_\lambda\},$$
$$\boldsymbol{Q}_{\lambda=0} = \boldsymbol{Q}, \quad \boldsymbol{Q}' = \boldsymbol{Q}_{\lambda=1}, \tag{23}$$

and the conservation of the classical properties of subsystem II means that (11) is invariant for the transformation defined by (23).

To demonstrate the invariance of (11) let us transform its right-hand part

$$\boldsymbol{A} = i[\boldsymbol{\rho}, \boldsymbol{H}] + \frac{\hbar}{2}\{\boldsymbol{\rho}, \boldsymbol{H}\} - \frac{\hbar}{2}\{\boldsymbol{H}, \boldsymbol{\rho}\}$$

according to (23). Then let us compare the result with the value

$$\boldsymbol{B}' = i[\boldsymbol{\rho}', \boldsymbol{H}'] + \frac{\hbar}{2}\{\boldsymbol{\rho}', \boldsymbol{H}'\} - \frac{\hbar}{2}\{\boldsymbol{H}', \boldsymbol{\rho}'\},$$

$\boldsymbol{H}'$ and $\boldsymbol{\rho}'$ in this expression are the transformed (according to (23)) quantities $\boldsymbol{H}$ and $\boldsymbol{\rho}$, respectively. The coincidence of $\boldsymbol{A}$ and $\boldsymbol{B}'$ means the invariance of (11); it takes place if the equations for $\boldsymbol{A}_\lambda$ and $\boldsymbol{B}_\lambda$ are the same.

Now it is easy to check that the equations for $\boldsymbol{A}_\lambda$ and $\boldsymbol{B}_\lambda$ become identical for $\boldsymbol{S} = R(p, q)\,\boldsymbol{1} + \boldsymbol{S}_0$, $\boldsymbol{S}_0 = \boldsymbol{const}$, i.e. for the canonical transformation of subsystem II along with the unitary transformation of subsystem I [1]. Such a transformation obviously does not mix the quantum and classical variables. In the more general case of (20) the equations for $\boldsymbol{A}_\lambda$ and $\boldsymbol{B}_\lambda$ differ from each other. But if the condition (21) is fulfilled this difference is $O(h^2)$, i.e. of the same order of magnitude as the precission of (11) itself. Therefore (11) is invariant within the limits of its accuracy.

One can conclude, that (20), (21) and (23) define the class of transformations that conserve the classical properties of subsystem II (subsystem II′ is a classical as subsystem II); (11) remains invariant under such a transformation. Note that the general equation (6) is invariant for any transformation defined by (23); the demonstration of this fact is equivalent to the demonstration of (16).

IV. The Adiabatic Approximation and the Perturbation Theory

Within the basis ψ_a the quantum-classical Hamiltonian $\boldsymbol{H}(p, q)$ (see (12)) is the matrix with the elements $H_{aa'} = H_{aa'}(p, q)$. For the moment we consider p, q as fixed parameters. Then one can transform $\boldsymbol{H}$ to the diagonal form $\boldsymbol{H}' = \boldsymbol{E}$. Let us denote the matrix S for this transformation by $S_{\mathrm{ad}} = \hbar \boldsymbol{S}_{\mathrm{ad}}$, so that $\boldsymbol{E} = \exp(-i\boldsymbol{S}_{\mathrm{ad}})\,\boldsymbol{H}\exp(i\boldsymbol{S}_{\mathrm{ad}})$, $E_{nn'} = E_n \delta_{nn'}$. The matrix $\boldsymbol{S}_{\mathrm{ad}}$ is to be found by the solution of the usual quantum problem $(H - E)\,\psi = 0$ for the subsystem I. For this problem p, q are the parameters, therefore $E_n = E_n(p, q)$, $\boldsymbol{S}_{\mathrm{ad}} = \boldsymbol{S}_{\mathrm{ad}}(p, q)$ and the new basis functions φ_n are equal to

$$\varphi_n = \sum_a b_{na}(p, q)\,\psi_a,$$
$$b_{na}(p, q) = (\exp\{i\boldsymbol{S}_{\mathrm{ad}}(p, q)\})_{na}. \tag{24}$$

Usually for the electron-nuclei system $\boldsymbol{S}_{\mathrm{ad}} = \boldsymbol{S}_{\mathrm{ad}}(q)$, φ_n is the adiabatic electron wave function, its dependence on q being essential in the small region of size l^* [3]. The same value l^* is the characteristic length for S_{ad}, as it is seen from (24). If the electronic state is φ_n, then $\mathscr{H}_n = \hbar E_n(p, q)$ is the classical Hamiltonian for the nuclear motion: $\mathscr{H}_n = K(p) + U_n(q)$. K is the kinetic energy, U_n the adiabatic potential.

Now let us use the matrix $\boldsymbol{S}_{\mathrm{ad}}$ to transform the Hamiltonian $\boldsymbol{H}$ according to (23). Neglecting the terms $O(\hbar^2)$ one finds

$$\boldsymbol{H}'(p, q) = \boldsymbol{E}(p, q) + \boldsymbol{V}^{\mathrm{nonad}}(p, q),$$
$$\boldsymbol{V}^{\mathrm{nonad}} = \frac{\hbar}{2}\int_0^1 \mathrm{d}\lambda\,(\{\boldsymbol{E}_\lambda, \boldsymbol{S}_{\mathrm{ad}}\} - \{\boldsymbol{S}_{\mathrm{ad}}, \boldsymbol{E}_\lambda\}). \tag{25}$$

$\boldsymbol{E}_\lambda$ is the solution for the equation

$$\frac{\partial \boldsymbol{E}_\lambda}{\partial \lambda} = i[\boldsymbol{E}_\lambda, \boldsymbol{S}_{\mathrm{ad}}], \quad \boldsymbol{E}_{\lambda=0} = \boldsymbol{H}. \tag{26}$$

If the nonadiabatic interaction $\boldsymbol{V}^{\mathrm{nonad}}$ can be neglected, that is if

$$|\, V^{\mathrm{nonad}}_{nn'} | \ll | E_n - E_{n'} |, \tag{27}$$

then (11) separates into independent equations

$$\dot{\varrho}_{nn'} = i(E_{n'} - E_n)\,\varrho_{nn'} + \{\varrho_{nn'}, \mathscr{H}_{nn'}\}, \tag{28}$$

$$\mathscr{H}_{nn'} = \frac{\hbar}{2}(E_n + E_{n'}). \tag{29}$$

That leads to the obvious result: in pure adiabatic approximation the motion of the classical subsystem for each quantum state n is controlled by the Liouville equation

$$\dot{\varrho}_n = \{\varrho_n, \mathscr{H}_n\}. \tag{30}$$

$\mathscr{H}_n \equiv \mathscr{H}_{nn}(p, q)$ is the classical Hamiltonian, obtained as the n^{th}-eigenvalue of the quantum subsystem.

Note that for the electron-nuclei system $|V^{\text{nonad}}| \approx v/l^*$ (v is the nuclear velocity) as it is seen from (25). Therefore in this case (27) can be written in the form

$$\hbar v/l^* \ll \Gamma, \tag{31}$$

Γ is the energy gap between the adiabatic potentials U_n and $U_{n'}$.

The trivial equation (30) describes the classical motion; any transitions between different adiabatic states of the quantum subsystem are forbidden. For small values of the nonadiabatic interaction V^{nonad} it is possible to take these transitions into account by the following procedure, which is the quantum-classical version of the perturbation theory:

Consider some basis for the subsystem I (not necessarily an adiabatic one) in which the Hamiltonian can be written as $\boldsymbol{H} = \boldsymbol{E} + \boldsymbol{V}$; $\boldsymbol{E}$ is the diagonal matrix and $\boldsymbol{V}$ the small nonsecular perturbation. For $\boldsymbol{V} = 0$ (the zeroth-order approximation) (11) separates into independent equation (28). We shall denote by $G_{nn'}(p, q; t; p_0, q_0)$ the fundamental solution of (28); $G_{nn'}(p, q; 0; p_0, q_0) = \delta(p - p_0) \cdot \delta(q - q_0)$. For $\boldsymbol{V} \neq 0$, at the right-hand side of (11) stand the terms $i[\boldsymbol{\rho}, \boldsymbol{V}]$ and $\hbar/2(\{\boldsymbol{\rho}, \boldsymbol{V}\} - \{\boldsymbol{V}, \boldsymbol{\rho}\})$. We shall keep the term $i[\boldsymbol{\rho}, \boldsymbol{V}]$ only, as it presents the lowest power of $\hbar$. Then (11) leads to the set of equations

$$\begin{aligned}\dot{\varrho}_{nn'} &= i(E_{n'} - E_n)\varrho_{nn'} + \{\varrho_{nn'}, \mathscr{H}_{nn'}\} \\ &\quad + i\sum_{n''} V_{n''n'}\varrho_{nn''} - i\sum_{n''} V_{nn''}\varrho_{n''n'}.\end{aligned} \tag{32}$$

Suppose that the initial condition corresponds to the quantum state n_0 (not necessarily an adiabatic one); the initial classical distribution is $f(p, q)$:

$$\varrho_{nn'}(p, q; 0) = f(p, q)\,\delta_{nn_0}\,\delta_{n'n_0}. \tag{33}$$

For the moment we suggest that $f(p, q)$ is the equilibrium solution of (30) with $n = n_0$.

Let us look for the solution of (32) applying the iteration method. We start with the zeroth-order values, given by (33). The first iteration creates the values $\varrho_{n_0n}(p, q; t) = \varrho^*_{nn_0}(p, q; t)$,

$$\begin{aligned}\varrho_{n_0n} = -i\int_0^t \mathrm{d}t'' \int \mathrm{d}p''\,\mathrm{d}q''\, V_{n_0n}(p'', q'') \\ \cdot f(p'', q'')\, G_{n_0n}(p, q; t - t''; p'', q''),\end{aligned} \tag{34}$$

and the next iteration produces the diagonal distributions for $n \neq n_0$:

$$\begin{aligned}\varrho_n(p, q; t) = 2\,Re\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \int \mathrm{d}p'\,\mathrm{d}q' \\ \cdot \int \mathrm{d}p''\,\mathrm{d}q''\, V_{n_0n}(p'', q'') \\ \cdot f(p'', q'')\, V_{nn_0}(p', q') \\ \cdot G_{nn}(p, q; t - t'; p', q') \\ \cdot G_{n_0n}(p', q'; t' - t''; p'', q'').\end{aligned} \tag{35}$$

(34) and (35) are the quantum-classical analogues of the perturbation theory expressions for the density matrix elements in the first nonvanishing approximation.

Usually one has to calculate only the probability $\mathscr{P}_{n_0n}(t)$ to find the quantum state n at the moment t:

$$\mathscr{P}_{n_0n}(t) = \int \mathrm{d}p\,\mathrm{d}q\,\varrho_n(p, q; t). \tag{36}$$

As far as G_{nn} is the Green function for the classical equation (30), one has:

$$\int G_{nn}(p, q; t; p_0, q_0)\,\mathrm{d}p\,\mathrm{d}q = 1.$$

Thus, using (35), from (36) one finds out that

$$\begin{aligned}\mathscr{P}_{n_0n}(t) = 2\,Re\int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \int \mathrm{d}p'\,\mathrm{d}q' \\ \cdot \int \mathrm{d}p''\,\mathrm{d}q''\, V_{n_0n}(p'', q'') \\ \cdot f(p'', q'')\, V_{nn_0}(p', q') \\ \cdot G_{n_0n}(p', q'; t' - t''; p'', q'').\end{aligned} \tag{37}$$

Note that, if $f(p, q)$ is not the steady state solution for (28), then the value of $f(p'', q'')$ in (34), (35) and (37) must be replaced by the expression $\varrho^{(1)}_{n_0} = \varrho^{(1)}_{n_0}(p'', q''; t'')$,

$$\begin{aligned}\varrho^{(1)}_{n_0}(p, q; t) = \int \mathrm{d}p_0\,\mathrm{d}q_0\, f(p_0; q_0) \\ \cdot G_{n_0n_0}(p, q; t; p_0, q_0).\end{aligned} \tag{38}$$

In many cases the function

$$\begin{aligned}g_{n_0n}(t) = \int \mathrm{d}p\,\mathrm{d}q \int \mathrm{d}p'\,\mathrm{d}q'\, V_{n_0n}(p', q')\, f(p', q') \\ \cdot V_{nn_0}(p, q)\, G_{n_0n}(p, q; t; p', q')\end{aligned}$$

vanishes very rapidly with the time t. Then the probability to find the state n at the moment t is proportional to t, $\mathscr{P}_{n_0n}(t) = W_{n_0n} t$, and for the transition probability per unit time one has

$$\begin{aligned}W_{n_0n} &= \int_{-\infty}^{\infty} g_{n_0n}(t)\,\mathrm{d}t, \\ g_{n_0n}(-t) &= g^*_{n_0n}(t).\end{aligned} \tag{39}$$

If $\tilde{p} = \tilde{p}(p_0, q_0, t)$ and $\tilde{q} = \tilde{q}(p_0, q_0, t)$ are the trajectories for the classical Hamiltonian $\mathscr{H}_{nn}(p, q)$, then g_{n_0n} can be expressed as

$$g_{n_0n}(t) = \int \mathrm{d}p_0 \, \mathrm{d}q_0 \, V_{n_0n}(p_0, q_0) f(p_0, q_0) \cdot V_{nn_0}(\tilde{p}, \tilde{q}) \exp\Big(i \int\limits_0^t \Delta E_{nn_0}(\tilde{p}, \tilde{q}) \, \mathrm{d}t'\Big),$$
$$\Delta E_{nn'} = E_n - E_{n'} . \tag{40}$$

Thus, to obtain W_{n_0n} one can use the classical trajectories for the "middle" Hamiltonian $\mathscr{H}_{n_0n}(p, q)$. That certainly does not mean that the classical subsystem moves according to $\mathscr{H}_{n_0n}(p, q)$. Indeed, in (28) the "middle" Hamiltonian equation (29) appears in the equation for $\varrho_{nn'}$. However, the nondiagonal element $\varrho_{nn'}$ has no analogy at all in the pure classical theory.

The condition of validity of the perturbation theory (35), (37) and (39) can be established by the next step iteration calculation. In case of an $a \to a'$ transition between the crossing diabatic terms this condition becomes similar to that known for the Landau formulae [3]:

$$\hbar v / l^* \gg \Gamma, \quad \Gamma = \hbar H_{aa'}, \tag{41}$$

which is a condition opposite to (31). Therefore, for small interaction between the diabatic states (small Γ) the perturbation theory can be used in the diabatic basis ψ_a, while for large Γ it can be helpful in the adiabatic basis φ_n. Because of this fact one is able to consider some particular transition in the electron-nucleus system both for large and small interaction within the same Equation (11).

Let us also note that for large kinetic energy of the classical subsystem the trajectories $\tilde{p}$ and $\tilde{q}$ are practically the same for $\mathscr{H}_n$, $\mathscr{H}_{nn_0}$ and $\mathscr{H}_{n_0}$. Therefore from (40) it is seen that for large kinetic energy ($K(p) \gg \Delta E_{nn'}$) (11) leads to the same results as the trajectory [2] or the half-classical [3] approximations.

V. Examples and Discussion

In many electron-nucleus problems one can take into account only two quantum electronic states ("two levels model"). For this model any matrix A can be expressed by the linear combination of the 2×2 unity matrix σ_0 and the Pauli matrixes σ_α, $\alpha = 1, 2, 3$. Usually one considers the Hamiltonian that in the quantum-classical representation is written as

$$\hbar \boldsymbol{H} = (K + U)\sigma_0 + \Delta U \sigma_3 + \Gamma \sigma_2 , \tag{42}$$
$$U = \tfrac{1}{2}(U_a + U_b), \quad \Delta U = \tfrac{1}{2}(U_a - U_b),$$

$U_{a,b}$ are the diabatic potentials, Γ is the interaction between the diabatic states ψ_a and ψ_b. We suggest that the crossing diabatic potentials are the wells with shifted minima. Then one assumes that the quasi-equilibrium states a and b are in the vicinity of these minima. We consider the transition $a \to b$. First we shall discuss the case of small interaction, which is the case of (41) with the perturbation theory valid in the diabatic basis. To compare our result with the known quantum one let $U_{a,b}$ be the shifted oscillator potentials:

$$U_{a,b} = \frac{1}{2} \sum_j M_j \omega_j^2 \Big(q_j \pm \frac{\delta_j}{2}\Big)^2 . \tag{43}$$

M_j are the masses and ω_j the frequencies of the oscillators, δ_j are the shifts of the oscillators equilibrium positions for the states a and b.

The unperturbed system is represented by the diagonal matrix $\hbar \boldsymbol{E} = (K + U)\sigma_0 + \Delta U \sigma_3$, therefore $\hbar \boldsymbol{E}_a = K + U_a$, $\hbar E_b = K + U_b$, $E_{ab} = E_{ba} = 0$. The functions $\tilde{p}_j$ and $\tilde{q}_j$ (see (40)) are

$$\tilde{p}_j = - M_j \omega_j q_{j_0} \sin \omega_j t + p_{j_0} \cos \omega_j t ,$$
$$\tilde{q}_j = q_{j_0} \cos \omega_j t + (p_{j_0} / M_j \omega_j) \sin \omega_j t .$$

The integral in the exponent of (40) is

$$\begin{aligned} \int\limits_0^t \Delta E_{ab}(p, q) \, \mathrm{d}t' &= 2 \int\limits_0^t \Delta U(\tilde{q}) \, \mathrm{d}t' \\ &= \sum_j M_j \delta_j \omega_j^2 \int\limits_0^t \tilde{q} \, \mathrm{d}t' \\ &= \sum_j (M_j \omega_j q_{j_0} \sin \omega_j t \\ &\quad + p_{j_0}(\mathrm{dos}\, \omega_j t - 1)) . \end{aligned} \tag{44}$$

The initial distribution $\boldsymbol{\rho}_0$ corresponds to the quasi-equilibrium with the potential U_a:

$$\boldsymbol{\rho}_0 = \frac{1}{2}(\sigma_0 + \sigma_3) f(p, q) , \tag{45}$$
$$f = \exp\Big(-\frac{U_a}{T}\Big) \Big/ \int \mathrm{d}p \, \mathrm{d}q \exp\Big(-\frac{U_a}{T}\Big) .$$

By substituting (44) and (45) in (40) one finds

$$g_{ab} = \frac{\Gamma^2}{\hbar^2} \exp \sum_j \frac{E_R}{\hbar \omega_j} \cdot [-(2\bar{n}_j + 1) + (\bar{n}_j + 1) e^{i\omega_j t} + \bar{n}_j e^{-i\omega_j t}] . \tag{46}$$

$E_{R_j} = M_j \omega_j^2 \delta_j^2/2$ is the "reorganisation energy" for the oscillator j. The average number of phonons $\bar{n}_j$ is defined by the equation

$$\hbar \omega_j (\bar{n}_j + \tfrac{1}{2}) = T. \qquad (47)$$

The form of (46) is the same as the known quantum result [7], but (47) coincides with the quantum definition of n_j for high temperatures only, i.e. for $T \gg \hbar \omega_j$. It is just the condition for the classical statistical treatment of the oscillators [6]. Therefore one concludes that our result in the region of its validity (see Sect. III) coincides with the quantum calculation.

For the large reorganisation energy $E_R = \sum_j E_{R_j} \gg \hbar \omega_j$, (46) and (39) lead to the known result [8]:

$$W_{ab} = \frac{\Gamma^2}{\hbar^2} \sqrt{\frac{\pi}{E_R T}} \exp\left(-\frac{U_A}{T}\right),$$
$$U_A = \frac{E_R}{4}. \qquad (48)$$

Now let us consider the problem with the same Hamiltonian (42) in the adiabatic approximation, i.e. in the case of (31). The eigenvalue of the 2×2 matrix equation (42) are

$$\hbar E_1 = k + U_1, \quad \hbar E_2 = K + U_2,$$
$$E_{12} = E_{21} = 0,$$
$$U_{1,2} = U \mp \sqrt{\Delta U^2 + \Gamma^2}, \qquad (49)$$

and it is easy to verify that the matrix S_{ad} in (24) is

$$S_{\mathrm{ad}} = \tfrac{1}{2} \vartheta \sigma_2, \quad \operatorname{tg} \vartheta = \Gamma/\Delta U. \qquad (50)$$

For the diabatic terms in question the adiabatic potential U_1 presents two wells, divided by the barrier. The transition $a \to b$ is now the classical penetration from one well to another. One can calculate W_{ab} within the pure adiabatic approximation, therefore $W_{ab} = \nu \exp(-E_A/T)$, the activation energy E_A for $\Gamma \ll E_R$ is approximatly the same as U_A in (48), but the preexponential ν is different. In the paper [9] it is shown that the values of $\nu = \nu(\Gamma)$ calculated with the help of (11) in the adiabatic approximation ($\Gamma \gg hv/l^*$) and by the perturbation theory ((48), $\Gamma \ll hv/l^*$) match well for the intermediate values of Γ (i.e. for $\Gamma \approx hv/l^*$). Thus in this case indeed (11) permits to evaluate W_{ab} for an arbitrary value of the interaction Γ.

According to (49) the exited adiabatic potential U_2 is the well with the minimum near the crossing of the terms U_a and U_b. The $2 \to 1$ transition corresponds to the nonadiabatic desactivation, its rate is W_{21}. To calculate W_{21} by the perturbation theory one has to establish the expression for V^{nonad}. Let us illustrate the latter procedure explicitly.

For the value of S_{ad}, given by (50), the solution for (26) is

$$\hbar (E_\lambda)_{11} = K + U - \Delta U \cos \lambda \vartheta - \Gamma \sin \lambda \vartheta,$$
$$\hbar (E_\lambda)_{22} = K + U + \Delta U \cos \lambda \vartheta + \Gamma \sin \lambda \vartheta,$$
$$\hbar (E_\lambda)_{12} = \hbar (E_\lambda)_{21} = \Gamma \cos \lambda \vartheta - \Delta U \sin \lambda \vartheta. \qquad (51)$$

For $\lambda = 1$ that gives just (49). By substituting (51) in the expression for V^{nonad} (see (25)) one finds

$$V^{\mathrm{nonad}} = \tfrac{1}{2} \sigma_2 \sum (\nabla_j \vartheta) p_j / M_j.$$

Using this expression for the perturbation V in (40) ($\tilde{p}$ and $\tilde{q}$ are the trajectories for the potential U) one can now calculate W_{21} with the help of (39).

The quantum-classical approach, discussed in this paper, is presently the only way to analyse theoretically the elementary processes in liquids starting with "first principles". The quantum equation (1) is useless for such purposes as there is no quantum-statistical model for liquids such as those for solids or gases. At the same time a simple classical consideration is often not satisfactory as one has to take into account the mutual dependence of the classical motion of the heavy particles of the liquid and the quantum motion of the electrons. The practical use of the quantum-classical consideration was already demonstrated in the papers [9—11] (in a manner, slightly different from the straightforward way of (11), but nevertheless equivalent).

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