Internal Time Peculiarities as a Cause of Bifurcations Arising in Classical Trajectory Problem and Quantum Chaos Creation in Three-Body System

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Abstract

A new formulation of the theory of quantum mechanical multichannel scattering for three-body collinear systems is proposed. It is shown, that in this simple case the principle of quantum determinism in the general case breaks down and we have a micro-irreversible quantum mechanics. The first principle calculations of the quantum chaos (wave chaos) were pursued on the example of an elementary chemical reaction \( Li^+(FH) \rightarrow (LiFH)^* \rightarrow (LiF) + H \).

1 Introduction

At the early stage of quantum mechanics development A. Einstein had asked the question that attracted close attention several decades later \[1\]. The question was: what will the classic chaotic system become in terms of quantum mechanics. He has particularly set apart the three-body system.

In an effort to formulate and obtain the solution for the problem of quantum chaos M. Gutzwiller has tentatively subdivided all the existing knowledge in physics into three areas \[2\]:

1) regular classical mechanics (area \( R \));
2) classical chaotic systems or dynamical systems of Poincaré (\( P \) area);
3) regular quantum mechanics (\( Q \) area).

The above areas are connected by certain conditions. Thus, the Bohr’s correspondence principle works between \( R \) and \( Q \) areas, transferring the quantum mechanics into classical Newton’s mechanics within the limit \( \hbar \rightarrow 0 \). Areas \( R \) and \( P \) are connected by Kolmogorov’s - Arnold’s - Moser’s theorem (KAM). In spite of well known work by F. Nelson \[3\], which allows to describe \( Q \)-systems with the help of \( P \)-systems in the thermodynamical limit under certain circumstances, the general principle connecting \( P \) and \( Q \) is not determined yet. Assuming the existence of a fourth area - quantum chaos area \( Q_{ch} \), M. Gutzwiller adds that the ”quantum chaos” conception is rather a puzzle than a well formulated problem. It is evident that the task formulated correctly in \( Q_{ch} \) area is a most general one and under specific conditions must transform into the above-mentioned limiting areas.

The problem of quantum chaos was studied by the authors taking as an example the quantum mechanical multichannel scattering in collinear three-body system \[4\]-\[5\]. It was shown than this task can be transformed into a problem of anharmonic oscillator with non-trivial time (internal time), which in the general case can have a chaotic behaviour. In the present work the study of the problem of quantum chaos is continued using numerical calculations based on the example of an elementary chemical reaction.

2 Formulation of the problem

The quantum multichannel scattering in the framework of collinear model is formulated in such a way:

\[
A + (BC)_n \rightarrow \begin{cases} 
A + (BC)_m \\
(AB)_m + C \\
A + B + C \\
(ABC)^* \rightarrow \begin{cases} 
A + (BC)_m \\
(AB)_m + C \\
A + B + C 
\end{cases}
\end{cases}
\]  \hspace{1cm} (1)
where \( m \) and \( n \) are the vibrational quantum numbers corresponding to \((in)\) and \((out)\) scattering channels. As was shown elsewhere \(8\) one can formulate the problem of quantum multichannel scattering \(8\) as the motion of an image point with reduced mass \( \mu_0 \) on the manifold \( M \), that is a lamination of the Lagrange surface within a local coordinate system moving on \( S_p \). In our case there is a standard definition of the surface \( S_p \)

\[
S_p = \{ x^1, x^2 : 2\mu_0 (E - V(x^1, x^2)) > 0 \}, \quad \mu_0 = \left\{ \frac{m_A m_B m_C}{m_A + m_B + m_C} \right\}^{1/2},
\]

(2)

where \( m_A, m_B, m_C \) are the masses of corresponding particles, \( E \) and \( V(x^1, x^2) \) are respectively the total energy and interaction potential of the system. The metric on the surface \( S_p \) in our case is introduced in the following way

\[
y_{ik} = P_0^2(x^1, x^2) \delta_{ik}, \quad P_0^2(x^1, x^2) = 2\mu_0 (E - V(x^1, x^2)).
\]

(3)

The motion of the local coordinate system is determined by the projection of the image point motion over the extremal ray \( \Sigma_{ext} \) of the Lagrange manifold \( S_p \). Note, that for scattering problem \(8\) there are two extremal rays on a surface \( S_p \): one connecting the \((in)\) channel with the \((out)\) channel of particle rearrangement and the other connecting the \((in)\) channel with the \((out)\) channel, where all three particles are free. From now on we shall study only the case of particles rearrangement at the collision. Let us introduce curvilinear coordinates \( (x^1, x^2) \) in Euclidean space \( R^2 \) along the projection of the rearrangement extremal ray \( \Sigma_{ext} \) in a such way, that \( x^1 \) is changing along \( \Sigma_{ext} \) and \( x^2 \) is changing in the orthogonal direction. In such a case the trajectory of the image point is determined by the following system of second order differential equations:

\[
x^{k}_{;ij} + \left\{ k \atop ij \right\}_{S_p} x^{i}_{;j} x^{j}_{;i} = 0, \quad (i, j, k = 1, 2)
\]

(4)

where \( x^i = \frac{dx^i}{d\tau} \) and \( \left\{ k \atop ij \right\}_{S_p} = \frac{1}{2} \gamma^{kl} \left( \frac{\partial g_{ik}}{\partial x^l} + \frac{\partial g_{il}}{\partial x^k} - \frac{\partial g_{il}}{\partial x^k} \right) \).

The differential equations of second order \(8\) with initial conditions

\[
x^i_0 = x^i(-\infty), \quad \dot{x}^i_0 = x^i_0(-\infty)
\]

(5)

at any moment of time \( t \) defines the only solutions \( x^i(t) \) and \( \dot{x}^i(t) \) - the geodesic trajectory and geodesic velocity.

Now we pass to quantum description of rearrangement process. Let’s note that in quasiclassical limits such description equivalent to consideration of geodesic trajectories flow on Lagrange surface \( S_p \). It is convenient to describe the flow in a local coordinate system given by solution \( x^i(s) \) of the system \(8\). The quantization of corresponding trajectory flow should be carried out in indicated coordinate system on stratification \( M \) of Lagrange surface \( S_p \).

Taking into account the Schrödinger equation for arbitrary curvilinear coordinate system \( (x^1, x^2) \) and keeping in mind aforesaid one can obtain the full wave function of the noted system in moving local coordinates:

\[
\{ \hbar^2 \Delta_{(x^1(s), x^2)} + P_0^2(x^1(s), x^2) \} \Psi = 0,
\]

(6)

with the operator \( \Delta_{(x^1(s), x^2)} \) of the form

\[
\Delta_{(x^1(s), x^2)} = \gamma^{-1} \left\{ \partial_{x^1(s)} \left[ \gamma^{ij} \gamma^{kl} \partial_{x^1(s)} \right] + \partial_{x^2} \left[ \gamma^{ij} \gamma^{kl} \partial_{x^2} \right] \right\}, \quad \partial_{x^1(s)} = \partial / \partial x^i(s).
\]

(7)

The metric tensor of the manifold \( M \) has the following form \(8\):

\[
\gamma_{11} = \left( 1 + \lambda(x^1(s)) \right)^2, \quad \gamma_{12} = \gamma_{21} = 0,
\]

\[
\gamma_{22} = \left( 1 + \frac{x^2}{\rho_2(x^1(s))} \right)^2, \quad \gamma = \gamma_{11} \gamma_{22} > 0,
\]

(8)

where \( \lambda \) is de Broglie wave length on \( \Sigma_{ext} \), \( \rho_1 \) and \( \rho_2 \) being the principal curvatures of the surface \( S_p \) in the point \( x^1 \in \Sigma_{ext} \) in the directions of coordinates \( x^1 \) and \( x^2 \) which are changed as

\[
\rho_i^{-1} = \frac{P_{0;x^i}(x^1(s), x^2)}{P^2_0(x^1(s), x^2)} \bigg|_{x^2 = 0}, \quad \lambda = \left. \frac{\hbar}{P_0(x^1(s), x^2)} \right|_{x^2 = 0}, \quad P_{0;x^i} = \frac{dP_0(x^1(s), x^2)}{dx^i}, \quad i = 1, 2.
\]

(9)
Note, that the main difference of (6) from Schrödinger equation comes from the fact, that one of the independent coordinates $x^1$ is the solution of system of nonlinear differential equations and as such, it is not a natural parameter of our system and can in certain situations be a stochastic function.

Our purpose is to find a solution of equation (6) that satisfy the following asymptotic conditions for the total wave function of the system

$$
\lim_{x^1 \to -\infty} \Psi^{(+)} (x^1, x^2) = \Psi_{in} (n; x^1, x^2) + \sum_{m \neq n} R_{mn} \Psi_{in} (n; x^1, x^2),
$$

$$
\lim_{x^1 \to +\infty} \Psi^{(+)} (x^1 (s), x^2) = \sum_{m} S_{mn} R_{mn} \Psi_{out} (m; x^1, x^2),
$$

(10)

where the coefficients $R_{mn}$ and $S_{mn}$ are the excitation and rearrangement amplitudes respectively.

3 Reduction of the scattering problem to the problem of quantum harmonic oscillator with internal time

Let us make a coordinate transformations in Eq.(6):

$$
\tau = (E_k^i)^{-1} \int_0^{x^1(s)} P (x^1, 0) \sqrt{\gamma_0} dx^1, \quad z = (\hbar E_k^i)^{-\frac{1}{2}} P (x^1, 0) x^2,
$$

$$
(11)
$$

where $E_k^i$ is the kinetic energy of particle $A$ in the (in) channel and the function $P (x^1, x^2)$ is the momentum of image point on the curve $\mathcal{Z}_{ext}$.

By expanding $P (x^1, x^2)$ in the coordinate $x^2$ up to the second order we can reduce the scattering equation (3) to the problem of a quantum harmonic oscillator with variable frequency in an external field, depending on internal time $\tau (x^1 (s))$. (3) + (4). E.g., in the case of zero external field the exact wave function of the system has the form

$$
\Psi^{(+)} (n; \tau) = \left[ \frac{(\Omega_m / \pi)^{1/2}}{2^n n! |k|} \right]^{\frac{1}{2}} \exp \left\{ i \left[ \frac{E_k^i \tau}{\hbar} - i \left( n + \frac{1}{2} \right) \Omega_m \int_{-\infty}^\tau \frac{d\tau'}{|\xi'|^2} + \frac{1}{2} \xi^{-1} \right] \right\} H_n \left( \frac{\sqrt{\Omega_m}}{|k|} z \right),
$$

(12)

$$
\dot{\xi} = d_s \xi, \quad \dot{p} = d_s p, \quad P (x^1 (s)) = P (x^1, 0),
$$

where the function $\xi (\tau)$ is the solution of the classical oscillator equation

$$
\ddot{\xi} + \Omega^2 (\tau) \dot{\xi} = 0,
$$

$$
\Omega^2 (\tau) = - \left( \frac{E_k^i}{p} \right)^2 \left\{ \frac{1}{\beta_2^2} + \sum_{k=1}^2 \left[ \frac{p_{kk}^i}{p} + \left( \frac{p_{kk}}{p} \right)^2 \right] \right\}, \quad p_{kk} = \frac{d p}{dx^k}
$$

(13)

with asymptotic conditions

$$
\xi (\tau) \sim \exp (i \Omega_m \tau),
$$

$$
\xi (\tau) \sim C_1 \exp (i \Omega_{out} \tau) - C_2 \exp (i \Omega_{out} \tau).
$$

(14)

Note, that the internal time $\tau$ is directly determined by the solution of $x^1 (s)$ and therefore includes all peculiarities of $x^1$ solution.

The transition probability for that case is of the form (3) + (4) + (5) + (6):

$$
W_{mn} = \frac{n_<!}{n_>!} \sqrt{1 - \rho} \left| P_{n_> + n_<} (1 - \rho) \right|^2, \quad \rho = \frac{C_2}{C_1},
$$

(15)

where $n_<= \min (m, n)$, $n_> = \max (m, n)$ and $P_m$ being the Legendre polynomial.
4 The study of the internal time dependence versus standard time - the natural parameter of the problem

Now we can turn to the proof of the chaos initiation possibility in the wave function of the three-body system (12) for the case of zero external field, that we shall name as quantum chaos. Let’s stress, that in this case the transition probability dependence over classical trajectory features will be nonregular too. It will be sufficient to show, that the solution \( x^1(s) \) under some initial conditions is unstable or chaotic. For that purpose we studied in detail the behaviour of the image point trajectories on Lagrange surface \( S_n \) on example of elementary chemical reaction \( Li + (FH)_n \rightarrow (LiFH)^* \rightarrow (LiF)_n + H \). The potential surface of this reaction was reproduced using the quantum-mechanical calculations carried out in work [10]. It was shown, that if the beginning of geodesic trajectory \( x^2_0 \) in the \((in)\) channel (i.e. \( x^1 \rightarrow -\infty \)) is fixed, then for the collision energy \( E^i_k \geq 1.4eV \) the behaviour of that trajectory is regular (Fig.1a,1b). In this case the regular interchange of passing and reflection areas on the energy scale is observed (Fig.2). The same observations are true for the case when the energy \( E^i_k \) is fixed and the value of \( x^2_0 \) changes.

Starting from \( E^i_k \approx 1.4eV \) up to reaction threshold energy \( 1.1eV \) unstable behaviour of system motion can be seen in the flows of passing and reflecting geodesic trajectories, that results in complete mixing in the intermediate area at further reduction of \( E^i_k \) energy and causes the \( (LiFH)^* \) resonant complex generation.

It was shown by numerical calculations, that the largest Lyapunov exponents are positive for all energy values. However, up to energy values of \( 1.4eV \) and greater its growth is very slow. And at energy interval from \( 1.4eV \) to \( 1.1eV \) the quick increasing of largest Lyapunov exponents occurs. The last fact shows the exponential divergence of trajectories. For the area of collision energy \( E^i_k \) mentioned the regular interchange of passing and reflection fields is violated and the fields of unstable behaviour arises. The numerical investigations of such fields shows theirs self-similarity relative to scale transformation that characterizes them as fractal type objects (see Fig.3).

Thus for those initial conditions the evolution in the correspondent classical problem is chaotic and so the motion of the local coordinate system is chaotic too. It is easy to see that in such situation the behaviour of \( x^1(s) \) is also chaotic and the same is true for internal time \( \tau (x^1(s)) \), that is the chronologization parameter of quantum evolution in three-body system.

It can be shown, that chaotic behaviour of the internal time \( \tau (x^1(s)) \) is followed by the stochastic behaviour of the model equation solution \( \xi (\tau (x^1(s))) \). The same is true for the wave function representation (12) and transition probability (13). In such a way on the example of the simple multichannel scattering model wave function the possibility of violation of quantum determinism and quantum chaos initiation was shown.

5 Conclusion

In this work it was shown that the representation developed by the authors includes not only Plank’s constant \( \hbar \), but new energy parameter as well. Thus, when the energy of the particles collision exceeds a certain critical value (which is different for the different systems), solution for internal time \( \tau \) coincides with an ordinary time - natural parameter \( s \). In this case, the evolution equation for the system of bodies transforms to ordinary nonstationary Schrödinger’s equation. The scattering process is in fact single-channel for this case.

But everything is quite different when the collision occurs below the critical energy. As it is shown, in such a case the solution for internal time \( \tau \) in a definite range of \( s \) has an oscillatory character. Moreover, for all the extreme points the derivative of \( \tau \) with respect to \( s \) has a jump of the first kind, while the phase portrait of reactive (parametrical) oscillator has bifurcations. Let us note that these are the collision modes that increase the interference effects, i.e. the problem becomes essentially multichannel and includes the phase of resonant state formation. At a small decrease of collisions energy, a number of internal time oscillations grows dramatically. In this case the system loses all the information about its initial state completely. Chaos arises in a wave function, which then self-organizes into a new order within the limit \( \tau \rightarrow \infty \). Mathematically it becomes possible as a result of common wave equation irreversibility by time (natural parameter \( s \)).

Let us stress that the result obtained supports the transitional complex theory, developed by Eyring and Polanyi in the thirties [1] on the basis of heuristic considerations, the essence of which is statistical description of chemical reactions. The amplitude of rearrangement transition in three-body system is investigated in this work on the example of \( Li + (FH)_n \rightarrow (LiFH)^* \rightarrow (LiF)_n + H \) reaction and it is shown, that in the area where the quantity of internal time peculiarities is high, it has a stochastic nature. It is also been shown that the representation developed here satisfies the limit conditions in the specified areas, including transition from \( Q_{ch} \) area into \( P \) area. The latter occurs under \( \hbar \rightarrow 0 \) and at \( E^i_k < E_c \), where \( E_c \) is critical energy and \( E^i_k \) is a collision energy.
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Figure 1: Geodesic trajectories and dependence of internal time over natural parameter for a) direct rearrangement reaction, b) direct reflection reaction and c) rearrangement reaction going through resonance state.

Figure 2: The regular map of collision energy $E_k^i$ and $x_0^2$ coordinate initial values for passing (white fields) and reflecting (black fields) geodesic trajectories.
Figure 3: The irregular map of collision energy $E_k^i$ and $x_{0}^{2}$ coordinate initial values for passing (white fields) and reflecting (black fields) geodesic trajectories. One can see that there is the selfsimilarity relative to scale transformation in chaotic field.
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