

# CHAOS IN POLYATOMIC MOLECULES

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**ABSTRACT.** Polyatomic molecules can perform internal rotational motion of two types: torsional oscillation and free rotation of one part of the molecule with respect to the other part. On the phase plane these two types of motions are separated by the separatrix. Phase trajectories, originated as a result of periodical external force action on the system have stochastic nature. At the quantum consideration of the motion near to the classical separatrix, transition from the pure quantum-mechanical state to the mixed one takes place. Originated at that mixed state, it must be considered as the quantum analogue of the classical dynamic stochasticity and named as the quantum chaos. This work is devoted to the investigation of the quantum chaos manifestation, in the polyatomic molecules, which have property to perform internal rotation. For the molecule of ethane  $C_2H_6$ , the emergence of quantum chaos and possible ways of its experimental observation have been studied. It is shown, that radio-frequency field can produce the non-direct transitions between rotational and oscillatory states. These transitions, being the sign of the existence of quantum chaos, are able to change levels population sizeably and due to this phenomenon experimental observation of the infrared absorption is possible.

## 1. INTRODUCTION

The traditional notion of an area, where the laws of statistical physics are effective, consists in the assumption that the number of interacting particles is sufficiently large. However, a lot of examples of systems with a small number of degrees of freedom, where chaotic motions occur, had become known [1,2] by the end of the last century. A new stage in the development of notions about a chaos and its origin appeared in the last two decades of the past century. It turned

out that classical Hamiltonian system may experience special kind of instability. Because of this instability various dynamic characteristics of the system randomly change with time. Such a property of the system to perform random motion is called dynamic stochasticity. Dynamic stochasticity is an internal property of the system and is not associated with the action of some a priori random forces. Stochasticity as an internal property of the system is rather frequently encountered in physical problems. The difficulty of revealing it is due to the fact that it occurs either in a very narrow range of parameters or manifests itself on very large time intervals or is veiled by other stronger processes. Quantum analogue of dynamic stochasticity is usually called quantum chaos. By a quantum chaos we understand a quantum state appearing when the ratios of the parameters of a system are the same as those at which, in the case of classical consideration, dynamic stochasticity takes place.

## 2. A PHASE PORTRAIT OF THE PENDULUM AND FORMATION OF A STOCHASTIC LAYER

In the general theory of stochasticity of Hamiltonian systems the dominating role is played by the problem of a pendulum, the function of whose Hamiltonian has the form

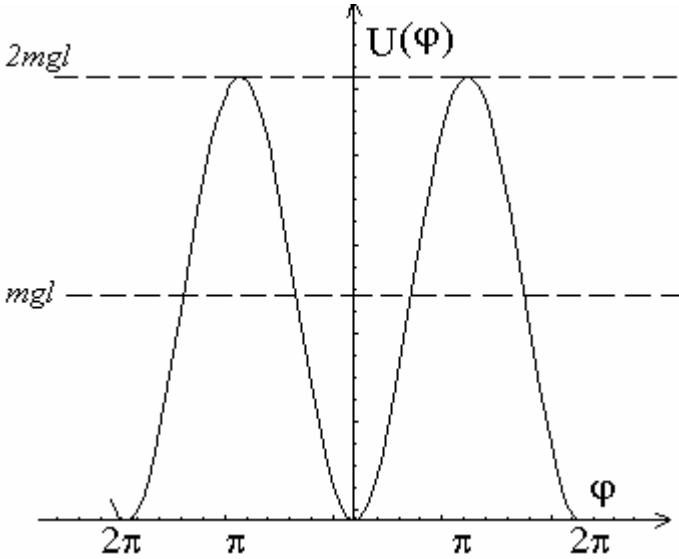
$$H = \frac{P_\varphi^2}{2m} + U(\varphi), \quad (1)$$

where  $P_\varphi = m\dot{\varphi}$  is a pulse and

$$U(\varphi) = mgl(1 - \cos \varphi) \quad (2)$$

is the periodic potential of the point body of mass  $m$ , which is suspended by a thread of length  $l$  (see Fig.1).

Using the law of energy conservation



**Fig.1.** The periodic potential of the pendulum. The angle  $\varphi$  is an angle of deviation of the pendulum from the equilibrium state. The equilibrium state of the pendulum is assumed to be a zero value of potential energy.

$$\frac{m\dot{\varphi}^2}{2} + U(\varphi) = E(t=0) = \text{const} \quad (3)$$

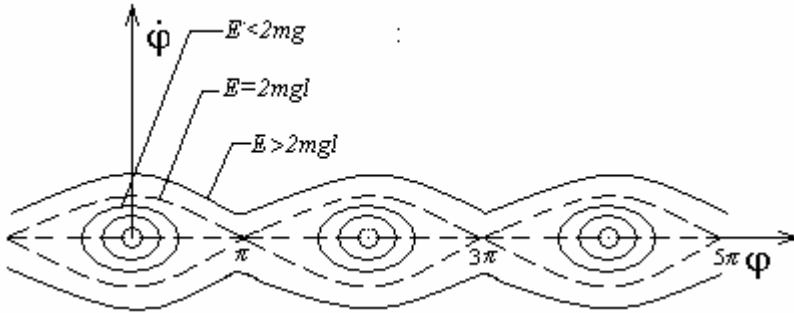
we can construct a phase picture of the pendulum (see Fig.2).

Using the energy integral (3) and potential (2), we can obtain an expression for a period of rotational motion of the pendulum

$$T_+ = \frac{m}{2} \int_0^{2\pi} \frac{d\varphi}{\sqrt{E - U(\varphi)}} = \frac{2m}{\sqrt{E}} K(k), \quad (4)$$

where

$$K(k) = \int_0^{\pi/2} \frac{d\varphi}{\sqrt{1 - k^2 \sin^2 \varphi}} \quad (5)$$



**Fig.2.** A phase picture of the pendulum. The closed curves  $E < 2mgl$  correspond to oscillatory motions. The wave curves  $E > 2mgl$  correspond to rotational motions. To the energy  $E = mgl$  there corresponds a special trajectory called a separatrix. On the phase plane it separates trajectories with different topology.

is the complete elliptic integral,  $k = (2mgl/E)^{1/2}$  is called the module of the integral. For the period  $T_c$  of trajectories in the neighborhood of the separatrix ( $k \rightarrow 1$ ) we obtain,

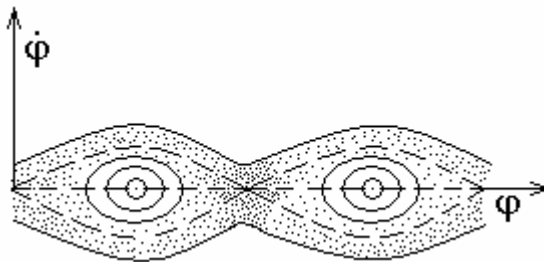
$$\lim_{k \rightarrow +1} T_+ = T_c$$

$$T_c = \frac{2m}{\sqrt{E}} K(k \rightarrow +1) \rightarrow \frac{2m}{\sqrt{E}} \ln \frac{4}{\sqrt{1-k^2}} = \frac{2m}{\sqrt{E}} \ln 4 \sqrt{\frac{E}{E-2mgl}}. \quad (6)$$

From expression (6) it follows that with the approach to the separatrix from above ( $k \rightarrow +1$ ) the motion period logarithmically tends to infinity. The oscillatory motion period  $T_-$  can be calculated analogously, but we do not do this here. We would like only to note that the approach to the separatrix from below

$$\lim_{k \rightarrow -1} T_- = T_c$$

is analogous to (6). That is, the periods of oscillatory and rotational motions coincide in the limit ( $k \rightarrow \pm 1$ ) and, in doing so, they tend to  $T_c$ . Motion along the trajectories near the separatrix is not uniform. It stops at the singular points  $\varphi_n = (2n+1)\pi$ , but quickly (within the time  $\sim (l/g)^{1/2}$ ) gets over the remaining (greater) part of the trajectory. Now let us assume that the considered system is under the action of perturbation, periodic with respect to time. In limiting cases of small oscillations  $E \ll 2mgl$  and free rotation  $E \gg 2mgl$ , such a perturbation leads to the modulation of phase trajectories. Points of intersection of a perturbed trajectory with an unperturbed one arise on the phase plane regularly. The position of each point completely depends on the position of the preceding point. The situation changes radically if an unperturbed trajectory lies near the separatrix ( $E \approx 2mgl$ ). Since in that case the motion makes a prolonged, though unstable, stop in the neighborhood of nodal singular points, even small perturbations may strongly affect the trajectory. Then points of intersection of perturbed trajectories with unperturbed ones appear on the phase plane irregularly (randomly). An area of the phase space occupied by random trajectories is called a stochastic layer (see Fig.3). Thus the main condition for the formation of a stochastic layer is motion near separatrix ( $E \approx 2mgl$ ). The stochastic layer width is defined by a difference  $E - 2mgl$  and a variable field amplitude.



**Fig.3.** The formation of a stochastic layer near the separatrix.

Note that even at first glance we see that in the considered case, dynamic stochasticity appears in the completely deterministic dynamic

system. Motion stochasticity is directly connected with the availability of the separatrix on the phase plane. On stepping over the separatrix, phase trajectories abruptly change their form. In the neighborhood of singular points, lying on the separatrix, there arises a strong instability which is the main cause for the appearance of stochasticity. To explain the phenomenon of dynamic stochasticity it is necessary to take into consideration a small dispersion of the initial conditions. This dispersion is insignificant for trajectories lying at a large distance from the separatrix ( $E \gg 2mgl$ ,  $E \ll 2mgl$ ), while for trajectories near the separatrix ( $E \approx 2mgl$ ), the initial dispersion grows so that, with a lapse of time, motion becomes completely unpredictable. A detailed study of the criterion of stochasticity formation in classical nonlinear systems can be found in [1,2]. We do not discuss this issue here.

### 3. QUANTUM CONSIDERATION. INTERNAL ROTATION IN POLYATOMIC MOLECULES

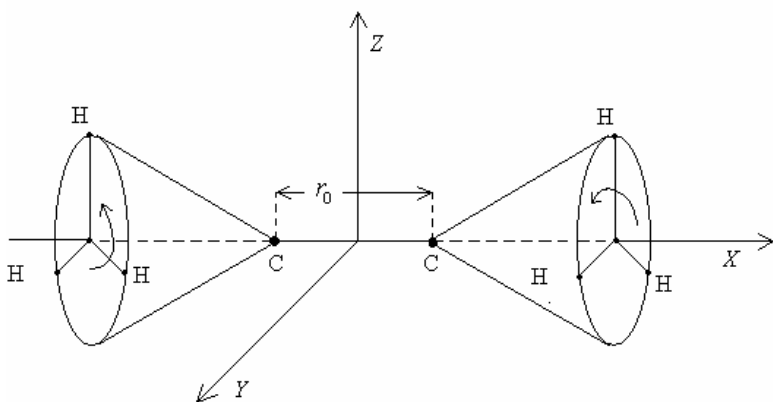
Let us now consider a quantum analogue of the pendulum (quantum pendulum). The corresponding Hamiltonian can be obtained from (1) if we replace there the pulse  $P_\varphi$  by its operator  $\hat{P}_\varphi = i\hbar\partial/\partial\varphi$ . Then we have

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{d\varphi^2} + U(\varphi) \quad (7)$$

Note that this form of the Hamiltonian is usually used to describe internal rotation in polyatomic molecules. As is known [3,4], one of the forms of internal motion in polyatomic molecules is torsional oscillation which for sufficiently large amplitudes transforms to rotational motion. In order to describe the corresponding motion in Hamiltonian (7) we assume that  $\varphi$  is the angle of torsion of one part of the molecule with respect to the other part and replace the mass  $m$  by the reduced moment of inertia  $I = I_1 I_2 / (I_1 + I_2)$ , where  $I_1$  and  $I_2$  are the inertia moments of rotation of the parts of the molecule with respect to its symmetry axis. Thus we obtain

$$U(\varphi) = \frac{V_0}{2}(1 - \cos n\varphi),$$

where  $V_0$  defines the height of potential barrier that separates torsional oscillations from the rotation of one part of the molecule with respect to the other part, and  $n$  defines the quantity of equilibrium orientations of one part of the molecule with respect to the other part. For the molecule of ethane  $H_3C-CH_3$ , dimethylacetylene  $H_3C-C \equiv C-CH_3$  and for other organic molecules we have  $n = 3$  equilibrium configurations (see Fig.4).



**Fig.4.** A schematic drawing of the molecular structure of ethane  $H_3C-CH_3$ . The circular arrow shows the torsion phase  $\varphi$ ,  $r_0$  is the equilibrium distance between two parts of molecule

The configuration shown in Fig.4 corresponds to an energy maximum and is a nonequilibrium configuration (cis-configuration). Other nonequilibrium configurations are obtained by rotating by the

angles  $\frac{2\pi}{3}$  and  $2\frac{2\pi}{3}$ . Equilibrium configurations (trans-configurations) are obtained by rotating of the angles  $\frac{\pi}{3}, \frac{\pi}{3} + \frac{2\pi}{3}, \frac{\pi}{3} + 2\frac{2\pi}{3}$ .

Below we give the numerical values [3,4] of other parameters of some organic molecules having the property of internal rotation. Thus for the molecule of ethane  $C_2H_6$  we have  $I_1 = I_2 \approx 5.3 \cdot 10^{-47} \text{ kg} \cdot \text{m}^2$ ,  $V_0(C_2H_6) \approx 2.1 \cdot 10^{-20} \text{ J}$ , and for the molecule of dimethylacetylene  $C_4H_6$  we have  $I_1 = I_2 \approx 10.6 \cdot 10^{-47} \text{ kg} \cdot \text{m}^2$ ,  $V_0(C_4H_6) \approx 0.34 \cdot 10^{-20} \text{ J}$ .

The Schrodinger equation corresponding to Hamiltonian (7) has the form

$$\frac{d^2\psi}{d\varphi^2} + \frac{2I}{\hbar^2} \left[ \varepsilon_k - \frac{1}{2} V_0 (1 - \cos n\varphi) \right] \psi = 0, \quad (8)$$

where  $\varepsilon_k$  the eigenenergy of the  $k$ -th state. Note that  $\varepsilon_k \equiv \varepsilon_k(V_0)$  is the function of barrier height  $V_0$ . The condition of motion near the separatrix (near a potential maximum) is written in the form  $\varepsilon_k \approx V_0$ .

If we introduce the new variable  $\alpha = \frac{n\varphi}{2}$ , then equation (8) can be rewritten as

$$\frac{d^2\psi(\alpha)}{d\alpha^2} + [E - 2l_0 \cos 2\alpha] \psi(\alpha) = 0 \quad (9)$$

where

$$E = \frac{8I}{n^2\hbar^2} (\varepsilon - V_0/2) \quad (10)$$

plays the role of energy in dimensionless units, and the parameter

$$l_0 = \frac{2I}{n^2\hbar^2} V_0 \quad (11)$$

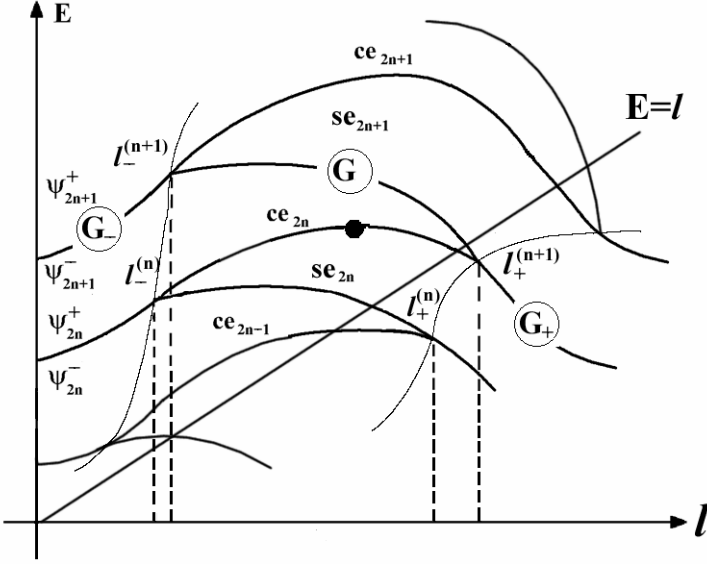


is the half-height of the barrier in dimensionless units and plays the same role as the length of the thread does in the classical pendulum problem. Equations (8) and (9) are called the Mathieu-Schrodinger equations. It describes the dynamics of the "quantum pendulum".

The Mathieu-Schrodinger equation (9) is a linear equation, which gives us the grounds to believe that for the quantum pendulum no instability, which leads to chaos and the instability of trajectories, might develop as this happens in the classical case. Another property of dynamic stochasticity is a jump-like change of the form of phase trajectories when they pass across the separatrix. In the case of quantum consideration, a smooth transition from the discrete energy spectrum to the continuous one takes place near the maxima of the periodic potential (Fig.1), which is connected with a possible tunneling through the barrier. Thus this fact does not work in favor of chaos either. However, as is shown in [5-7], the basic properties of dynamic stochasticity (in particular the irreversibility of the process) manifest themselves in the case of quantum consideration too. It can be assumed that a mixed state is a quantum analogue of classical stochastic motion. In our problem the transition from the pure state to the mixed one occurs due to special properties of the Mathieu-Schrodinger equation to be discussed below. A peculiar feature of the Mathieu-Schrodinger equation consists in the specific dependence of eigenvalues  $E_n(l)$  and eigenfunctions  $\psi_n(\varphi, l)$  on the parameter  $l$  (see Fig.5). On the plane  $(E, l)$ , on which the spectral characteristics (so-called Mathieu characteristics [6]) are drawn, this peculiarity manifests itself in the alternation of areas of twice degenerate  $G_{\pm}$  and nondegenerate states  $G$ . The boundaries between these areas pass across the branch points of energy terms  $E_n(l)$ .

The presence of degenerate and nondegenerate states of the quantum mathematical pendulum was established by studying the symmetry properties of the Mathieu-Schrodinger equation. In [5] the eigenfunctions were defined for each one of the areas of degenerate states  $G_{\pm}$  and nondegenerate states  $G$  :

$$\psi_{2n+1}^{\pm}(\varphi) = \frac{1}{\sqrt{2}}(ce_{2n+1}(\varphi) \pm ise_{2n+1}(\varphi)),$$



**Fig.5.** A fragment of a parametrically dependent energy spectrum of the quantum mathematical pendulum. The straight line  $E = l$  corresponds to the separatrix of classical motion. By  $l_{\pm}^{(m)}$  are denoted the points of branching of energy terms to the left and to the right of the separatrix

$$\psi_{2n}^{\pm}(\varphi) = \frac{1}{\sqrt{2}}(ce_{2n}(\varphi) \pm ise_{2n}(\varphi)), \quad (G_{-})$$

$$ce_{2n}(\varphi); ce_{2n+1}(\varphi); se_{2n}(\varphi); se_{2n+1}(\varphi), \quad (G)$$

$$\xi_{2n}(\varphi) = \frac{1}{\sqrt{2}}(ce_{2n}(\varphi) \pm ise_{2n+1}(\varphi)), \quad (G_{+})$$

$$\zeta_{2n+1}(\varphi) = \frac{1}{\sqrt{2}}(ce_{2n+1}(\varphi) \pm ise_{2n+2}(\varphi)).$$

Here  $ce_n(\varphi)$  and  $se_n(\varphi)$  denote the periodic Mathieu functions [8]. Let us consider two limiting cases of a low and a high energy barrier. In the limit of a low barrier  $V_0 \rightarrow 0$ , the Mathieu-Schrodinger equation (8) implies the equation for free rotation

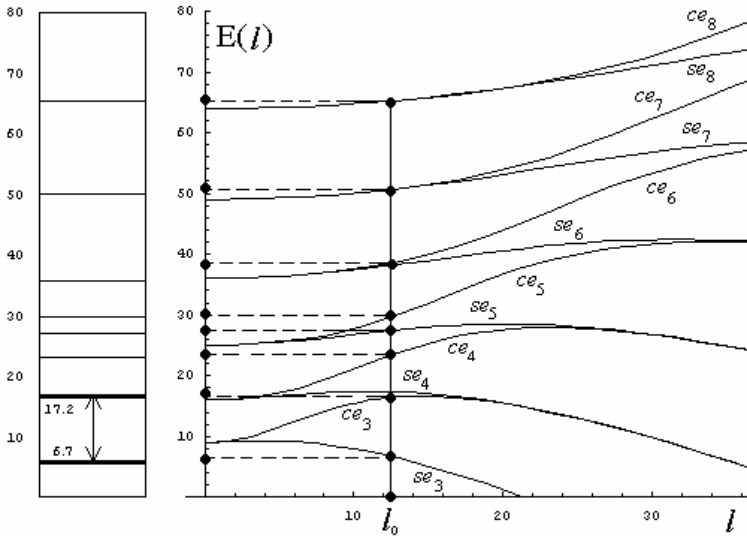
$$\frac{d^2\psi}{d\varphi^2} + \frac{2I}{\hbar^2} \varepsilon_r \psi = 0.$$

From which for the energy spectrum we obtain  $\varepsilon_r = (\hbar^2/2I)r^2$ , where  $r=0, 1, 2, \dots$  are integer numbers. Using the above-given numerical estimates for the molecule of ethane  $C_2H_6$ , we obtain  $\varepsilon_r \approx 0.21 \cdot 10^{-21} r^2 J$ , which corresponds to the cyclic frequency of rotation  $\approx 2.0 \cdot 10^{12} r^2 \text{ rad/s}$ . Comparing the expression for energy with the value of the ethane molecule barrier we see that only levels with a sufficiently large quantum number ( $r > 10$ ) are located high above the barrier and it is only for such levels that the considered limit is valid.

In another limiting case of a high barrier  $V_0$  the rotator is most of the time inside one of the potential wells where it performs torsional motions. In that case  $\alpha$  can be treated as a small angle. After expanding the potential energy in the Schrodinger equation (9) into small angles  $\cos 2\alpha \approx 1 - 2\alpha^2$ , we obtain a quantum equation for the oscillator, whose energy spectrum has the form  $\varepsilon_r = (r+1/2)\hbar\omega$ , where  $\omega = n\sqrt{V_0/2I} \approx 6.0 \cdot 10^{13} \text{ rad/s}$ . For the energy spectrum of small torsional oscillations we obtain  $\varepsilon_r \approx (r+1/2) \cdot 0.63 \cdot 10^{-20} J$ . If we compare the obtained expression for the spectrum with the corresponding numerical value of the barrier, then we can see that only the first three levels  $\varepsilon_0 \approx 0.32 \cdot 10^{-20} J$ ,  $\varepsilon_1 \approx 0.95 \cdot 10^{-20} J$  and  $\varepsilon_2 \approx 1.58 \cdot 10^{-20} J$  are located in the well but not at a sufficiently large depth that would allow us to assume that passages between them correspond to small oscillations. Thus we can conclude that for

internal rotation of the molecule of ethane  $C_2H_6$  the approximation of small oscillations is not carried out sufficiently well, while the approximation of free rotation is carried out for large quantum numbers.

A real quantitative picture of the internal rotation spectrum can be obtained by means of the Mathieu-characteristics when the points of intersection of the line  $l=l_0$  with the Mathieu-characteristics is projected on to the energy axis (see Fig.6).



**Fig.6.** The graphic method of finding energy terms of internal

rotation. For the ethane molecule  $l_0 = \frac{2I}{9\hbar^2} V_0 \approx 12.4$

These conclusions are in good agreement with experimental data. In particular, in the experiment we observed the infrared absorption by molecules of  $C_2H_6$  at a frequency  $\sim 8.7 \cdot 10^{12} Hz$  [9]. For an energy difference between the levels participating in the absorption process we have the estimate  $\Delta\varepsilon_{\text{exper}} \sim 0.54 \cdot 10^{-20} J$ . Comparing the

experimental result with the energy difference between two neighboring levels in the case of approximation of small oscillations, we obtain

$$\Delta\varepsilon_0 = 2\pi\nu_0\hbar,$$

where  $\nu_0 = \frac{3}{2\pi}\sqrt{V_0/2I}$  is the frequency of small oscillations.

Inserting the parameters values for molecules of  $C_2H_6$ , we obtain the estimate  $\Delta\varepsilon_0 = 0.63 \cdot 10^{-20} J$ . After comparing the obtained estimates with the energy difference between the states described by the wave functions  $ce_3(\varphi, l_0)$ ,  $se_3(\varphi, l_0)$  and applying formula (10), we obtain  $\Delta\varepsilon(ce_3(\varphi, l_0) \leftrightarrow se_3(\varphi, l_0)) \sim 0.54 \cdot 10^{-20} J$ .

Comparative analysis of the obtained estimates gives us the grounds to conclude that the energy levels corresponding to the states  $ce_3(\varphi, l_0)$ ,  $se_3(\varphi, l_0)$  participate in the infrared absorption revealed in the experiment.

#### 4. FORMATION OF A QUANTUM CHAOS

Let us assume that the considered quantum system is subjected to a radiofrequency (RF) monochromatic pumping whose frequency  $\Omega$  satisfies the condition  $\Omega \ll V_0/\hbar$ . This causes a slow modulation of quick electrone motions in a molecule. The formation of an energy barrier  $V_0$  is a result of the averaging over quick electrone motions and thus it is obvious that due to the pumping effect the barrier value is time-dependent,

$$V_0 \rightarrow V_0 + \Delta V \cos \Omega t \quad (12)$$

The depth of modulation  $\Delta V$  depends on a pumping power. By replacing (12) we obtain the time-dependent Hamiltonian

$$\hat{H} = \hat{H}_0(\varphi) + \hat{H}'(\varphi, t),$$

$$\hat{H}_0(\varphi) = -\frac{\partial^2}{\partial \varphi^2} + l_0 \cos 2\varphi, \quad (13)$$

$$\begin{aligned} \hat{H}'(\varphi, t) &= \Delta l \cos 2\varphi \cos \Omega t, \\ \Delta l &= \frac{2I}{n^2 \hbar^2} \Delta V \end{aligned} \quad (14)$$

Simple calculations show that the matrix elements of perturbation  $\hat{H}'(\varphi, t)$  with respect to the wave functions of the nondegenerate area  $G$  are equal to zero

$$\langle ce_n | \hat{H}'(\varphi, t) | se_n \rangle \sim \Delta l \int_0^{2\pi} ce_n(\varphi) \cos 2\varphi se_n(\varphi) d\varphi = 0 \quad (15)$$

where  $n$  is any integer number. Therefore perturbation (14) cannot bring about passages between nondegenerate levels.

The interaction  $\hat{H}'(\varphi, t)$ , not producing passages between levels, should be inserted in the unperturbed part of the Hamiltonian. The Hamiltonian obtained in this manner can be considered as slowly depending on time.

Thus, in the nondegenerate area the Hamiltonian can be written in the form

$$\hat{H} = -\frac{\partial^2}{\partial \varphi^2} + l(t) \cos 2\varphi. \quad (16)$$

Because of the modulation of the parameter  $l(t)$  the system passes from one area to another, getting over the branch points.

As different from the nondegenerate state area  $G$ , in the areas of degenerate states  $G_-$  and  $G_+$ , the nondiagonal matrix elements of perturbation  $\hat{H}'(\varphi, t)$  (14) are not equal to zero. For example, if we take the matrix elements with respect to the wave functions  $\psi_{2n+1}^\pm(\varphi)$ , then for the left degenerate area  $G_-$  it can be shown that

$$\begin{aligned}
H'_{+-} = H'_{-+} &= \langle \psi_{2n+1}^+ | \hat{H}'(\varphi, t) | \psi_{2n+1}^- \rangle \\
&\sim \Delta l \int_0^{2\pi} \psi_{2n+1}^+ \psi_{2n+1}^{-*} \cos 2\varphi \, d\varphi \neq 0
\end{aligned} \tag{17}$$

Note that the value  $H'_{+-}$  has order equal to the pumping modulation (14) depth  $\Delta l$ .

Analogously to (17), we can write an expression for even  $2n$  states as well.

An explicit dependence of  $\hat{H}'(\varphi, t)$  on time given by the factor  $\cos \Omega t$ , is assumed to be slow as compared with the period of passages between degenerate states that are produced by the nondiagonal matrix elements  $H'_{+-}$ . Therefore below the perturbation  $\hat{H}'_{+-}(\varphi, t)$  will be assumed to be the time-independent perturbation that can bring about passages between degenerate states.

In a degenerate area the system may be in the time-dependent superpositional state

$$\psi_{2n}(t) = C_n^+(t) \psi_{2n}^+ + C_n^-(t) \psi_{2n}^- \tag{18}$$

The probability amplitudes  $C_n^\pm(t)$  are defined by means of the fundamental quantummechanical equation, expressing the causality principle. We write such equations for a pair of doubly degenerate states:

$$\begin{cases}
-i\hbar \frac{dC_n^+}{dt} = (E_{0n} + H'_{++}) C_n^+ + H'_{+-} C_n^-, \\
-i\hbar \frac{dC_n^-}{dt} = H'_{+-} C_n^+ + (E_{0n} + H'_{--}) C_n^-,
\end{cases} \tag{19}$$

where the matrix elements are taken with respect to degenerate wave functions (see (17)) and  $E_{0n}$  is the energy of the  $n$ -th degenerate level near a branch point.

Let us assume that at the initial moment of time the system was in the degenerate state  $\psi_{2n}^-$ . Then as initial conditions we should take

$$C_n^-(0) = 1, \quad C_n^+(0) = 0 \quad (20)$$

Having substituted (18) into (17), for the amplitudes we obtain

$$\begin{aligned} C_n^+(t) &= i \exp\left(\frac{i}{\hbar} Et\right) \sin \omega t, \\ C_n^-(t) &= \exp\left(\frac{i}{\hbar} Et\right) \cos \omega t, \end{aligned} \quad (21)$$

$$E = E_{0n} + H'_{\pm \pm},$$

where  $\omega = \frac{2\pi}{\tau} = \frac{H'_{+-}}{\hbar}$  is the frequency of passages between degenerate states,  $\tau$  is the passage time.

Note that the parameter  $\omega$  has (like any other parameter) a certain small error  $\delta\omega$ , which during the time of one passage  $t \sim 2\pi/\omega$ , leads to an insignificant correction in the phase  $2\pi(\delta\omega/\omega)$ . However, if during the time  $t \sim \Delta T$ , when the system is the degenerate area ( $\Delta T < T$ ,  $T = 2\pi/\Omega$ ) there occurs a great number of passages ( $\Delta T \gg \tau$ ), then for  $\Delta T \delta\omega \approx 2\pi$ , a small error  $\delta\omega$  leads to the phase uncertainty. Then we say that the phase is self-chaotized. The self-chaotization formed in this manner can be regarded as the embryo of a quantum chaos which, as we will see in the sequel, further spreads to other states.



## 5. SPREAD OF THE QUANTUM CHAOS TO ENERGY TERMS

The spread of the quantum chaos, formed as a result of self-chaotization, can be described in the energy space by means of the density matrix.

Let us introduce the density matrix averaged over a small dispersion  $\delta\omega$  :

$$\rho_n^{+-}(t) = \begin{pmatrix} W_n^+(t) & iF_n(t) \\ -iF_n^*(t) & W_n^-(t) \end{pmatrix} \quad (22)$$

where  $W_n^\pm(t) = \overline{|C_n^\pm(t)|^2}$ ,  $F_n(t) = \overline{C_n^+(t)C_n^{*-}(t)}$ . The overline denotes the averaging over a small dispersion  $\delta\omega$

$$\overline{A(\omega, t)} = \frac{1}{2\delta\omega} \int_{\omega-\delta\omega}^{\omega+\delta\omega} A(x, t) dx. \quad (23)$$

To solve (21) we can write that

$$W_n^+(t) = \overline{\sin^2 \omega t}, \quad W_n^-(t) = \overline{\cos^2 \omega t}, \quad F_n(t) = \frac{1}{2} \overline{\sin 2\omega t}. \quad (24)$$

After a simple integration of the averaging (23), for the matrix element (24) we obtain

$$\begin{aligned} W_n^\pm(t) &= \frac{1}{2} (1 \mp f(2\delta\omega t) \cos 2\omega t), \\ F_n(t) &= F_n^*(t) = \frac{1}{2} f(2\delta\omega t), \\ f(2\delta\omega t) &= \frac{\sin 2\delta\omega t}{2\delta\omega t}. \end{aligned} \quad (25)$$

At small values of time  $t \ll \bar{\tau}$  ( $\bar{\tau} = 2\pi / \delta\omega$ ), insufficient for self-chaotization ( $f(2\delta\omega t) \approx 1$ ), we obtain

$$W_n^+(t \ll \bar{\tau}) = \sin^2 \omega t, \quad W_n^-(t \ll \bar{\tau}) = \cos^2 \omega t,$$

$$F_n(t \ll \bar{\tau}) = \frac{1}{2} \sin 2\omega t.$$

Comparing these values with the initial values (24) of the density matrix elements, we see that the averaging procedure (23), as expected, does not affect them. Thus, for small times we have

$$\rho_n^{+-}(t \ll \bar{\tau}) = \begin{pmatrix} \sin^2 \omega t & \frac{i}{2} \sin 2\omega t \\ -\frac{i}{2} \sin 2\omega t & \cos^2 \omega t \end{pmatrix}. \quad (26)$$

One can easily verify that matrix (26) satisfies the condition  $\rho^2(t \ll \bar{\tau}) = \rho(t \ll \bar{\tau})$ , which is a necessary and sufficient condition for the density matrix of the pure state.

On relatively large time intervals  $t \geq \bar{\tau}$ , in which the self-chaotization of phases takes place, for the matrix elements we should use general expressions (25). The substitution of these expressions for the matrix elements (25) into the density matrix (22) gives

$$\rho(t) = \frac{1}{2} \begin{pmatrix} 1 - f(2\delta\omega t) \cos 2\omega t & if(2\delta\omega t) \sin 2\omega t \\ -if(2\delta\omega t) \sin 2\omega t & 1 + f(2\delta\omega t) \cos 2\omega t \end{pmatrix}. \quad (27)$$

Hence, for times  $t \geq \bar{\tau}$  during which the phases get completely chaotized after passing to the limit  $\delta\omega t \gg 1$  in (27), we obtain

$$\rho_n^{+-}(t) = \frac{1}{2} \begin{pmatrix} 1 - O(\varepsilon) & iO(\varepsilon) \\ -iO(\varepsilon) & 1 + O(\varepsilon) \end{pmatrix}, \quad (28)$$

where  $O(\varepsilon)$  is an infinitesimal value of order  $\varepsilon = 1/2\delta\omega t$ .

The state described by the density matrix (28) is a mixture of two quantum states  $\psi_{2n}^+$  and  $\psi_{2n}^-$  with equal weights. The comparison of the corresponding matrix elements of matrices (28) and (26) shows that they differ in the terms that play the role of quickly changing fluctuations. When the limit is  $t \geq \bar{\tau}$ , fluctuations decrease as  $\sim 1/2\delta\omega t$ .

Thus the system, which at the time moment  $t = 0$  was in the pure state with the wave function  $\psi_{2n}^-$ , gets self-chaotized with a lapse of time  $t \gg \bar{\tau}$  and passes to the mixed state (28). In other words, at the initial moment the system had a certain definite "order" expressed in the form of the density matrix  $\rho^{+-}(0) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$ . With a lapse of time

the system got self-chaotized and the fluctuation terms (27) appeared in the density matrix. For large times  $t \gg \bar{\tau}$ , a new "order" looking like a macroscopic order, is formed, which is defined by matrix (28).

After a halfperiod, the system passes to the area of nondegenerate states  $G$ . In passing through the branch point, there arise nonzero probabilities for passages both to the state  $ce_{2n}(\varphi)$  and to the state  $se_{2n}(\varphi)$ . Thus, in the nondegenerate area the mixed state is formed, which is defined by the density matrix

$$\rho_{2n}^{ik} \left( t \sim \frac{T}{2} \gg \tau \right) = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (29)$$

where  $i$  and  $k$  number two levels that correspond to the states  $ce_{2n}(\varphi)$  and  $se_{2n}(\varphi)$ .

As follows from (29), at this evolution stage of the system, the populations of two nondegenerate levels get equalized. It should be noted that though the direct passage (15) between the nondegenerate levels is prohibited, perturbation (14) essentially influences "indirect" passages. Under "indirect" passages we understand a sequence of

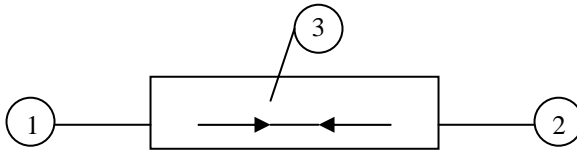
events consisting a passage  $G \rightarrow G_-$  through the branch point, a set of passages between degenerate states in the area  $G_-$ , and the reverse passage through the branch point  $G_- \rightarrow G$ . The "indirect" passages occurring during the modulation halfperiod  $T/2$  result in the equalization (saturation) of two nondegenerate levels.

Thus "indirect" passages are directly connected with a quantum chaos. Hence, by fixing "indirect" passages we thereby fix the presence of a quantum chaos.

Let us assume that the investigated molecule is a component of gaseous or liquid state. Then the molecular thermal motion, which tries to establish an equilibrium distribution of populations according to Boltzman's law, will be a competing process for the quantum chaos described above. Using thermodynamic terminology, we can say that the considered quantum system is located between two thermostats. One of them with medium temperature  $T_0$  tries to retain thermal equilibrium in the system, while the other, having an infinite temperature, tries to equalize the populations.

An equation describing the change of populations according to the scheme shown in Fig.7 has the form

$$\frac{dn_i}{dt} = -2W n_i - \frac{n_i - n_i^{(0)}}{T_1}, \quad (30)$$



**Fig.7.** A thermodynamic scheme of the process. Subsystem 1 is a usual thermostat with temperature  $T_0$ , subsystem 2 is a thermostat having an infinite temperature and consisting of the interaction  $\hat{H}'(\varphi, t)$  (14); the subsystem 3 is the quantum system corresponding to internal rotations of molecules and being able to receive energy from subsystem 2 and to transfer it to subsystem 1.

where  $2W$  is probability of indirect passages and  $T_1$  is the time of thermal chaotization. Bloembergen, Parcell and Pound used equation (30) to describe the process of saturation of nuclear magnetic resonance in solid bodies [11]. For a stationary distribution of populations from (30) we obtain

$$n_i = n_i^{(0)} \frac{1}{1+s}, \quad (31)$$

where  $s = 2WT_1$  is called the saturation parameter. For  $s \gg 1$  indirect passages have a stronger effect on the system than thermal processes.

Thus, along with the conditions  $\Omega \ll V_0/\hbar$ ,  $\Delta T \gg \tau$ ,  $\Delta T \delta\omega \approx 2\pi$ ,  $\delta\omega \ll \omega$ ,  $\Delta T < T$  the condition  $s \gg 1$  is a necessary condition for the formation of a quantum chaos.

In the opposite limiting case  $s \ll 1$ ,  $n_i \approx n_i^{(0)}$ , the quantum chaos will be completely suppressed by thermal motion.

In the case of gases the thermal chaotization time is estimated by the formula  $T_1 \approx \frac{d}{\bar{v}}$ , where  $d$  is the molecule size,  $\bar{v} = \sqrt{\bar{v}^2} = \sqrt{3/2} \cdot (2kT_0/m)^{1/2}$  is a mean motion velocity of molecules. After substituting the numerical values for  $C_2H_6$ , we obtain  $T_1 \approx 0.3 \cdot 10^{-11} \sqrt{1/T_0}$  s. Hence it follows that thermal chaotization in gaseous ethane occurs so quickly that the quantum chaos is completely veiled by a usual thermal chaos ( $s \ll 1$ ).

In the case of liquid under  $T_1$  we should understand the mean time of the settled life of a molecule, which is about  $10^{-8}$  s. Relatively large times of relaxation in liquids ensure the fulfilment of the saturation condition ( $s \geq 1$ ). As mentined above, infrared absorption by the molecules of  $C_2H_6$  was observed at frequencies  $\sim 289\text{cm}^{-1}$  [9], which corresponds to passages  $se_3 \rightarrow ce_3$  between the ground level and the first excited level.

Let us assume that the RF pumping gets involved into the process simultaneously with infrared passages absorption. If the pumping is so strong that indirect induced by it saturate the working levels  $s \geq 1$ ,

then infrared absorption will stop. This is regarded as a manifestation of the quantum process.

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## ქაოსი მრავალატომიან მოლეკულებში

დასკვნა

შესწავლილია შინაგანი ბრუნვითი მოძრაობა ეთანის მოლეკულებში რადიოსიხშირული მონოქრომატული დატუმბვის ზემოქმედებისას. ნაჩვენებია, რომ დატუმბვამ შეიძლება გამოიწვიოს გრესითი რხევებისა და მოლეკულის ნაწილების ერთმანეთის მიმართ რხევის გამმიჯნავი პოტენციური ბარიერის მოდულაცია. ამოცანა დაიყვანება მათიე-შრედინგერის არასტაციონარულ განტოლებაზე. ნაჩვენებია, რომ ბარიერის სიდიდის მოდულაციის გამო შესაძლებელი ხდება არაპირდაპირი გადასვლები შინაგანი ბრუნვითი მოძრაობის ენერგეტიკულ დონეებს შორის, რომელთა შორის პირდაპირი გადასვლები აკრძალულია. ასეთი გადასვლის სიხშირეები შედარებულია ექსპერიმენტზე დამზერილ ინფრაწითელ შთანთქმასთან. ექსპერიმენტული მონაცემები შედარებულია აგრეთვე მცირე რხევების შესაბამის სიხშირეებთან. დამტკიცებულია, რომ ინფრაწითელი შთანთქმა ეთანის მოლეკულების მიერ განპირობებულია არაპირდაპირი გადასვლებით შესაბამის ენერგეტიკულ დონეებს შორის.