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## Trajectory Analysis of the Rotational Dynamics of Molecules

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**Abstract**—A method for analysis of the rotational dynamics of molecular systems has been proposed on the basis of the calculation of the set of exact classical vibrational–rotational trajectories. It has been proposed to compose and to numerically solve the complete system of dynamic equations consisting of Hamilton's equations and generalized Euler equations for an arbitrary system. The computer algebra system can be applied to automatize the process of derivation and subsequent solution of dynamic equations. The variation of the picture of known bifurcation in the rotational dynamics of symmetric triatomic hydride molecules with an increase in vibrational excitation has been studied within the proposed approach. It has been shown that manifestations of bifurcation completely disappear at a quite high level of vibrational excitations.

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### 1. INTRODUCTION

The role of classical mechanics method in theoretical molecular spectroscopy has been noticeably weakened in the recent years mainly because of an increase in available computer capabilities. On one hand, a highly accurate quantum solution has become possible for a large number of molecular systems. On the other hand, in fields where an adequate quantum consideration of the problem will be hardly possible even in near future, molecular dynamics methods based on computational capabilities, rather than on traditional classical mechanics approaches are used. Nevertheless, the analysis of classical trajectories of an isolated molecular system in some spectroscopic problems can successfully compete with both quantum computations and calculations involving an erroneous number of particles. In particular, these are the simulation of collision-induced continuous spectra of loosely bound systems [1] and the calculation of the parameters of the collisional broadening of rotational lines [2].

The value of classical mechanics methods is not only in the possibility of obtaining approximate quantitative results when a problem is too difficult for quantum mechanics. In view of a close relation between quantum and classical mechanics, classical representations can often be used for better understanding of quantum phenomena. An example is the classical description of the dynamics of a molecular system when, because of the strong vibration–rotation interaction, the rotation of a molecule cannot even roughly be considered as the rotation of a solid top. As was established experimentally (see references 1–18 in [3]), quantum rotational spectra of highly symmetric molecules at quite high angular momenta include groups of four and more quasidegenerate levels, so-

called clusters, which are atypical for spectra of solid tops.

Dorney and Watson [4] interpreted the clustering of quantum energy levels in terms of classical rotation about the axes of symmetry of a molecule. Then, this idea was used to develop the concept of the rotational energy surface [3], which represents the classical energy of rotation of the molecule as a function depending on the direction of the angular momentum at a given its length. This function can be obtained from, e.g., the effective rotational Hamiltonian, where the operators of the angular momentum components are replaced by their classical analogs. Stationary points on the rotational energy surface always exist pairwise (because the rotational problem is invariant with respect to the center of inversion) and the axis passing through pair points is a stationary molecular rotation axis. The doubled number of equivalent stationary axes specifies the number of quasidegenerate energy levels in a certain part of the rotational multiplet. Then, Zhilinskii and Pavlichenkov [5] revealed that some axes become unstable with an increase in the angular momentum  $J$ ; in this case, new stable molecular rotation axes can appear. Such bifurcations in the rotational dynamics of the molecule just correspond to the arrangements of quantum energy levels in rotational multiplets.

Being productive, the concept of the rotational energy surface has two serious demerits. First, there is no a universal method for obtaining this surface adequately describing the rotational dynamics of a molecule for the entire set of vibrational–rotational states. Second, quantitative results obtained by means of the rotational energy surface will certainly be only approximate.

The solution of the complete system of dynamic equations contains exhausting information on the classical vibrational–rotational dynamics. In application to symmetric triatomic hydrides, an approximate variant of such an approach was implemented in [6], where the solution of linearized dynamic equations was used to analyze vibrational–rotational motion near steady states.

In this work, we also focus on symmetric triatomic hydride molecules (such as  $\text{H}_2\text{O}$ ) and on bifurcation in the rotational dynamics characteristic of such molecules. We consider the complete system of dynamic equations and its solutions in the form of vibrational–rotational motion trajectories. To describe the system under study and to obtain the corresponding trajectories, we use an additional simplification by fixing the distances between heavy central and light peripheral atoms.

It is noteworthy that the proposed approach is applicable not only to systems with an extremely small number of vibrational degrees of freedom with the use of model potentials or other simplifications of a physical model. In this work, we consider an extremely simple model for two reasons. First, we want to demonstrate the successive application of the proposed approach from writing the Hamiltonian of the system to obtaining vibrational–rotational trajectories. All intermediate transformations in the case of a complex system would be too lengthy for clear demonstration. Second, the simplest model is sufficient for revealing some features of the vibrational–rotational dynamics of symmetric triatomic hydrides that have not yet been discussed, as far as we know.

## 2. GENERALIZED EULER EQUATIONS

The Born–Oppenheimer approximation allows the consideration of the vibration–rotation problem as a problem of the dynamics of a many-body system with a given interaction potential. In the absence of external fields, the angular momentum of the system in the laboratory coordinate system with the origin at the center of mass is conserved:

$$\dot{\mathbf{j}} = 0. \quad (1)$$

In the vibration–rotation problem, it is more convenient to use a moving (noninertial) reference frame with the same origin and axes certainly connected to a molecule. Both reference frames are related to each other by an orthogonal transformation matrix  $\hat{S}$  [7], so that the components of any vector in the laboratory system are linearly related to the components of the same vector in the moving reference frame:

$$\mathbf{J} = \hat{S}\mathbf{j}. \quad (2)$$

The elements of the matrix  $\hat{S}$  can be expressed in terms of three independent parameters, e.g., three Euler angles.

Using the properties of orthogonality of the matrix  $\hat{S}$ , instead of Eq. (1), we obtain

$$\dot{\mathbf{J}} + \boldsymbol{\Omega} \times \mathbf{J} = 0, \quad (3)$$

where  $\boldsymbol{\Omega}$  is the angular velocity of the moving reference frame with respect to the laboratory system, which depends on the Euler angles and their time derivatives. The angular velocity components  $\boldsymbol{\Omega}$  are the arguments of the Lagrangian and the angular momentum components  $\mathbf{J}$  are the arguments of the Hamiltonian  $H$ . According to the Donkin theorem [8],

$$\boldsymbol{\Omega} = \frac{\partial H}{\partial \mathbf{J}}, \quad (4)$$

and Eq. (3) is modified to the form

$$\dot{\mathbf{J}} + \frac{\partial H}{\partial \mathbf{J}} \times \mathbf{J} = 0. \quad (5)$$

For the simplest solid top model of the molecular rotation, Eqs. (3) or Eqs. (5) are well-known Euler equations. Beyond the solid top model, the rotational Hamiltonian is more complex (e.g., a classical analog of the effective rotational Hamiltonian constructed using experimental data). Nevertheless, Eqs. (5) remain valid and will be called in this case the generalized Euler equations.

In the most general case, the Hamiltonian depends not only on the angular momentum components, but also on the internal generalized coordinates<sup>1</sup>  $\mathbf{q}$  and the corresponding canonically conjugate momenta  $\mathbf{p}$ :

$$H = H(\mathbf{q}, \mathbf{p}, \mathbf{J}). \quad (6)$$

In this case, generalized Euler equations (5) should be considered together with equations for the dynamic variables  $\mathbf{q}$  and  $\mathbf{p}$ ; it is natural to take these equations in the form of Hamilton's equations

$$\dot{\mathbf{q}} = \frac{\partial H}{\partial \mathbf{p}}, \quad \dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}}.$$

Hamiltonian (6) can be obtained as follows. The kinetic energy of the system of particles in the Lagrangian form,

$$T_L = \frac{1}{2} \sum_i m_i \dot{\mathbf{r}}_i^2,$$

where  $\mathbf{r}_i$  is the radius vector of the  $i$ th particle, in the moving reference frame has the form

$$T_L = \frac{1}{2} \sum_i m_i \dot{\mathbf{R}}_i^2 + \frac{1}{2} \sum_i m_i [\boldsymbol{\Omega} \times \mathbf{R}_i]^2 + \boldsymbol{\Omega}^+ \sum_i m_i [\mathbf{R}_i \times \dot{\mathbf{R}}_i], \quad (7)$$

<sup>1</sup> Coordinates  $\mathbf{q}$  formally correspond to vibrational degrees of freedom although they can describe not only simple intramolecular vibrations, but also the “internal rotations” of the fragments of molecules and intermolecular motions when a pair of colliding molecules is considered as a united system.

where  $\mathbf{R}_i = \hat{\mathbf{S}}\mathbf{r}_i$ , and superscripts “+” indicates the transposition operation. In view of the relation between the Cartesian and internal coordinates,  $\mathbf{R} = \mathbf{R}(\mathbf{q})$ , it is easy to obtain

$$T_L = \frac{1}{2}\mathbf{\Omega}^+\hat{I}\mathbf{\Omega} + \frac{1}{2}\dot{\mathbf{q}}\hat{a}\dot{\mathbf{q}} + \mathbf{\Omega}^+\hat{A}\dot{\mathbf{q}}, \quad (8)$$

where  $\hat{I}$  is the inertia tensor matrix,  $\hat{a}$  is the relative kinetic energy matrix, and  $\hat{A}$  is the Coriolis interaction matrix (all these matrices depend on the internal coordinates  $\mathbf{q}$ ). According to the Donkin theorem [8], the kinetic energy is written in the Hamiltonian form<sup>2</sup>

$$T_H = \frac{1}{2}\mathbf{J}^+\hat{I}^{-1}\mathbf{J} + \frac{1}{2}\mathbf{p}^+(\hat{a}^{-1} + \hat{b}\hat{A}\hat{a}^{-1})\mathbf{p} - \mathbf{p}^+\hat{b}\mathbf{J}, \quad (9)$$

and the Hamiltonian is obtained by adding the potential energy of interacting particles to Eq. (9). In Eq. (9),  $\hat{I} = \hat{I} - \hat{A}\hat{a}^{-1}\hat{A}^{-1}$  is the modified inertia tensor matrix and  $\hat{b} = \hat{a}^{-1}\hat{A}^+\hat{I}^{-1}$ .

The quantity  $J = |\mathbf{J}|$  is an integral of motion; for this reason, only two of three generalized Euler equations can be used. To this end, the angular momentum components are expressed in terms of the new dynamic variables  $\Theta$  and  $\Phi$ :

$$\begin{aligned} J_x &= J\sin\Theta\cos\Phi, \\ J_y &= J\sin\Theta\sin\Phi, \\ J_z &= J\cos\Theta. \end{aligned} \quad (10)$$

The angular variables  $\Theta$  and  $\Phi$  specify the direction of the angular momentum  $\mathbf{J}$  in the moving reference frame. In principle, in terms of the Euler angles and corresponding canonically conjugate momenta as the dynamic variables, Hamilton's equations can be considered instead of the generalized Euler equations. However, first, the number of equations in this case is larger and, second, the dynamic variables  $\Theta$  and  $\Phi$  determining the direction of the angular momentum are physically much more informative than the Euler angles and their conjugate momenta.

According to the above consideration, the complete system of dynamic equations can be represented in the form

$$\begin{aligned} \dot{\Phi} &= \left( \frac{\partial H}{\partial J_x} \cos\Phi + \frac{\partial H}{\partial J_y} \sin\Phi \right) \cot\Theta - \frac{\partial H}{\partial J_z}, \\ \dot{\Theta} &= \frac{\partial H}{\partial J_x} \sin\Phi - \frac{\partial H}{\partial J_y} \cos\Phi, \\ \dot{\mathbf{q}} &= \frac{\partial H}{\partial \mathbf{p}}, \\ \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{q}}, \end{aligned} \quad (11)$$

<sup>2</sup> Intermediate lengthy algebra is omitted and only the final result is presented.

where the partial derivatives of the Hamiltonian with respect to the angular momentum components are functions of  $\Theta$  and  $\Phi$  (as well as of  $\mathbf{q}$  and  $\mathbf{p}$ ) and  $J$  is the parameter of the problem. The angles  $\Theta$  and  $\Phi$  specify a two-dimensional sphere, which is the phase space of the rotational problem and is a subspace of the  $(2s + 2)$ -dimensional (taking into account integrals of motion) phase space of the vibration–rotation problem with  $s$  degrees of freedom.

Solving the system of Eqs. (11) and excluding the time from the resulting dependences  $\Theta = \Theta(t)$  and  $\Phi = \Phi(t)$ , we obtain a rotational phase trajectory, i.e., the trajectory of the end of the vector  $\mathbf{J}$  on the surface of the two-dimensional sphere with the radius  $J$ . Strictly speaking, this trajectory is the projection of a multidimensional phase trajectory on the two-dimensional sphere. The set of rotational phase trajectories with the same  $J$  value in a given energy range—phase portrait—can be associated with the quantum rotational multiplet with the same  $J$  value. The features of phase portraits make it possible to predict the structure of rotational multiplets of the molecule.<sup>3</sup>

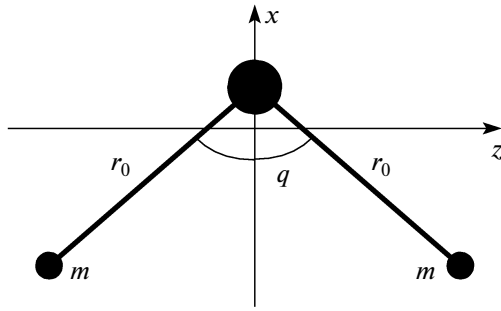
We note that system (11) for an arbitrary vibration–rotation problem with  $s$  vibrational degrees of freedom consists of the minimum possible number of dynamic equations,  $2s + 2$ ; i.e., the known integrals of motion of the vibration–rotation problem were maximally taken into account when deriving system (11). This distinguishes the described approach from those traditionally used for classical trajectory calculations, when the solved system contains a certainly excessive number of equations and the conservation of even energy and angular momentum, which are obvious integrals of motion, is controlled only numerically [2]. Another distinctive feature of the proposed approach is the use of the angular momentum components and intramolecular coordinates as the dynamic variables. Quantum numbers characterizing molecular energy levels correspond to these “natural” variables. Vibrational–rotational trajectories in terms of these variables make it possible to avoid the necessity of the “transformation” of the results of calculations to a space convenient for further analysis.

An example of the successive application of the described approach to the analysis of vibration–rotation dynamics will be given in the next section.

### 3. FEATURES OF THE ROTATIONAL DYNAMICS OF SYMMETRIC TRIATOMIC MOLECULES

We consider an extremely simple model of a water-like symmetric triatomic molecule  $\text{H}_2\text{X}$ . First, we fix

<sup>3</sup> This certainly does not mean that the proposed approach can be applied only to the analysis of only the rotational problem. Excluding the time from the dependences  $\mathbf{q}(t)$  and  $\mathbf{p}(t)$ , the phase trajectory of the vibrational problem can similarly be obtained.


 Fig. 1. Moving reference frame for the  $\text{H}_2\text{X}$  molecule.

distances from two light atoms to the central heavy atom; in this case, only one vibrational degree of freedom—valence angle—remains.<sup>4</sup> In addition, the mass of the central atom is assumed infinity.

In spite of seeming robustness, this model makes it possible to qualitatively analyze the vibration–rotation interaction [9]. It is adequate because the vibration–rotation interaction in real symmetric triatomic hydrides is due primarily to the interaction of the rotation of the molecule with deformation vibration.

The moving reference frame for the system under consideration is shown in Fig. 1, where the  $x$  axis is the bisector of the deformation angle  $q$ , the  $y$  axis is perpendicular to the plane of the molecule,  $m$  is the mass of a light particle, and  $r_0$  is the distance between the light and heavy particles.

The Hamiltonian has the form

$$H = \frac{J_x^2}{2I_{xx}} + \frac{J_y^2}{2I_{yy}} + \frac{J_z^2}{2I_{zz}} + \frac{p^2}{I_0} + V(q), \quad (12)$$

where  $I_{xx} = I_0(1 - \cos q)$ ,  $I_{yy} = 2I_0$ , and  $I_{zz} = I_0(1 + \cos q)$  are the moments of inertia with respect to the respective moving axes,  $I_0 = mr_0^2$ , and  $p$  is the momentum canonically conjugate to the angular coordinate  $q$ .

The complete system of dynamic equations (11) for this system has the form

$$\begin{aligned} \dot{q} &= \frac{2}{I_0} p, \\ \dot{p} &= -\frac{\partial V_{\text{eff}}}{\partial q}, \\ \dot{\Theta} &= \frac{J}{2I_0} \sin \Theta \sin \Phi \cos \Phi \frac{1 + \cos q}{1 - \cos q}, \\ \dot{\Phi} &= \frac{J}{I_0} \cos \Theta \left[ \frac{\cos^2 \Phi}{1 - \cos q} - (1 + \cos q)^{-1} + \frac{1}{2} \sin^2 \Phi \right], \end{aligned} \quad (13)$$

<sup>4</sup> Such a model is usually called the rigid bender.

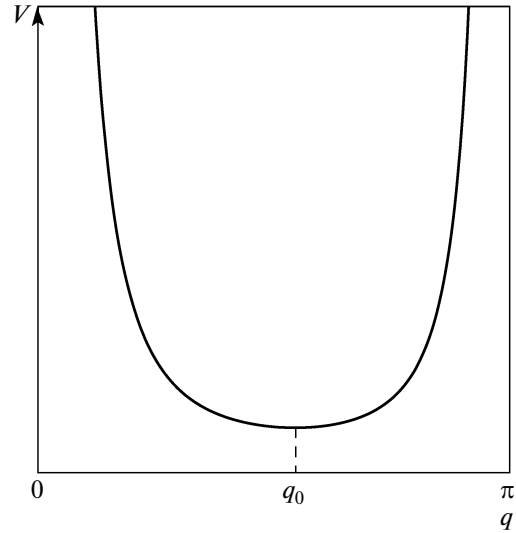


Fig. 2. Pöschl–Teller potential [10].

where the effective potential is given by the expression

$$V_{\text{eff}} = V(q) + \frac{1}{2I_0} \left( \frac{J_x^2}{1 - \cos q} + \frac{1}{2} J_y^2 + \frac{J_z^2}{1 + \cos q} \right), \quad (14)$$

and the angular momentum components are specified by Eqs. (10). The intramolecular potential  $V(q)$  is taken in the form of the Pöschl–Teller potential [10] (Fig. 2)

$$V = \frac{1}{2I_0} \left( \frac{V_-}{1 - \cos q} + \frac{V_+}{1 + \cos q} \right). \quad (15)$$

Here,

$$V_{\pm} = \frac{1}{4} I_0^2 \omega_0^2 (1 \pm \cos q_0)^2,$$

where  $q_0$  is the equilibrium angular coordinate and  $\omega_0$  is the harmonic frequency. This molecular potential was chosen because it allows the exact solution of the quantum oscillation problem whose energy spectrum has the form [11]

$$\begin{aligned} E_n &= \frac{1}{I_0} \hbar^2 \left[ n + \frac{1}{2\hbar} (\sqrt{V_-} + \sqrt{V_+}) \right] \\ &\times \left[ n + 1 + \frac{1}{2\hbar} (\sqrt{V_-} + \sqrt{V_+}) \right], \quad n = 0, 1, 2, \dots \end{aligned} \quad (16)$$

Since the analytical dependence of effective potential (14) on the coordinate  $q$  is similar to the potential  $V(q)$ , the quantum oscillation problem with the potential  $V_{\text{eff}}$  can be considered with the classical components  $J_\alpha$  as parameters [12]. The spectrum of eigenvalues is given by Eq. (16) with the replacement of  $V_-$  and  $V_+$  by  $V_- + J_x^2$  and  $V_+ + J_z^2$ , respectively. Each of the energy levels  $E_n$  existing in the absence of rotation is

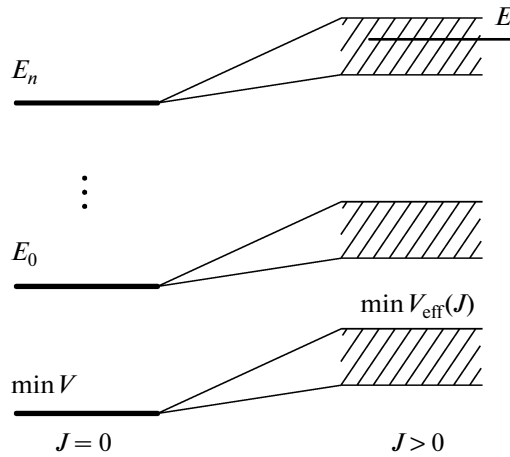


Fig. 3. System of vibrational levels for the one-dimensional problem with the Pöschl–Teller potential.

transformed to a band whose width is determined by the range of possible directions of the vector  $\mathbf{J}$  with a fixed length, as is shown in Fig. 3. Each of the energy bands can be considered as a classical analog of a quantum rotational multiplet and the solution of the system of dynamic equations (13) and the corresponding phase trajectories in the energy range of interest can be analyzed by specifying the appropriate initial conditions. In this work, we analyze only states with the energy corresponding to the upper part of rotational multiplets, i.e., states that change sharply owing to classical bifurcations. It is reasonable to begin with the lowest energy band (see Fig. 3).<sup>5</sup>

The phase portrait of the system under study is determined primarily by its rest points (equilibrium states of the system), i.e., by the time-independent solution of Eqs. (13). These solutions can be obtained from the condition of vanishing the right-hand sides of Eqs. (13). One of these solutions has the form

$$\begin{aligned} p_e &= 0, \\ q_e &= \arccos \frac{\sqrt{V_+ + J^2} - \sqrt{V_-}}{\sqrt{V_+ + J^2} + \sqrt{V_-}}, \\ \Theta_e &= 0. \end{aligned} \quad (17)$$

The energy corresponding to this solution<sup>6</sup> is the upper edge of the lowest energy band in the right-hand part of Fig. 3. The angular momentum in this state is directed along the  $z$  axis of the moving reference frame. Another interesting solution is given by the expressions

$$\begin{aligned} p_e &= 0, \\ q_e &= \frac{\pi}{2}, \\ \Phi_e &= 0 \quad \text{or} \quad \Phi_e = \pi, \end{aligned} \quad (18)$$

$$\Theta_e = \arcsin \sqrt{\frac{1}{2} \left( 1 - \frac{V_- - V_+}{J^2} \right)}.$$

This solution exists only if  $J \geq \sqrt{V_- - V_+}$ . This means that each molecule is characterized by a certain critical angular momentum determined by the parameters of this molecule:

$$J_{\text{cr}} = \sqrt{V_- - V_+} = I_0 \omega_0 \sqrt{|\cos q_0|}. \quad (19)$$

The four points on the phase sphere  $[(\Theta_e, \Phi_e = 0), (\Theta_e, \Phi_e = \pi), (\pi - \Theta_e, \Phi_e = 0), (\pi - \Theta_e, \Phi_e = \pi)]$  specify two straight lines (new rotation axes) as is shown in Fig. 4b. The angular momentum in equilibrium states (18) is directed along one of these straight lines and two directions of  $\mathbf{J}$  are possible for each of these straight lines. The energy in each of states (18) is equal to the energy of state (17) at  $J = J_{\text{cr}}$  and is above the latter at  $J > J_{\text{cr}}$ , i.e., becomes the upper edge of the lowest energy band in Fig. 3.

The character of the stability of equilibrium states (17) and (18) is determined by the form of phase trajectories near these points. As is seen in Fig. 4a, the north and south poles are stable at  $J < J_{\text{cr}}$  and the angular momentum precesses about the axis passing through these points (i.e., the  $z$  axis). Each of these points becomes unstable at  $J = J_{\text{cr}}$ , but a pair of new stable points appears near each pole, which diverge from each other with an increase in  $J$  (Fig. 4b). The angle  $\Theta_e$  varies from 0 at  $J = J_{\text{cr}}$  to  $\pi/4$  at  $J \rightarrow \infty$ . The angular momentum can precess about each of two new axes shown in Fig. 4b.<sup>7</sup>

The described bifurcation in classical dynamics (predicted for the first time for the water molecule in [14]) corresponds to the appearance of quadruple clusters in the upper part of the quantum rotational multiplet. Clustering was experimentally observed in the ground vibrational state for the  $\text{H}_2\text{Se}$  [15] and  $\text{H}_2\text{Te}$  [16] molecules and was revealed in highly accurate variational calculations [17]. Formula (19) provides the following critical angular momenta in units of  $\hbar$ : 22, 14, 8, and 5 for the  $\text{H}_2\text{O}$ ,  $\text{SiH}_2$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$ , respectively. These values are in agreement with those previously obtained in [12, 17, 18].

<sup>5</sup> The analysis of the corresponding vibrational dynamics is also of interest, but it is beyond the scope of this work.

<sup>6</sup> Taking into account the center of inversion, we have two equivalent solutions with  $\Theta_e = 0$  and  $\Theta_e = \pi$  and any  $\Phi_e$  value.

<sup>7</sup> We emphasize that the solution of system (13) near the equilibrium states can negligibly differ from the solution of the linearized system of equations, but this statement is not universal. In particular, trajectories of the initial system of dynamic equations for “center”-type equilibrium states (as in Fig. 4) can be significantly different from those of the linearized version of this system [13].

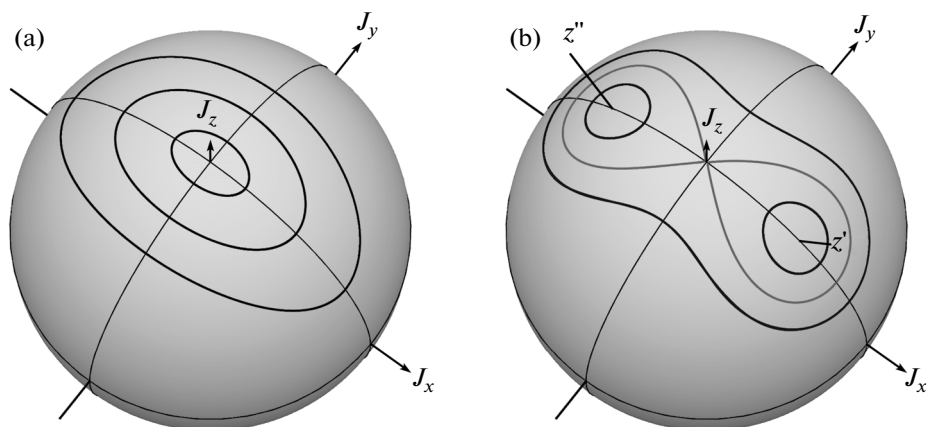


Fig. 4. Rotational phase trajectories near stationary points for (a)  $J < J_{cr}$  and (b)  $J > J_{cr}$ ;  $z'$  and  $z''$  are new stable rotation axes.

Equilibrium states (17) and (18) and solutions close to them (see Fig. 4) correspond to the minimum of effective potential (14). Such approximate solutions can be obtained for any molecule if the generalized Euler equations in the complete system of dynamic equations (11) are artificially decoupled from Hamilton's equations. Then, considering the components of the vector  $\mathbf{J}$  as parameters, it is possible to find stationary solutions of Hamilton's equations,  $\mathbf{q}_e = \mathbf{q}_e(\mathbf{J})$  and  $\mathbf{p}_e = \mathbf{p}_e(\mathbf{J})$ . Substituting these solutions into Hamiltonian (6) and returning the status of the dynamic variables to the angular momentum components, we obtain the effective rotational Hamiltonian  $H_r = H(\mathbf{q}_e(\mathbf{J}), \mathbf{p}_e(\mathbf{J}), \mathbf{J})$ . The rotational dynamics of the molecule will be described only by generalized Euler equations (5) with the Hamiltonian  $H_r$ . It is easy to obtain the Hamiltonian in the explicit form [19, 20]:

$$H_r = \frac{1}{2} \mathbf{J}^+ \hat{I}^{-1}(\mathbf{q}_e) \mathbf{J} + V(\mathbf{q}_e). \quad (20)$$

The rotation of the molecule described by the approximate rotational Hamiltonian given by Eq. (20) can be called the rotation of a "soft body" taking into account that the equilibrium geometry of the molecule is determined by the rotation state:  $\mathbf{q}_e = \mathbf{q}_e(\mathbf{J})$ . Stationary states, where  $\dot{\mathbf{J}} = 0$ , are of particular interest among solutions describing the rotation of the soft body. In this case, the stationary solutions of Hamilton's equations,  $\mathbf{q}_e = \mathbf{q}_e(\mathbf{J})$  and  $\mathbf{p}_e = \mathbf{p}_e(\mathbf{J})$ , follow from the conditions  $\dot{\mathbf{q}} = 0$  and  $\dot{\mathbf{p}} = 0$ , which is exactly satisfied. In this case, intramolecular vibrations are absent and the molecule rotates about an axis fixed in the space. Solutions (17) and (18) for the description of the dynamics of triatomic water-like molecules exemplify such a rotation.

However, with an increase in the total vibrational-rotational energy, it is necessary to solve the complete system of dynamic equations (11) with the appropriate initial conditions. In particular, for the above model of a triatomic molecule, it is convenient to take the initial

coordinate  $q_0 = q_e$ , where  $q_e$  is the value at which the effective potential given by Eq. (14) has a minimum. Then, since the energy is an integral of motion, the initial momentum is given by the expression

$$p_0 = \sqrt{I_0[E_n - V_{\text{eff}}(q_e)]}. \quad (21)$$

The solution of system (13) with initial conditions  $q_0$  and  $p_0$ , describes the vibration-rotation dynamics of the molecule corresponding to the  $n$ th vibrational state.

The  $q_0$  and  $p_0$  values naturally depend on the direction of the vector  $\mathbf{J}$ . Consequently, the position of  $E_n$  inside the  $n$ th energy band is determined by the initial values  $\Phi_0$  and  $\Theta_0$ . The initial value  $\Theta_0$  at  $\Phi_0 = 0$  can be chosen according to the dependence  $E_n = E_n(\Theta)$  (Eqs. (16) and (10)). Stationary solutions in which the vector  $\mathbf{J}$  is parallel to the  $z$  axis exist (as in the case of the soft-body model) for system (13) at  $J < J_{cr}$  at any  $n$  value. Phase trajectories for near-steady states are also local (Fig. 5), but are less smooth than in the case of the soft-body model (see Fig. 4).

Phase trajectories for the vibrational level  $n = 0$  are complicated. New steady states similar to Eq. (18) do not appear at  $J > J_{cr}$ , but localized trajectories continue to exist near the point  $(\Theta_e, \Phi_e)$  (point of the maximum of  $E_n$ ). However, their form significantly differs from those shown in Fig. 4: the phase trajectories are not closed and completely fill a small vicinity of the point  $(\Theta_e, \Phi_e)$  on the phase sphere (Fig. 5b). Nevertheless, the existence of four such equivalent (with the same energy) trajectories indicates the possible appearance of quadruple clusters in the upper part of quantum rotational multiplets in the ground vibrational state.

With a further increase in vibrational excitation, the dimension of localization domains of rotational trajectories increases significantly (Fig. 6a). It is seen that the delocalization of phase trajectories increases significantly with  $n$ . With a further increase in vibrational excitation, it becomes impossible to find trajectories localized near new stationary rotation axes on the rotational phase portrait (Fig. 6b). In application

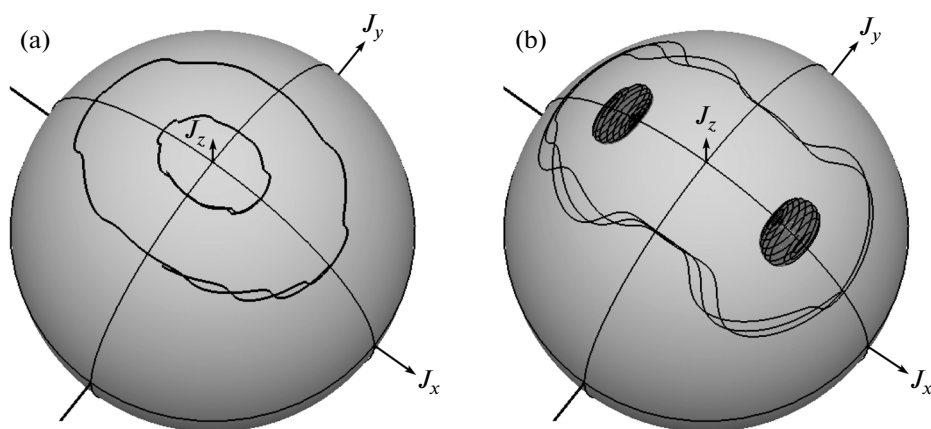


Fig. 5. Rotational phase trajectories for the ground vibrational state at (a)  $J < J_{cr}$  and (b)  $J > J_{cr}$ .

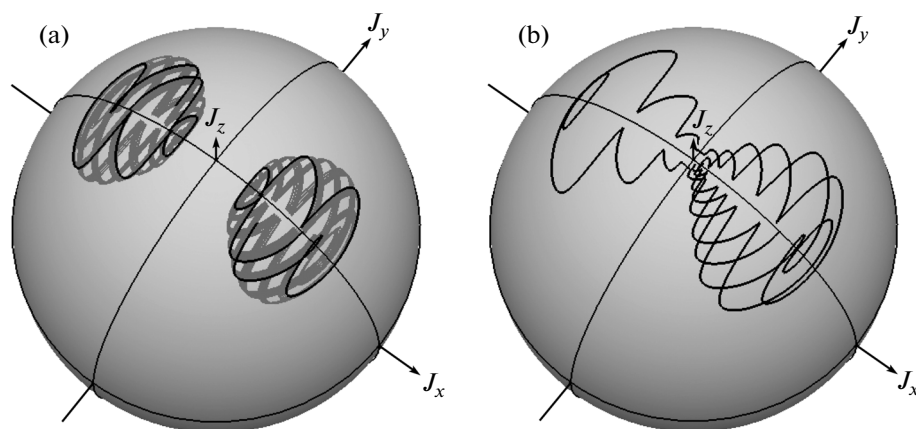


Fig. 6. Rotational phase trajectories for the excited vibrational states with  $n$  (a) 2 and (b) 3 at  $J > J_{cr}$ .

to quantum spectra, this means the inevitable disappearance of quadruple clusters in spectra of highly excited vibrational states even at angular momenta above the critical value.

#### 4. CONCLUSIONS

An approach to the analysis of the vibrational–rotational dynamics of molecular systems (molecules, molecular pairs, etc.) has been proposed on the basis of the solution of a derived complete system of dynamic equations. For an arbitrary molecule with  $N$  internal degrees of freedom, it has been proposed to supplement the standard system of  $2N$  Hamilton’s equations by a pair of equations (5), which we refer to as the generalized Euler equations. Resulting system (11) consists of only  $2N + 2$  equations, but allows the complete description of the classical vibrational–rotational dynamics of a molecule system without any additional approximation.

For the calculation of the set of classical trajectories (e.g., collisional), a small number of equations in

a dynamic system give in principle obvious computational advantages. However, an excessive number of equations are often compensated in practice by their simple and compact form. For this reason, the proposed system of dynamic equations can possibly give no significant computational gain as compared to other modern methods of classical trajectory calculations [2].

Nevertheless, we believe that the main value of the proposed approach is not a potential increase in the rate of the calculation of the set of classical trajectories but is the possibility of such a calculation in terms of the natural variables of the vibration–rotation problem. As a result, trajectories are obtained in the form of time dependences of the internal coordinates and total angular momentum components. The stage of the “transformation” of the calculated trajectories to a space convenient for further analysis is thus excluded.

The successive application of the proposed approach to the analysis of the vibrational–rotational dynamics of a simple model system imitating a symmetric triatomic hydride molecule ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , etc.)

has been demonstrated in Section 3. The variation of the picture of the known bifurcation in the rotational dynamics of such molecules with an increase in vibrational excitation has been determined. It has been shown that manifestations of bifurcation completely disappear in the classical phase portrait of the system when the level of vibrational excitation is quite high and, therefore, the corresponding rearrangements of quantum energy levels will not be observed in the spectra of highly excited vibrational states of triatomic hydride molecules.

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