Critical phenomena in rotational spectra

B. I. Zhilinskiĭ

Moscow State University

I. M. Pavlichenkov

Kurchatov Atomic Energy Institute

(Submitted 26 February 1986; resubmitted 3 September 1986)
Zh. Eksp. Teor. Fiz. **92**, 387–403 (February 1987)

Nonlinear effects produced in rotational spectra of molecules and atomic nuclei by centrifugal distortion at large values of the angular quantum number J are investigated. The theoretical analysis is based on a new concept, that of an effective rotational Hamiltonian. It is shown that at a certain value J_c of the quantum number J there can occur in the rotational spectra of these systems phenomena that lead to qualitative changes of the rotation dynamics. These phenomena, which are in some sense analogs of phase transitions in macroscopic systems, are called critical. Their counterpart in classical mechanics is bifurcation. Critical phenomena for pure rotation is classified on the basis of a local symmetry group $\mathfrak{g}$. Local critical phenomena that cover a bounded region of the phase space of the rotational motion are singled out among the five types of critical phenomena that can exist in rotational spectra. In the classical limit, local critical phenomena are characterized by breaking of the $\mathfrak{g}$ symmetry, by a change of the degeneracy multiplicity, and by discontinuity of the second derivative of the rotation energy with respect to J at the point J_c. It is shown that for local critical phenomena there exists a universal rotational-motion Hamiltonian that is independent, accurate to the constants it contains, of the internal structure of the system. The universal Hamiltonian is used to develop a phenomenological theory of local critical phenomena and to show their deviation from second-order phase transitions in macroscopic systems.

1. INTRODUCTION

The spectra connected with quantum rotational motion have so far been investigated in detail only for two microscopic systems, molecules and atomic nuclei. Rotational excitations of these systems are grouped into rotational bands with a regular sequence of levels, each described by an energy and by the total angular momentum J as the quantum number. Rotational states are therefore relatively simply separated by investigating the complex excitation spectra of these multiparticle systems. Even at the large values of J attained by modern methods of molecular and nuclear spectroscopy, the rotational states are quite pure, i.e., they contain negligible admixtures of other types of excitation. From the standpoint of the study of the dynamics of a finite multiparticle system, hwoever, interest attaches not to the regularity indicated above, but to deviations from it, due to the interaction of the rotation with other degrees of freedom. We consider in this article the simplest among the distortions of rotational spectra, viz., centrifugal distortion, which becomes appreciable at large J.

For most typical molecules, the electron-excitation energy exceeds considerably the energies of the vibrational and rotational excitations, so that the Born-Oppenheimer adiabatic approximation is quite suitable. If the electron ground state is not degenerate, it suffices to consider the vibrational-rotational motion, whose Hamiltonian is of the form[1]

$$H = {}^1/_2 \sum_{\alpha,\beta} \{ (J_\alpha - \pi_\alpha)\mu_{\alpha\beta}(J_\beta - \pi_\beta) - {}^1/_4 \delta_{\alpha\beta}\mu_{\alpha\alpha} \} + {}^1/_2 \sum_{k=1}^{3n-6} \omega_k p_k{}^2 + U(q_1, \ldots, q_{3n-6}), \quad (1)$$

where J_α $(\alpha = x,y,z)$ are the components of the total-angular-momentum operator along the axes of the body coordinate frame (BCF), π_α are the vibrational angular-momentum operator, $\mu_{\alpha\beta}$ is a matrix inverse to the inertia tensor and depends on the coordinates q_i of the normal vibrations of an n-atom molecule, while p_i are the momenta conjugate to them; U is the potential energy of the molecule in the electronic ground state. The vibrational-rotational interaction reduces to effects of centrifugal distortion that results from the dependence of $\mu_{\alpha\beta}$ on the coordinates q_i, and to Coriolis-interaction effects due to the operators π_α.

There is no analog of the Born-Oppenheimer approximation in atomic nuclei, but the rotation in well-deformed nuclei is nonetheless adiabatic. The ground state of a deformed nucleus is an axisymmetric ellipsoid. Deviations from the adiabatic approximation for rotational states with $J \leqslant 10$ are small in bands based on lower excited heavy deformed nuclei. For larger J, the lower band, named the "yrast band" and made up of nuclear levels that have the lowest energy for the given J, is not homogeneous. It consists of levels of rotational bands based on quasistatic excitations, which turned out for some reasons to be the lowest for the given spin region.

The deformation of a nucleus in the lowest band begins to change noticeably when the centrifugal energy of the rotation becomes comparable with the energy gap beween the shells; this occurs at $J \sim 30$. The deformation change is such as to minimize the rotational energy of the nucleus. The largest moment of inertia is possessed by an oblate nucleus rotating about its symmetry axis. Therefore, when J is increased in the lowest band, the nucleus tends to change from prolate to oblate, but this is hindered by shell effects. As a

0038-5646/87/020221-09$04.00

result, starting with $J \sim 40$, the nucleus becomes nonaxial, and the lowest band corresponds to its rotation about the axis with maximum moment of inertia.

Centrifugal effects are thus common for molecules and atomic nuclei. The centrifugal distortion determines the structure of the rotational excitations in these systems at sufficiently large angular momenta. Usually the effects of centrifugal distortion are taken into account phenomenologically, viz., with the aid of the variable moment of inertia in nuclei, and with the aid of the so-called reduced effective rotational Hamiltonians[3] in molecules. In both cases, a large number of rotational levels are fairly well described quantitatively. One can cite as an example the rotational band for the ground vibrational state of the H_2S molecule, for which 29 adjustment parameters permit a good description of 426 experimental transitions with $J \leqslant 22$ (Ref. 4). It is important that if $J \sim 20$ the succeeding terms of the Hamiltonian are no longer small compared with the preceding ones. The convergence of the power-law series is even worse for the H_2O molecule. This situation is typical of the rotational structure, since an expansion near $J = 0$ cannot describe large-J states in which the essentially nonlinear features of rotational dynamics manifest themselves.

Nonlinearity at large J leads to qualitatively new effects, which have heretofore been little investigated. In Ref. 5 is considered 90° rotation of the vector **J** relative to the BCF upon excitation of the levels of the lowest rotational band. This phenomenon is similar to a first-order transition. In Ref. 6 is described the appearance of equivalent rotation axes in an isolated band of a five-atom molecule in the form of a weak aspherical top. This is the analog of a second-order phase transition. Both effects lead to an irregular change of the levels of the rotational multiplet (RM)[1] near a certain critical value J_c. Qualitative effects of this type in microsystems will hereafter be called critical phenomena, bearing in mind their difference from phase transitions in macroscopic systems. Critical phenomena were heretofore investigated mainly for model systems. The most popular is the Lipkin-Meshkov-Glick model.[7] Different approaches to the description of a critical phenomenon in this model was considered in Refs. 8–10. Phase transitions for a more complicated collective motion in a model of interacting bosons was investigated in Ref. 11.

A critical phenomenon comprises a qualitative change in the dynamic motion of a microsystem, and takes place at certain values of its integrals of motion (number of particles, angular momentum, energy). It is manifested in a restructuring of the system's collective-excitations spectrum. Critical phenomena are a fundamental and as yet unsolved problem in the physics of finite multiparticle systems. Three problems are faced in the investigation of critical phenomena.

1. Classification, i.e, determination of all the possible types of critical phenomena for a given collective motion of the system. This problem reduces to an investigation of the classical-energy surface of the collective motion and is solved in the spirit of catastrophe theory. An analog of a critical phenomenon in classical mechanics is bifurcation. An important aspect during this stage is the introduction of the concept of a local symmetry group $\mathfrak{g}$ that characterizes a small region of the collective-motion phase space. The critical phenomena are classified in accordance with the group $\mathfrak{g}$. All types of critical phenomena can be divided into two groups: local which occur in a finite region of phase space, and global which are not so restricted.

2. Investigation of the spectrum of the collective excitations near the critical point. This problem, which can naturally be called the theory of quantum bifurcations, can be solved for local critical phenomena for which there exists in the vicinity of the critical point a closed collective Hamiltonian capable of describing the lower collective excitations of the system. This Hamiltonian should be universal, i.e., be independent of the internal structure of the system, apart from the constants it contains. Solution of this problem, meaning construction of a phenomenological theory of critical phenomena, makes it possible to determine the change of the spectrum of the lower collective excitations on passing through the critical point. In a finite system this change is the only attribute by which the critical phenomenon can be identified.

3. A microscopic theory of universal critical phenomena should indicate whether a critical phenomenon exists for a given type of collective motion in the considered system. If this phenomenon exists, the theory must predict the parameters of the universal collective Hamiltonian.

We solve in this paper only the first two problems for the simplest type of collective motion—rotation. The results are general and independent of the specific form of the system.

2. EFFECTIVE ROTATIONAL HAMILTONIAN AND ITS SYMMETRY

It is convenient to study the critical phenomena with the aid of an effective rotational Hamiltonian

$$H_{eff}=h+\sum_{\alpha} h_\alpha J_\alpha+\sum_{\alpha,\beta} h_{\alpha\beta} J_\alpha J_\beta+\sum_{\alpha,\beta,\gamma} h_{\alpha\beta\gamma} J_\alpha J_\beta J_\gamma+\dots, \qquad (2)$$

which is an infinite series in powers of the operator J_α. The coefficients of this series depend on the operators of the internal motion of the system. The Hamiltonian (2) can be obtained by the generalized-density matrix method used to describe the collective excitations of an atomic nucleus.[12] For molecules, expression (2) is obtained from the vibrational-rotational motion Hamiltonian (1).[13]

If the state of the internal (rotational, single-particle, etc.) motion is not degenerate, there are no Coriolis forces in the band based on it, and $h_\alpha = h_{\alpha\beta\gamma} = \dots = 0$ in the Hamiltonian (2). In this case $H_{\rm eff}$ describes the centrifugal-distortion effects. We shall study these effects in an isolated rotational band weakly coupled to the other rotational bands.[2] The coefficients h, $h_{\alpha\beta}$, etc. for such a band are c-numbers.

The effective rotational Hamiltonian of an isolated band based on a nondegenerate state is invariant to time reversal and to inversion of the BCF. Additional contraints on the coefficients of the Hamiltonian (2) stem from the point symmetry group of the system. The aggregate of the operations of the point group and of the inversion forms the symmetry group G of the effective rotational Hamiltonian. For a nucleus this is the group D_2. The point groups of the molecules are more varied. They include elements such as the symmetry plane σ, the nth order symmetry axis C_n, the mirror-rotation axes[3] S_n, and combinations of these elements.

We represent $H_{\rm eff}$ in the form of an expansion

$$H_{eff}=\sum_{k=0}^{\infty}\sum_{m=0}^{2k}\{t_{k,m}T_{2k,m}+(-1)^{m}t^{*}_{k,m}T_{2k,-m}\} \qquad (3)$$

in irreducible spherical tensor operators of the form

$$T_{l,m}=(-1)^{m}T^{+}_{l,-m}=(-1)^{m}f_{l,m}(\mathbf{J}^{2},J_{z})J_{-}^{m}, \qquad (4)$$

where $\mathbf{J}^2=J_x^2+J_y^2+J_z^2$, $J_\pm=J_x\pm iJ_y$ (in the BCF, J_- and J_+ are respectively raising and lowering operators), and f are real functions given explicitly in Ref. 14. We shall find it convenient to regroup the terms of (3) and write the effective Hamiltonian in the form

$$H_{eff}={}^{1}/_{2}\sum_{m=0}^{\infty}\{J_{+}^{m}g_{m}^{*}(\mathbf{J}^{2},J_{z})+g_{m}(\mathbf{J}^{2},J_{z})J_{-}^{m}\}, \qquad (5)$$

where the function g_m satisfies the relation

$$(-1)^{m}g_{m}(\mathbf{J}^{2},-J_{z})J_{+}^{m}=J_{+}^{m}g_{m}(\mathbf{J}^{2},J_{z}) \qquad (6)$$

and depends on the coefficients of t_{km} (i.e., h, $h_{\alpha\beta}$, ...).

Characterizing the RM levels are, besides the quantum number J, irreducible representations of the group G. The fine structure of the levels of the multiplet is called in molecular spectroscopy the cluster structure.[15] A lucid description of the RM cluster structure is obtained by using the concept of precession. We introduce the classical notion of a stationary rotation axis whose orientation relative to the BCF is determined from the equations

$$\{H_{eff},J_{\alpha}\}=0,\quad \alpha=x,y,z, \qquad (7)$$

where $H_{\rm eff}$ is the classical analog of the Hamiltonian (3) or (5), and {...} are Poisson brackets. Each stable stationary rotation axis is connected in the RM with a level group corresponding to precession of the vector **J** about this axis. Corresponding to an unstable stationary axis is a group of levels located in the transition region between the states corresponding to the precession of the vector **J** about different stable axes. Symmetry makes possible several equivalent stable rotation axes, precessions about which are equal accurate to a symmetry transformation. The precession of **J** about equivalent axes is independent only in the zeroth approximation. Tunneling through the barrier between regions of equivalent precessions leads to splitting of the levels making up the cluster.

We shall distinguish between regular and critical changes in the RM level structure. In the former case a change of the quantum number J (assumed hereafter to be large enough) changes only the orientation of the stationary axes, which leads to a monotonic dependence of the level energies in the RM on J. Critical phenomena are accompanied by a change of the number of stationary axes and of the character of their stability. At the critical point J_c, some of the RM levels corresponding to precession about the changed rotation axes are restructured. The appearance or vanishing of equivalent stable rotation axes leads to a change of the cluster structure of the RM levels.

We consider a subgroup $\mathrm{g}\subset G$ making up the z axis of the BCF invariant, and call it the local-symmetry group. It determines the form of the Hamiltonian $H_{\rm eff}$ (5) near the selected direction of the z axis. Let the z axis lie in a symmetry plane σ that coincides with the xz plane. It is easy to prove with the aid of (6) that $g_m^*=g_m$. If the z axis is a C_n symmetry axis, then the nonzero function s_m in (5) are those with $m=np$, where $p=1, 2, \ldots$. For axes of type C_{nv} the function g_m must satisfy simultaneously the first and second requirements. The symmetry axes C_{nh} contribute nothing new to the properties of the Hamiltonian $H_{\rm eff}$, isnce the C_{nh} axis is identical for it with the C_n axis if n is even, and is identical with C_{2n} if n is odd.

The functions g_m in the Hamiltonian (5) are undoubtedly determined by the symmetry of the system as a whole, i.e., by the group G. For a description of some of the RM levels, however, the decisive group is g, in accordance with which it is convenient to classify the critical phenomena. The concept of a local-symmetry group is closely related with the fundamental difference between the considered theory of rotational spectra and other approaches based in some way or another on the use of the adiabaticity of the rotation. The sum (5) is not a power series, and can be conveniently used, as will be shown below, to describe nonlinear effects in rotational spectra.

As a first step towards the solution of our problem we use the Hamiltonian (5) to determine the energy of classical rotation in that part of phase space which corresponds to rotation of the system around an axis close to the z axis of the BCF. The phase space of the rotational motion is made up of three Euler angles ϕ, ϑ, ψ and three momenta p_ϕ, p_ϑ, and p_ψ conjugate to them. The absolute value of the angular-momentum vector **J** and its component $J_{z'}=p_\phi$ on the z' axis of the laboratory frame are integrals of the motion. It is therefore convenient to transform canonically to new conjugate variables J and q_J, $J_{z'}$ and $q_{z'}$, and J_z and q_z (Ref. 16). Since q_J and $q_{z'}$ are cyclic variables, the phase space of the rotating body is in fact two-dimensional. It is convenient to map it on the surface of a sphere of radius J with center at the BCF origin (phase sphere).[4)] A point on the sphere with coordinates θ,φ ($\cos\theta=J_z/J$, $\varphi=\pi/2-q_z$ for $J_{z'}=q_J=0$) determines the orientation of the vector **J** in the BCF. Thus, the trajectories of end point of the vector **J** on the phase sphere are classical trajectories of the system in its collective rotational phase space. From the Hamiltonian (5) we obtain in the classical limit the rotation energy (the rotational-energy surface).

$$E(\theta,\varphi)=\varepsilon_{0}(J^{2},\cos^{2}\theta)+{}^{1}/_{2}\sum_{m=0}^{\infty}[\varepsilon_{m}^{*}(J^{2},\cos\theta)e^{im\varphi}+\varepsilon_{m}(J^{2},\cos\theta)e^{-im\varphi}]\sin^{m}\theta. \qquad (8)$$

3. TYPES OF CRITICAL PHENOMENA FOR DIFFERENT LOCAL-SYMMETRY GROUPS

1. We consider first the case $\mathrm{g}=C_1$, when the z axis is a general position axis and all the functions g_m in (8) differ from zero. We expand the rotation energy $E(\theta,\varphi)$, assuming the angle θ to be small, and write this expansion in terms of the Cartesian coordinates $\xi=\theta\cos\varphi$, $\eta=\theta\sin\varphi$ in the vicinity of the north pole of the phase sphere (the axes ξ and η are directed along the axes x and y of the BCF, respectively):

$$E(\xi,\eta)=E_{z}(J)+a_{10}\xi+a_{01}\eta+a_{11}\xi\eta+a_{20}\xi^{2}+a_{02}\eta^{2}+a_{30}\xi^{3}+a_{21}\xi^{2}\eta+a_{12}\xi\eta^{2}+a_{03}\eta^{3}+\ldots, \qquad (9)$$

where $E_z(J)$ is the energy of the system rotation about the z axis, and the coefficients a_{ij} depend on J. Let the z axis be at $J=J_0$ the stationary rotation axis of the system, i.e.,

$a_{10}(J_0) = a_{01}(J_0) = 0$. In this case we can restrict the expansion in (9) to terms quadratic in ξ and η. If J is varied, the local behavior of the function $E(\xi,\eta)$ does not change qualitatively. The system, as before, has a stationary axis of rotation, but one displaced from it position at $J = J_0$. This is the regular variation of the precession axis.

The critical point[5)] (if it exists) is determined by the condition that the rotation axis be stationary and by the equation $a_{11}^2(J_c) - 4a_{02}(J_c)a_{20}(J_c) = 0$. In the vicinity of the critical point is is necessary to take into account the cubic terms in the expansion (9). A nonlinear transformation of the coordinates can reduce (9) to the canonical form of a catastrophe function of the "fold" type,[17] which takes in our case the form

$$E(\xi,\eta)=E_z(J)-\alpha(J-J_c)\xi+a_{02}\eta^2+a_{30}\xi^3, \tag{10}$$

where the values of a_{02} and a_{30} are specified at the point J_c.

Analysis of the surface (10) shows that the considered critical phenomenon is connected with the onset of two stationary rotation axes, one stable and the other unstable, whose directions are close to that of the z axis. Near the critical point, a singularity arises in the second derivative, with respect to J, of the energy of rotation about the stable axis, $E''(J) \sim \mp |J + J_c|^{-1/2}$. Figure 1 shows the classical trajectories on the left and right of the critical point J_c in that part of the phase space where the stationary axes appear. For $J < J_c$ all the trajectories are global and encompass the entire phase sphere, in view of the absence of a stationary rotation axis. For $J > J_c$, the local trajectories describe the precession of the vector $\mathbf{J}$ around the stable axis of rotation. The local trajectories are separated from the global ones by a separatrix S that passes through the saddle point of the surface (10). The separatrix is a global curve, and therefore this critical phenomenon is not local.

2. Critical phenomena for the local symmetry groups C_s, C_2, and C_{2v} are the same, and are described in the classical limit by the energy surface.

$$E(\xi,\eta)=E_z(J)-\alpha(J-J_c)\eta^2+a_{20}\xi^2+a_{04}\eta^4. \tag{11}$$

Depending on the signs of the coefficients a_{20} and a_{04} in expression (11), two types of critical phenomena exist. If a_{20} and a_{04} differ in sign, the critical phenomenon is not local and reduces to a change in the character of the stability of the stationary rotation axis z. At equal signs of the coefficients α and a_{20}, the rotation axis z which is stable for $J < J_c$ becomes unstable for $J > J_c$. In addition, the two equivalent unstable axes of rotation with energy $E_k = E_z - \alpha^2(J + J_c)^2/4a_{04}$ vanish at the point J_c.

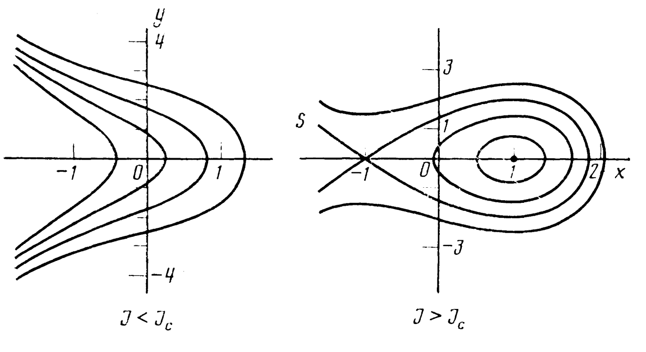

FIG. 1. Classical trajectories near the north pole of the phase sphere for a critical phenomenon corresponding to the local symmetry group $C_1(\alpha > 0, a_{02} > 0, a_{30} > 0)$.

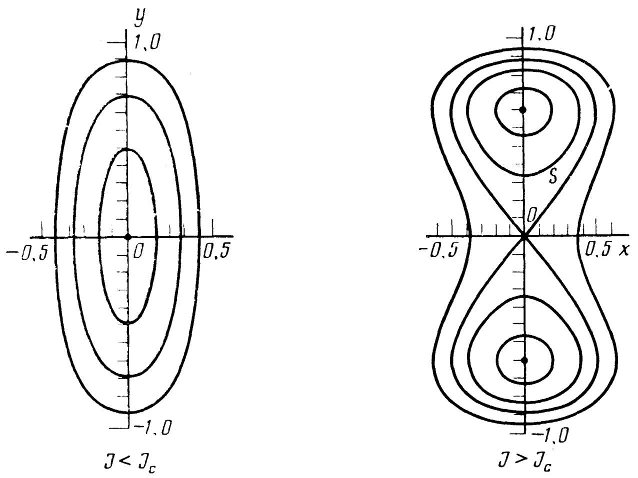

FIG. 2. Classical trajectories for local critical phenomenon C_{2v}.

If the coefficients a_{20} and a_{04} are of like sign, the classical picture of the change of the rotation of the system at the critical point J_c is the following. If the sign of α coincides with that of the coefficients a_{20} and a_{04} the rotation around the z axis, with energy $E_z(J)$, goes over at $J > J_c$ into rotation around one of the two equivalent axes $\mathbf{k}(\theta_0,\pi/2)$ or $\mathbf{k}'(\theta_0,3\pi/2)$, $(\theta_0^2 = \alpha(J - J_c)/2a_{04})$ with energy $E_k(J)$. The classical solution is then no longer invariant, and the second derivative with respect to J of the energy rotation about the stable axis becomes discontinuous at the point J_c. Figure 2 shows a family of classical trajectories near the north pole of the phase sphere on the left and right of the point J_c. The energy $E_z(J)$ at the saddle point of the surface (11) corresponds to the separatrix S between the trajectories of the local precession and the global trajectories. The localization of the separatrix for values of J close to J_c is an attribute of the local critical phenomenon that takes place in a bounded volume of phase space.

For a quantum description of the investigated critical phenomenon we consider, for simplicity, the effective rotational Hamiltonian (5) for the local group C_{2v}. Corresponding to that part of phase space in which the local trajectories of Fig. 2 are located are the RM quantum states satisfying the condition $\langle Jv|J^2 - J_z^2|Jv\rangle/J^2 \ll 1$, which we shall call hereafter the lower RM states. These states can be described by using an approximate Hamiltonian obtained from (5) by expanding the functions g_m $(m = 0,2,4)$ in powers of the small quantity $(J_z^2 - J^2)/J^2$. This Hamiltonian, which has all the symmetry properties of the initial one, is of the form

$$\begin{aligned}H_{C_{2v}}=&E_z(J)+[\alpha(J-J_c)-2b_1]\frac{J_z^2-J^2}{J^2}+a_2\left(\frac{J_z^2-J^2}{J^2}\right)^2\\&+b_1\frac{J_+^2+J_-^2}{J^2}+\frac{b_2}{2J^4}([J_z^2-J^2,J_+^2]_++[J_z^2-J^2,J_-^2]_+)\\&+c_1\frac{J_+^4+J_-^4}{J^4},\end{aligned} \tag{12}$$

where the regular part $E_z(J) = g_0(\mathbf{J}^2,J^2)$ is the energy of the classical rotation of the system about the z axis, and the constants α, a_2, b_1, b_2, and c_1 depend on the internal structure of the system.

To clarify the character of the change of the rotation dynamics of the system on going through the critical point, we obtain first the solutions of the Hamiltonian (12) in the harmonic approximation (see the Appendix). At $J<J_c$ the lower states correspond to precession of the vector **J** about the z axis. Their energies are given, according to (A4), by the expression

$$E_{JM}=E_z(J)+[2b_1-\alpha(J-J_c)]\frac{2J-1}{2J^2}-\frac{a_2}{2}\left(\frac{2J-1}{J^2}\right)^2+\omega_z\left(J-|M|+\frac{1}{2}\right), \tag{13}$$

where the precession frequency is approximately

$$\omega_z\approx4[b_1\alpha(J_c-J)]^{1/2}/J. \tag{14}$$

The states are doubly degenerate[6)] relative to the sign of the projection M.

At $J>J_c$ the frequency (14) becomes imaginary, meaning instability of the precession about the z axis. A new axis appears, or more accurately, two equivalent precession axes **k** and **k**′. We consider first the precession of the vector **J** about the first axis. We rotate the BCF with the aid of the operator $R(\pi/2,\theta_0,-\pi/2)$ (Ref. 18) in such a way that the **k** axis coincides with the z axis, and change in the transformed Hamiltonian $RH_{C_{2v}}R^{-1}$ to the harmonic approximation. Since rotation of the BCF is equivalent in this approximation to a shift of the origin, to describe the precession about the **k** axis we must set the coefficients of the operators b and b^+ equal to zero in the resultant Hamiltonian. This requirement allows us to determine the angle θ_0. The energy of the lower RM levels for $J>J_c$ is specified by the quantum number K of the projection of the angular momentum on the precession axis **k**:

$$E_{JK}=E_{\mathbf{k}}(J)+\omega_{\mathbf{k}}(J-|K|+{}^1/_2),\quad K=\pm J,\ \pm(J-1),\ldots, \tag{15}$$

where $E_{\mathbf{k}}(J)$ becomes in the classical approximation the energy of the rotation about the **k** axis. The precession frequency if given for small θ_0 by

$$\omega_{\mathbf{k}}\approx4[2b_1\alpha(J-J_c)]^{1/2}/J. \tag{16}$$

The wave function of the lower RM level with $K=J$ is obtained from expression (A6) with the aid of the rotation R:

$$\varphi_{J,J}(\mathrm{k},q)=\left[\frac{2b_1}{\pi\alpha(J-J_c)}\right]^{1/2}\times\exp\left\{-\left[\frac{b_1}{2\alpha(J-J_c)}\right]^{1/2}(q-\theta_0J^{1/2})^2\right\}. \tag{17}$$

The function $\varphi_{J,J}(\mathbf{k}',q)$, which describes the precession about the **k**′ axis differs from the function (17) in the sign of the angle θ_0. The functions $\varphi(\mathbf{k})$ and $\varphi(\mathbf{k}')$ which correspond to one and the same energy (15) determine the states of the Hamiltonian $H_{C_{2v}}$ with broken symmetry C_2. The operator of this symmetry element transforms $\varphi(\mathbf{k})$ into $\varphi(\mathbf{k}')$ and vice versa. We emphasize that the symmetry breaking is the result of using the harmonic approximation. The latter can be improved by using the symmetrized combinations $\varphi(\mathbf{k})\pm\varphi(\mathbf{k}')$, which are eigenfunctions of the transformation operator C_2. By averaging the Hamiltonian $H_{C_{2v}}$ over these functions we can determine the energy $\Delta E\sim\exp\{-\delta(J-J_c)\}$, where $\delta\sim1$, of the opposite-parity level splitting. The harmonic approximation helps prove the universality of the Hamiltonian $H_{C_{2v}}$ for the description of the lower RM states in the vicinity of the critical point J_c. We add to $H_{C_{2v}}$ the succeeding terms of the expansion of the initial Hamiltonian (5), which contain the operators J_α^6, J_α^8, etc. The added terms strengthen the precession anharmonicity that manifests itself noticeably in the higher RM states. It is easily shown, however, that they do not play a significant role in the harmonic approximation, which is valid for the lower RM states.

To track the restructuring of the lower RM levels, we must find an exact solution of the Hamiltonian $H_{C_{2v}}$ for a number of values of the quantum number J near J_c. It is natural to diagonalize $H_{C_{2v}}$ in the basis of the eigenfunction $|JM\rangle$ of the operator J_z. The $H_{C_{2v}}$ states are conveniently classifed in accordance with the irreducible representations (IR) A_1, A_2, B_1, and B_2 of the C_{2v} group (Ref. 19). The form of the representations is determined by the sequence of the quantum numbers M in the expansion of the $H_{C_{2v}}$ eigenfunctions in terms of the functions $|JM\rangle$. The results of the numerical diagonalization for a certain particular set of parameters is shown in Fig. 3, where the energies of the lower RM levels, reckoned from the regular part $E_z(J)$, are plotted against the quantum number J. At $J<J_c$ these levels form a system of doublets A_1+A_2 for the even and B_1+B_2 for the even sequence of the values of M. The splitting of the doublets is of the inversion type and is too small to show in the figure. As J approaches J_c the doublets A_1+A_2 and B_1+B_2 begin to approach each other and form at $J>J_c$ a quadruple cluster $A_1+A_2+B_1+B_2$, corresponding to delocalized precession about two equivalent axes. The same figure shows for comparison the results of harmonic-approximation calculation with Eqs. (13) and (15).

3. An investigation of the rotational-energy surface for the symmetry groups C_3 and C_{3v} shows that there exists only one nonlocal critical phenomenon, consisting of a change in the type of stability of the rotation axis.[20] On going through the critical point J_c, the stable rotation axis z with the maximal (minimal) moment of inertia becomes the axis with the minimal (maximal) moment of inertia.[7)]

To solve the quantum problem we use, as before, an expansion of the Hamiltonian (5)

$$H_{C_{3v}}=E_z(J)+\alpha(J-J_c)\frac{J_z^{\,2}-J^2}{J^2}+\frac{b}{J^4}\{[J_+^{\,3},J_z]_++[J_-^{\,3},J_z]_+\}. \tag{18}$$

Nonlocality of a critical phenomenon means that in the transition region it is necessary to take into account, generally speaking all the terms of the expansion (18), including the discarded ones. If, however, the parameter α is large enough in absolute value, the discrete character of J permits the region of substantial nonlocality to be excluded, and the first terms of the expansion (18) can be used. In the harmonic approximation it suffices to take into account only the first two terms in the Hamiltonian $H_{C_{2v}}$. The precession energy is

$$E_{JM}=E_z(J)-(2\alpha/J)(J-J_c)(J-|M|),\qquad M=\pm J,\ \pm(J-1),\ldots, \tag{19}$$

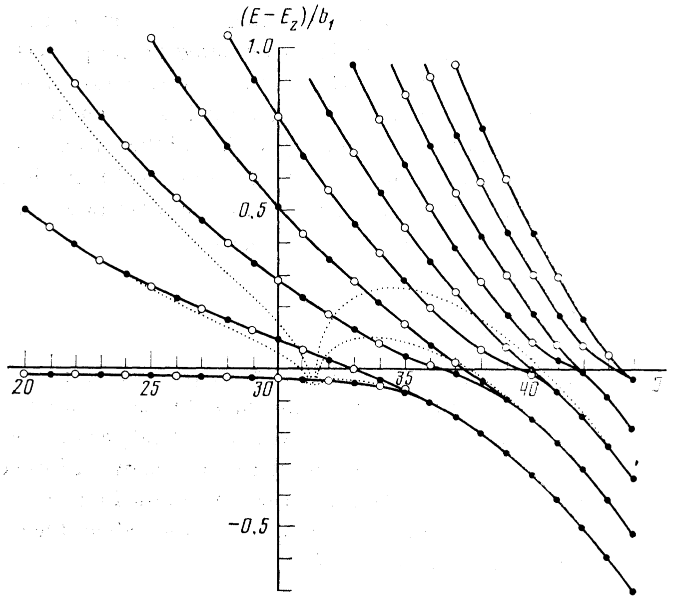

FIG. 3. Lower levels of rotational multiplet in the transition region for the local critical phenomenon C_2. Parameters of Hamiltonian $H_{C_{2v}}$: $J_c = 30$, $\alpha/b_1 = 0.3$, $b_2/b_1 = 1.0$, $a_2/b_1 = 7.0$, $c_1/b_1 = 0.5$; ○ doublets $A_1 + A_2$. ●—doublets $B_1 + B_2$, dashed curves—harmonic approximation.

and the wave function $|JM\rangle$ coincides with an eigenfunction of the operator J_z. These very same functions are used as the basis for obtaining the exact solution of the Hamiltonian (18) with allowance for the third term of the expansion. Its states are classified in accordance with the IR A_1, A_2, and E of the C_3 group (Ref. 19). Figure 4 shows a plot of the energy $E_{Jv} - E_z$ for the lower RM levels, referred to the precession frequency. On the left and right of the critical point these levels form a system of doublets $A_1 + A_2$ for the values $M = 3n$, and a system of doubly degenerate levels of type E for $M = 3n + 1$, $3n + 2$. It can be seen from the figure that the critical phenomenon manifests itself in a decrease of the number of equidistant levels corresponding to the precession of the vector $\mathbf{J}$ when the point J_c is approached and in a decrease of their number on moving away from this point. Passage through the critical point is accompanied by inversion of the levels relative to the abscissa axis.

4. The classical picture of a critical phenomenon for the symmetry groups C_4 and C_{4v} depends on the relations between the coefficients in the expression for the classical energy (see the Conclusion). If $|a| < 2b$, the critical phenomenon is nonlocal and reduces, in analogy with the phenomenon for the symmetry group C_{3v} to a change of the type of stability of the rotation axis. The critical phenomenon becomes more complicated when $|a| > 2b$. In this case, besides the stable rotation axis z, there appear or vanish four stable equivalent axes that are close to it in direction and turned through angles 90° relative to one another. The pattern of the phase trajectories is typical of a local critical phenomenon. It is characterized by violation of the invariance of the classical rotation relative to the symmetry element C_4 and by discontinuity of the second derivative, with respect to J, of the rotation energy at this point J_c.[20]

The locality of the considered critical phenomenon makes it possible to obtain from H_{eff} (5) an approximate universal Hamiltonian for the description of the lower RM levels:

$$H_{C_{4v}} = E_z(J) + \alpha(J - J_c)\frac{J_z^2 - J^2}{J^2} + a\left(\frac{J_z^2 - J^2}{J^2}\right)^2 + b\frac{J_+^4 + J_-^4}{J^4}. \tag{20}$$

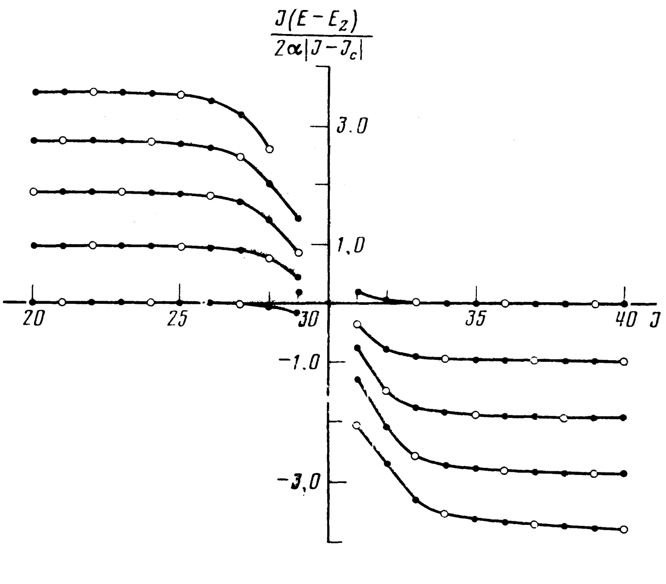

FIG. 4. Lower levels of rotational multiplet in the region of the transition for the critical phenomenon C_{3v} ($J_c = 30$, $\alpha/b = 0.8$); ○—doublets $A_1 + A_2$, ●—doubly degenerate levels of type E.

We consider first the change of the precession on going through the critical point J_c in the case $a > 2b > 0$ and $\alpha > 0$. The z axis is a stable axis of rotation on the left and right of J_c. The energy of the levels corresponding to precession about this axis is determined by the expression

$$E_{JM}=E_z(J)+\frac{2J-1}{J^2}\left\{\alpha(J_c-J)+a\frac{2J-1}{J^2}\right\}(J-|M|). \quad (21)$$

On going through the critical point, the precession about the z axis with maximum moment of inertia is transformed into precession with minimum moment of inertia. Four equivalent precession axes $\mathbf{k}_i$ appear if $J>J_c$. The energy of the levels corresponding to precession about any of these axes is equal to

$$E_{JK}=E_{\mathbf{k}}(J)+\omega(J-|K|+{}^1/_2), \quad K=\pm J,\ \pm(J-1),\ldots, \quad (22)$$

where $E_{\mathbf{k}}(J)$ is the energy of rotation about the $\mathbf{k}_i$ axis, K is the quantum number of the component of the angular momentum along this axis, and the precession frequency is

$$\omega=(8\alpha/J)(J-J_c)[b/(a-2b)]^{1/2}, \quad J>J_c. \quad (23)$$

The change of the precession is manifested by a regrouping of the lower RM levels, which can be tracked by using the exact solutions of the Hamiltonian $H_{C_{2v}}$. We shall classify its states in accordance with the IR A_1, A_2, B_1, B_2, E of the C_{4v} group.[19] Figure 5 shows the dependence of the RM lower-level energy, referred to the frequency of the precession about the z axis from (21). At $J<J_c$ the lower part of the RM is a system of approximately equidistant levels consisting of the doublets A_1+A_2 ($M=4n$), B_1+B_2 ($M=4n+2$) and of doubly degenerate levels of type $E(M=4n+1, 4n+3)$. With increase of J, these levels either come closer together to form an eightfold cluster $A_1+A_2+B_1+B_2+2E$ (delocalized precession about four equivalent axes), or is regrouped into the initial structure (precession about the z axis).

5. Local symmetries containing axes of order higher than fourth are either rarely encountered or are possessed only by heavy molecules whose rotational structure cannot be resolved spectroscopically. Analysis has shown that for the symmetry groups C_n and C_{nv} with $n\geqslant 5$ there exists only one type of critical phenomenon, the same as for the local symmetry C_{4v}, if $|a|>2b$ (Ref. 20). In this case, however, n rather than four equivalent axes appear.

4. CONCLUSION

Let us list all the considered critical phenomena in purely rotational excitations. It is convenient to use for the classification the classical picture, in which a critical phenomenon is characterized by a local-symmetry group $\mathfrak{g}$, by the form of the energy surface $E(\theta,\varphi)$ near the z axis of the BCF, and by the singularity of the energy $E(J)$ of rotation about the stable axis at the critical point J_c.

Local symmetry group C_1

Energy surface

$$E(\xi,\eta)=E_z(J)-\alpha(J-J_c)\xi+a_{02}\eta^2+a_{30}\xi^3.$$

Nonlocal critical phenomenon with singularity $E''(J)\propto\pm|J-J_c|^{-1/2}$.

Local symmetry groups C_s, C_2, C_{2v}

Energy surface

$$E(\xi,\eta)=E_z(J)-\alpha(J-J_c)\eta^2+a_{20}\xi^2+a_{04}\eta^4.$$

Critical phenomena of two types exist: 1) If $a_{20}a_{04}<0$, the critical phenomenon is nonlocal and alters the character of the stability of the stationary rotation axis, 2) if $a_{20}a_{04}>0$, the critical phenomenon is local and is characterized by a singularity $\Delta E''(J_c)=-\alpha^2/2a_{04}$.

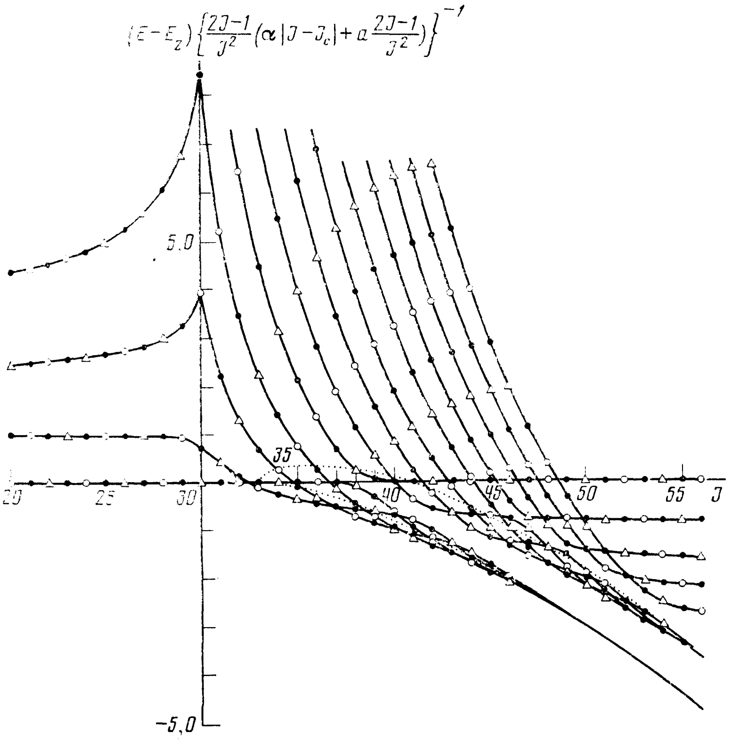

FIG. 5. Lower levels of rotational multiplet in the transition region for the local critical phenomenon C_{4v}. Parameters of Hamiltonian $H_{C_{4v}}$: $J_c=30$, $\alpha/b=0.18$, $a/b=8.0$; ○—doublets A_1+A_2, ●—doubly degenerate levels of type E, △—doublets B_1+B_2, dashed curves—harmonic approximation (22).

Local symmetry groups C_3 and C_{3v}

Energy surface

$$E(\theta, \varphi)=E_z(J)-\alpha(J-J_c)\theta^2+2b\theta^3 \cos 3\varphi.$$

The critical phenomenon is nonlocal and consists of a change of the type of stability of the rotation axis.

Local symmetry groups C_4 and C_{4v}

Energy surface

$$E(\theta, \varphi)=E_z(J)-\alpha(J-J_c)\theta^2+(a+2b \cos 4\varphi)\theta^4, \quad b>0.$$

Critical phenomena of two types exist: 1) if $|a| < 2b$ the critical phenomenon is nonlocal and is similar to that for groups C_3 and C_{3v}; 2) if $|a| > 2b$, the local critical phenomenon is characterized by a singularity $\Delta E''(J_c) = -\alpha^2/2(a-2b)$.

Local symmetry C_n, C_{nv}, $n \geqslant 5$

Energy surface

$$E(\theta, \varphi)=E_z(J)-\alpha(J-J_c)\theta^2+a\theta^4+2b\theta^n \cos n\varphi.$$

Local critical phenomenon of type 2) for groups C_4 and C_{4v} with singularity $\Delta E''(J_c) = -\alpha^2/2b$.

All the foregoing critical phenomena can be called elementary in the sense that they involve the vanishing, at the point J of one of the coefficients of the local rotational Hamiltonian. More complicated cases are possible, when several coefficients or a rather large number of them vanish. In the latter case a trough is produced on the energy surface, and the critical phenomenon, which leads to rotation of the vector **J** through a finite angle relative to the BCF, is an analog of a first-order phase transition.[5]

Two of the five essentially different types of elementary critical phenomena are local. In the classical limit local critical phenomena are characterized by degeneracy (equivalent rotation axes), breaking of symmetry relative to a local group $\mathfrak{g}$, and a discontinuity of the second derivative of the rotation energy at the point J_c with respect to J. In this sense, local critical phenomena are similar to second-order phase transitions. For quantum systems such as molecular and atomic nuclei, the classical picture is not more than an illustration. Local critical phenomena are revealed in rotational spectra by the change of the RM structure, viz., by the appearance of clusters of levels corresponding to delocalized precession of the vector **J** about the equivalent axes. With increase of $(J-J_c)$ the splitting of the levels that enter in the cluster decreases exponentially, but the precession is not localized on one axis, and the states in the cluster have a definite symmetry relative to the group $\mathfrak{g}$. Thus, no spontaneous symmetry breaking takes place in the critical phenomena[21,22]—the Hamiltonian and its solutions remain invariant to the symmetry group $\mathfrak{g}$. This is the fundamental difference between critical phenomena and phase transitions in macroscopic bodies.

At sufficiently large J, a perturbation that is arbitrarily small relative to $\mathfrak{g}$ takes the system out of a symmetric delocalized state into an asymmetric localized one that corresponds to the classical solution. This state is nonstationary, but its lifetime can be long enough (in view of the low penetrability of the barrier between the regions of the precessions about the equivalent axes) to be able to state that it really exists.

The common features of local critical phenomena and second-order phase transitions manifest themselves in the universality of the collective motion near the critical point. Universality in the case of phase transitions means that the details of the Hamiltonian of the macroscopic systems are of no importance in the scale of the long-wave fluctuations that determine the phase transition. Universality of a local critical phenomenon means that it takes place in a bounded region of the phase space of the collective motion. Therefore the form of the collective Hamiltonian in the vicinity of the critical point is independent, accurate to constant coefficients, of the internal structure of the system.

For rotational spectra of molecules and atomic nuclei, the universality property is of practical significance. It makes it possible to replace, in the description of the rotational bands, the expansion near $J=0$, which is patently unsuitable at large J, by an expansion near J_c. This possibility has therefore not been considered in either nuclear or molecular spectroscopy.

APPENDIX

Harmonic approximation for quantum precession

It is convenient to investigate the structure of a rotational multiplet by using the boson representation, proposed by Marshalek,[23] of the angular momentum of a quantum top. We shall be interested in angular-momentum operators in the BCF

$$J_z=J-b^+b, \quad J_+=J_-{}^+=b^+(2J-b^+b)^{1/2}, \tag{A1}$$

which act in the space of the wave functions

$$\varphi_{J,\nu}=\sum_{M=-J}^{J} a_M^{(\nu)} \frac{(b^+)^{J-M}}{[(J-M)!]^{1/2}} |0\rangle, \tag{A2}$$

corresponding to the states of an isolated RM; $|0\rangle$ is the vacuum state for the boson operators b^+ and b.

Consider precession about the z axis. Using Eqs. (A1) and one of the methods described in Ref. 24, we expand the Hamiltonian H_{eff} (5) in terms of the boson operators b^+ and b and confine ourselves to the quadratic terms:

$$H=E_z(J)+Sb^+b+(P+iQ)b^+b^++(P-iQ)bb. \tag{A3}$$

The coefficients E_z, P, Q, and S depend on the parameters of the Hamiltonian (5) and on the quantum number J. The Hamiltonian (A3) is diagonalized with the aid of a linear canonical transformation of the operators b^+ and b:

$$E_{JM}=E_z(J)-\frac{1}{2}S+\frac{S}{|S|}[S^2-4P^2-4Q^2]^{1/2}\left(J-|M|+\frac{1}{2}\right), \quad M=\pm J, \quad \pm(J-1), \ldots \tag{A4}$$

The result of the diagonalization shows that the states corresponding to precession of the vector **J** about the z axis can be classified with the aid of the projection M of the angular momentum on this axis. The condition $S^2>4(P^2+Q^2)$ is necessary for the state with $M=\pm J$ be a stable-equilibrium state. The value of J_c at which $S^2=4(P^2+Q^2)$, is a point of transition to other states corresponding to precession of the vector **J** about another axis (if it exists). The harmonic approximation is quite suitable if the condition $J-J_c| \gg J_c^{-2/3}$ is met.[10]

In the case of equivalent precession axes it is convenient to deal with a wave function in the coordinate representation. We introduce for this purpose a dimensionless coordinate $q(|q|<\infty)$ defined by the relations

$$b^{+}=2^{-1/2}(q-d/dq), \quad b=2^{-1/2}(q+d/dq). \tag{A5}$$

We substitute (A5) in the equation $\hat{H}\varphi_{JM}=E\varphi_{JM}$ and rewrite the resultant differential equation with the aid of the substitution

$$\varphi_{JM}(q)=\psi(q)\exp\{-iq^2Q/(S-2P)\} \tag{A6}$$

in the form

$$-\frac{1}{2}(S-2P)\frac{d^2\psi}{dq^2}+\frac{S^2-4P^2-4Q^2}{2(S-2P)}q^2\psi=\left(E-E_z+\frac{S}{2}\right)\psi. \tag{A7}$$

For Eq. (A7) to describe precession, i.e., small oscillations near the equilibrium position $q=0$, it is necessary that the quantities $S+2P$ and $S-2P$ be of the same sign, and $S^2-4P^2-4Q^2>0$. The wave function of the state with $|M|=J$ takes in the coordinate representation the form

$$\varphi_{J,\pm J}(q)=\left(\frac{f}{\pi}\right)^{1/4}\exp\left\{-\frac{1}{2}(f+ig)q^2\right\}, \tag{A8}$$

where

$$f=\frac{(S^2-4P^2-Q^2)^{1/2}}{S-2P}, \quad g=\frac{Q}{S-2P}.$$

---

[1] We define a rotational multiplet as an aggregate of rotational states with fixed value of the quantum number J.

[2] This requirement is met by the ground-state band of even-even deformed nuclei. Isolated rotational bands are quite frequently encountered in molecular spectra, both for asymmetric and high-symmetry molecules of the spherical-top type.

[3] The mirror-rotation axis S_n for a Hamiltonian invariant to the inversion transformation is identical with the C_{nh} axis for even n and C_{2nh} for odd n.

[4] It is called the Bloch sphere in quantum optics.

[5] More accurately, degenerate critical point according to the terminology of catastrophe theory.

[6] The degeneracy is a consequence of the symmetry of the Hamiltonian (12) with respect to inversion. In real molecular spectra this symmetry leads to the existence of level doublets having symmetries A and B_1 or B_2 and B_3 relative to the group D_2. In rotational spectra of nuclei and molecules that have nuclei with zero spin, only a fully symmetric state A exists in place of a doublet. The doublet splitting in local critical phenomena is small compared with level-restructuring effects, and we neglect them.

[7] The reference here is to the local characteristic of the moment of inertia for rotation about the z axis.

[1] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw, 1955. J. K. G. Watson, Mol. Phys. **15**, 479 (1968).

[2] M. A. J. Mariscotti and G. Scharf-Goldhaber, Phys. Rev. **178**, 1864 (1969); G. Scharf-Goldhaber, Nucl. Phys. A**347**, 31 (1980).

[3] J. K. G. Watson, in: Vibrational Spectra and Structure, J. R. Durig, ed., Elsevier, 1977, Vol. 6, p. 1. M. R. Aliev and J. K. G. Watson, in: Molecular Spectroscopy, Modern Research, Academic, 1985, Vol. III, p. 1.

[4] J. M. Flaud, C. Camy-Peyret, and J. W. C. Johns, Canad. J. Phys. **61**, 1462 (1983).

[5] I. M. Pavlichenkov, Zh. Eksp. Teor. Fiz. **82**, 9 (1982) [Sov. Phys. JETP **55**, 5 (1985)].

[6] I. M. Pavlichenkov and B. I. Zhilinskii, Chem. Phys. **100**, 339 (1985).

[7] H. Lipkin, N. Meshkov, and A. J. Glick, Nucl. Phys. **62**, 188 (1985).

[8] D. Agassi, H. J. Lipkin, and N. Meshkov, *ibid.* **86**, 321 (1966).

[9] R. Gilmore and D. H. Feng, *ibid.* **A301**, 189 (1978). R. Gilmore and D. H. Feng, Proc. Int. Meeting on Frontiers of Physics, N.Y. 1980, p. 1231.

[10] S. T. Belyaev and I. M. Pavlichenkov, Nucl. Phys. **A388**, 505 (1982).

[11] D. H. Feng, R. Gilmore, and S. R. Deans, Phys. Rev. **C23**, 1254 (1981). R. Gilmore and D. H. Feng, in: Contemp. Res. Topics in Nucl. Phys. N.Y., 1982, p. 401.

[12] S. T. Belyaev and V. G. Zelevinskiĭ, Yad. Fiz. **17**, 525 (1973) [Sov. J. Nucl. Phys. **17**, 269 (1973)].

[13] Yu. S. Makushkin and V. G. Tyuterev, Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy [in Russian], Nauka, Novosibirsk, 1984.

[14] H. A. Buckmaster, R. Chatterjee, and Y. H. Shing, Phys. Stat. Sol. **a13**, 9 (1972).

[15] W. G. Harter, C. W. Patterson, and F. J. daPaizao, Rev. Mod. Phys. **50**, 37 (1978). W. G. Harter and C. W. Patterson, J. Chem. Phys. **80**, 4241 (1984).

[16] S. D. Augustin and W. H. Miller, *ibid.* **61**, 3155 (1974).

[17] R. Gilmore, *Catastrophe Theory for Scientists and Engineers*, Wiley 1981.

[18] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton U. Press, 1957.

[19] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Nonrelativistic Theory*, Pergamon, 1978.

[20] B. I. Zhilinskiĭ and I. M. Pavlichenkov, Dokl. Akad. Nauk SSSR, **288**, 355 (1986) [Sov. Phys. Dokl. **31**, 423 (1986)].

[21] N. N. Bogolyubov, Collected Papers [in Russian], Nauk. dumka, Kiev, 1971, Vol. 3, p. 174.

[22] A. A. Grib, E. V. Damaskinskiĭ, and V. M. Maksimov, Usp. Fiz. Nauk **102**, 587 (1970) [Sov. Phys. Usp. **13**, 798 (1971)].

[23] E. R. Marshalek, Phys. Rev. **C11**, 1426 (1975).

[24] S. G. Pang, A. Klein, and R. M. Dreizler, Ann. Phys. (N.Y.) **49**, 477 (1968).

Translated by J. G. Adashko