

Critical Phenomena in Rotational Spectra

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Nonlinear effects in rotational spectra of molecules and atomic nuclei caused by a centrifugal distortion for high values of an angular momentum quantum number J are investigated. The theoretical analysis is based on a new expansion form of the effective rotational Hamiltonian. It is shown that qualitative changes of rotational motion may occur in the rotational spectra for some value J_c of the quantum number J . These phenomena which are in some sense analogous to the macroscopic phase transitions are called critical phenomena and correspond to bifurcations in classical mechanics. The classification of critical phenomena for a purely rotational motion is given. This classification is based on the concept of a local symmetry group \mathcal{G} . There exist five types of critical phenomena in the rotational spectra. The local critical phenomena occurring in a bounded region of the rotational motion phase space are specially discussed. In the classical limit the local critical phenomena are characterized by a broken symmetry \mathcal{G} and *discontinuity of the second derivative of the rotational energy with respect to J at J_c* . A universal rotational Hamiltonian is shown to exist in the neighborhood of J_c , which does not depend on the dynamical systems internal structure up to numerical values of its parameters. A phenomenological theory of the local critical phenomena is developed with the aid of universal Hamiltonians. The difference between the local critical phenomena and second-order phase transitions in macroscopic systems is shown. © 1988 Academic Press, Inc.

1. INTRODUCTION

Quantum rotation is a specific type of excitation of microscopic systems: molecules, atomic nuclei, and even hadrons, the spectra of which show regular sequences of the rotational type states (Regge trajectories). The rotational spectra of molecules and nuclei are studied in more detail. The energy levels of these systems are grouped in rotational bands having a regular sequence of energy levels characterized by the energy and quantum number J of the total angular momentum. Thus, the rotational states may be extracted rather easily from the complex excitation spectra of these many-particle systems. The rotational states are rather pure, i.e., they contain an almost negligible admixture of excitations of some other

origin, even for high J values achieved experimentally by using modern molecular and nuclear spectroscopy methods. From the point of view of the dynamical behaviour of the finite many-particle system, deviations from the above-mentioned regularity rather than the regularity itself are of primary interest. These deviations may be caused by the interaction of the rotation with other degrees of freedom. A centrifugal distortion is the simplest effect of such interactions which becomes essential for high J values. It is the centrifugal distortion effect that we consider in the present paper.

Electronic excitations are much higher than vibrational ones for most so-called "normal" molecules. Therefore they may be described adequately in the Born-Oppenheimer approximation. For a nondegenerate ground electronic state it is sufficient to consider the following rovibrational Hamiltonian [1],

$$H = \frac{1}{2} \sum_{\alpha, \beta} \left\{ (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) - \frac{1}{4} \delta_{\alpha\beta} \mu_{\alpha\alpha} \right\} + \frac{1}{2} \sum_{k=1}^{3n-6} p_k^2 + U(q_1, \dots, q_{3n-6}), \quad (1.1)$$

where J_α ($\alpha = x, y, z$) are the projections of the total angular momentum operator on the body-fixed frame axes; π_α are the vibrational angular momentum operators; and $\mu_{\alpha\beta}$ stands for the matrix elements of the inverse inertia tensor, which depend on the normal coordinates q_i of n -atomic molecules and on the conjugated momenta p_i . U is the molecular potential energy for the ground electronic state. The vibration-rotation interaction is reduced to the centrifugal distortion effects being due to the $\mu_{\alpha\beta}$ dependence on q_i and the Coriolis interaction due to π_α .

There is no analog of the Born-Oppenheimer approximation for atomic nuclei. Nevertheless, the formation of the bands with strong (of the order of 100 single particles) E-2 transitions between neighbouring states shows the existence of collective motion. All nuclei participate cooperatively into this collective motion with internal degrees of freedom being frozen completely or partly. During the last 10 years the application of new methods of rotational excitation based on heavy-ion reactions enabled one to demonstrate new types of rotational bands corresponding to different nuclear shapes: oblate, triaxial, superdeformed prolate. Light nuclei were shown to possess rotational bands based on cluster or quasimolecular states.

The type of deformation defines the character of rotation. So, it is very important to find the mechanism of the shape changes under an increase in momentum J . For example, the deformation of the axially deformed nucleus in the yrast band begins to change noticeably when the centrifugal energy in a rotating nucleus becomes comparable to the shell energy. It takes place typically at $J \approx 30$. The deformation changes so that the rotational energy of the nucleus is the minimum. The highest moment of inertia corresponds to the rotation of an oblate nucleus around its symmetry axis. Therefore, the nucleus tends to go over from the prolate into the oblate state with increasing J in the yrast band but the shell effects hinder it. As a result,

starting from $J \approx 40$, the nucleus becomes nonaxial and the yrast band corresponds to the rotation of the nucleus about the axis with the highest moment of inertia.

Thus, the centrifugal effects are common for both molecules and atomic nuclei. The centrifugal distortion is responsible for the structure of rotational excitations in these systems at sufficiently high angular momenta. Usually, the centrifugal distortion effects are treated phenomenologically: the model of a variable inertia moment is used in nuclear physics [2] and the so-called reduced effective rotational Hamiltonians are used in molecular problems [3]. These Hamiltonians are power series of J_x operators with a minimal number of phenomenological parameters which are necessary for the description of all rotational states with angular momentum quantum numbers varying from 0 to a given J value. Both methods enable one to obtain a rather good description of a great number of rotational levels. For example, the rotational band of the ground vibrational state of the H_2S molecule requires 29 adjustable parameters to reproduce 426 experimentally observed transitions with $J \leq 22$ [4]. It should be noted that for $J \approx 20$ the subsequent terms of the Hamiltonian are no smaller than the preceding ones. The convergence of the power expansion is worse for an H_2O molecule and the corresponding reduced Hamiltonian includes terms with higher powers of J_x . Such a situation is typical of the rotational structure of the ground vibrational states of a lot of molecules, since the expansion near $J=0$ cannot adequately describe rotational states with high J for which the nonlinear features of the rotational dynamics are essential.

The nonlinear behaviour at high J values results in qualitatively new effects which have not attracted much attention until now. The 90° rotation of the angular momentum vector \mathbf{J} relative to the body-fixed frame under the excitation of the yrast rotational band in nonaxially deformed nuclei was studied in Ref. [5]. This phenomenon is analogous to the phase transition of the first order. In [6] the appearance of the equivalent rotation axes for an isolated band of the five-atomic slightly aspherical molecules is shown. This phenomenon is an analog of the second-order phase transition. Both effects result in an irregular variation of the energy levels in the rotational multiplet¹ near some critical value J_c . Hereinafter, such qualitative effects in the microsystems will be called critical phenomena taking into account their difference from the phase transitions in the macroscopic systems. The notion "critical phenomena" is taken from the catastrophe theory. It will be shown below that each critical phenomenon is associated with a degenerate critical point on the classical energy surface of the system considered.

Until now the critical phenomena have been studied mainly for model systems. The Lipkin–Meshkov–Glick model is the most popular [7]. Different approaches to the study of the critical phenomena in this model were proposed in works [8–10]. The phase transitions for a more complicated collective motion in the interacting boson model were investigated in [11].

The critical phenomenon is a qualitative change of the collective motion dynamics of the microscopic system, occurring at certain values of its integrals of

¹ The rotational multiplet is a set of rotational levels with the same value of quantum number J .

motion (the particle number, angular momentum, energy). It manifests itself by changes in the spectra of the collective excitations. The study of critical phenomena is a principal and as yet unresolved problem in the physics of finite many-particle systems. Three main problems arise in studying critical phenomena:

(i) This is a problem of classification, i.e., determination, of all possible types of critical phenomena for a given collective motion of the microsystem. This problem may be reduced to the study of the classical energy surface of the collective motion and can be solved in the spirit of the catastrophe theory. The bifurcation is the analog of the critical phenomenon in classic mechanics. An important point here is the introduction of a local symmetry group \mathfrak{G} , which characterizes a small region of the collective motion phase space. The classification of critical phenomena is made in accordance with the group \mathfrak{G} . All critical phenomena can be divided into two classes: local ones occurring in a finite region of the phase space and global ones which do not obey the above-mentioned restriction.

(ii) Investigations of the excitation spectra near the critical point are a problem. It is only natural to call this problem a quantum bifurcation theory which can be solved rather easily only for local critical phenomena characterized by closed collective Hamiltonians describing the lowest collective excitations of the system. These Hamiltonians must be universal, i.e., independent of the internal structure of the system up to numerical values of their parameters. The solution of this problem is, the construction of a phenomenological theory of local critical phenomena. This theory explains the variation of the spectrum of the lowest collective excitation close to the critical point. This variation is the only evidence for a critical phenomenon in the finite-particle system.

(iii) The microscopic theory of the local critical phenomena should answer the question whether critical phenomena really exist for a given type of collective motion in the system considered. If the answer is positive, it should also predict the parameters of the universal collective Hamiltonian.

The first two problems are solved in the present paper for rotation which is the simplest type of collective motion. The results obtained are general and do not depend on a concrete type of system.

2. EFFECTIVE ROTATIONAL HAMILTONIAN AND ITS SYMMETRY

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

$$H_{\text{eff}} = h_0 + \sum_{\alpha} h_{\alpha} J_{\alpha} + \sum_{\alpha, \beta} h_{\alpha\beta} J_{\alpha} J_{\beta} + \sum_{\alpha, \beta, \gamma} h_{\alpha\beta\gamma} J_{\alpha} J_{\beta} J_{\gamma} + \dots, \quad (2.1)$$

which is an infinite power series in J_{α} operators. The coefficients of the series depend on the internal structure of the system. The Hamiltonian (2.1) may be

obtained using the generalized density matrix approach which is used for the description of collective excitations of atomic nuclei [12]. For molecular systems the expression (2.1) results from the rovibrational Hamiltonian (1.1) by using contact transformations or any type of operator perturbation theory [3, 13]. The terms of the series (2.1) converge rapidly if the rotation is adiabatic with respect to other degrees of freedom of the system.

If the internal state (vibrational, single-particle, etc.) is not degenerate, the Coriolis effects are absent from the corresponding rotational band. In such a case $h_\alpha = h_{\alpha\beta\gamma} = \dots = 0$ in (2.1) and H_{eff} describes the centrifugal distortion effects. We shall study these effects for an isolated rotational band whose coupling with other rotational bands is negligible.² For this band the coefficients h , $h_{\alpha\beta}$, etc. are the c -numbers.

The effective rotational Hamiltonian for an isolated band based on a non-degenerate internal state is invariant with respect to the time reversal and inversion of the body-fixed frame. Further restrictions on the coefficients of the Hamiltonian (2.1) are due to the point symmetry groups. Both the point group operations and the inversion form a symmetry group G of the effective rotational Hamiltonian. For nuclei the symmetry group D_2 is a point group. It consists of an identity operation and three rotations through 180° about the x , y , z axes (the C_2 symmetry axes). Molecular point groups are more various. They contain such elements as symmetry planes, σ ; n -fold symmetry axes, C_n ; n -fold mirror symmetry axes, S_n ;³ and their combinations.

We write H_{eff} for an isolated rotational band based on a nondegenerate state as an expansion

$$H_{\text{eff}} = \sum_{k=0}^{\infty} \sum_{m=0}^{2k} \{ t_{k,m} T_{2k,m} + (-1)^m t_{k,m}^* T_{2k,-m} \} \quad (2.2)$$

in terms of the irreducible spherical tensor operators

$$T_{l,m} = (-1)^m T_{l,-m}^+ = (-1)^m f_{l,m}(\mathbf{J}^2, J_z) J_-^m, \quad (2.3)$$

where $\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2$, $J_\pm = J_x \pm iJ_y$ (J_- is the raising operator and J_+ is the lowering one in the body-fixed frame), and f stands for the real functions, the explicit form of which is given, for example, in [14]. The t coefficients in (2.2) can be expressed in terms of h , $h_{\alpha\beta}$, ...

It is suitable to regroup the sum in (2.2) and to write the effective Hamiltonian in the form

$$H_{\text{eff}} = \frac{1}{2} \sum_{m=0}^{\infty} \{ J_+^m g_m^*(\mathbf{J}^2, J_z) + g_m(\mathbf{J}^2, J_z) J_-^m \}, \quad (2.4)$$

² The ground rotational band of the even-even deformed nuclei meets this requirement. The isolated rotational bands are common for either asymmetric or highly symmetric molecules.

³ The axis S_n is identical to C_{nh} for even n and to C_{2nh} for odd n if the Hamiltonian is invariant with respect to the body-fixed frame inversion.

where g_m satisfies the relation

$$(-1)^m g_m(\mathbf{J}^2, -J_z) J_+^m = J_+^m g_m(\mathbf{J}^2, J_z), \quad (2.5)$$

and depends on the coefficient $t_{k,m}$ and the symmetry group G .

In addition to the quantum number J , the energy levels of the rotational multiplet are characterized by irreducible representations of G . The fine structure of energy levels belonging to one multiplet is called a cluster structure [15] and can be described clearly by using the classical precession motion representation. Let us introduce a classical stationary rotation axis. Its orientation in the body-fixed frame is defined by the equations

$$\{H_{\text{eff}}, J_\alpha\} = 0, \quad \alpha = x, y, z, \quad (2.6)$$

where H_{eff} is the classical analog of the Hamiltonian (2.2) or (2.4), and $\{\dots\}$ is the Poisson bracket. Each stable stationary axis is connected with a set of energy levels in a multiplet having, as a classical analog, a precession of the vector \mathbf{J} around this axis. An unstable stationary axis is associated with a group of levels situated in the transition region between states corresponding to the precession of the vector \mathbf{J} around different stable axes. Sometimes several equivalent stable rotation axes may exist due to the symmetry. The precession around these axes is identical up to a symmetry transformation. The precession around equivalent axes is independent in the zero approximation only. Tunneling through the barrier separating the regions of equivalent precessions yields an intracluster splitting. Thus, the structure of the rotational multiplet is completely defined by a set of stationary axes and their stability.

We shall distinguish regular and critical changes in the structure of the rotational multiplet. In the first case only the orientation of the stationary axes changes, which results in the energy level monotonic dependence on J . Critical phenomena are connected with a change of the equivalent stationary axes number or variations of their stability. At J_c there takes place a reconstruction of that part of the rotational multiplet, which corresponds to the precession around new rotation axes. The appearance or disappearance of equivalent stable rotation axes leads to the variation of the cluster structure of the rotational multiplet.

To study the irregular variations of the energy levels of rotational multiplet, we consider the Hamiltonian (2.4) near a given direction which we choose to coincide with the z axis of the body-fixed frame. Let us consider a subgroup $\mathfrak{G} \subset G$ which leaves the z axis invariant. We call \mathfrak{G} a *local symmetry group*. It specifies the form of H_{eff} (2.4) close to a chosen z -axis direction. Let the z axis lie in a symmetry plane σ which coincides, for example, with the xz plane. The reflection in this plane is equivalent to a replacement of J_\pm with $-J_\mp$ and J_z with $-J_z$. Using (2.5) one can easily prove that the Hamiltonian (2.4) is invariant under σ if $g_m^* = g_m$. The invariance of the Hamiltonian H_{eff} with respect to the C_n symmetry axis requires that the only nonzero g_m functions are those with $m = np$, where $p = 0, 1, 2, \dots$. The invariance with respect to the C_{nv} axis requires that the g_m functions satisfy both

the above-mentioned requirements. The C_{nh} symmetry axis does not yield any new features of the Hamiltonian (2.4) due to the equivalence of the C_{nh} axis to C_n (for even n) or to C_{2n} (for odd n).

The functions g_m are obviously influenced by the total symmetry of the system, i.e., by the group G . Nevertheless, it is the group \mathfrak{G} which is suitable for the description of a part of the energy levels and for the classification of the critical phenomena. The concept of the local symmetry group is closely connected with the principal difference between the proposed theory of the rotational spectra and other approaches based, mainly, on the adiabaticity of the rotation and on the power expansion of the rotational Hamiltonian in J_α . The sum (2.5) is not a power series expansion and it will be shown to be appropriate for the description of a part of the states of the rotational multiplet.

As a first step to solving the problem mentioned above, we use the Hamiltonian (2.4) to calculate the classical rotation energy E for that part of the phase space which corresponds to the rotation around a an axis of the body-fixed frame. The phase space of the rotation motion of the rigid body is formed by three Euler angles ϕ, ν, ψ and three conjugated momenta p_ϕ, p_ν, p_ψ . The absolute value of the angular momentum J and its projection $J_z = p_\phi$ on the z' axis of the laboratory fixed frame are the integrals of motion. It is suitable to perform the canonical transformation to new canonically conjugated variables J and q_J, J_z and $q_{z'}, J_z$ and q_z [16]. The phase space of the rotating body is really two-dimensional as q_J and $q_{z'}$ are cyclic variables. It can be mapped on the surface of the sphere of the J radius with the centre in the origin of the body-fixed frame (the phase sphere).⁴ The point on the sphere specified by the coordinates θ, φ defines the orientation of the vector \mathbf{J} in the body-fixed frame. The canonical transformation enables us to relate the conjugated variables J_z and q_z to the angles θ and φ . The assumption of $J_z = q_J = 0$ yields

$$\cos \theta = \frac{J_z}{J}, \quad \varphi = \frac{\pi}{2} - q_z, \quad (2.7)$$

provided that $q_{z'}$ is arbitrary. Thus, the trajectories of the top of the vector \mathbf{J} on the phase sphere are classical trajectories of the system in its rotational phase space. From (2.4) we find the rotation energy in the classical limit

$$E(\theta, \varphi) = \varepsilon_0(J, \theta) + \frac{1}{2} \sum_{m=1}^{\infty} \{ \varepsilon_m^*(J, \theta) e^{im\varphi} + \varepsilon_m(J, \theta) e^{-im\varphi} \} \sin^m \theta. \quad (2.8)$$

3. CRITICAL PHENOMENA FOR DIFFERENT LOCAL SYMMETRY GROUPS

Only quantum mechanics can yield an adequate description of critical phenomena in an isolated microsystem. However, the classical approach is

⁴ In quantum optics it is called the "Bloch sphere."

appropriate for their classification and clear physical interpretation. So, we begin discussion of each type of critical phenomenon with the study of the rotational energy surface (2.8) close to a given direction of the z axis in a body-fixed frame.

3.1. Critical Phenomenon for Local Symmetry Group C_1

Let us consider the case of $\mathfrak{G} = C_1$, i.e., the axis z being a generic one. In such a case all the g_m functions in (2.8) are other than zero. We expand the rotation energy $E(\theta, \varphi)$ in series assuming θ small. We use the Cartesian coordinates $\xi = \theta \cos \varphi$, $\eta = \theta \sin \varphi$ in the neighborhood of the north pole of the phase sphere (the axes ξ and η are directed along the x and y axes of the body-fixed frame, respectively):

$$E(\xi, \eta) = E_0(J) + a_{10}\xi + a_{01}\eta + a_{20}\xi^2 + a_{11}\xi\eta + a_{02}\eta^2 + a_{30}\xi^3 + a_{21}\xi^2\eta + a_{12}\xi\eta^2 + a_{03}\eta^3 + \dots \quad (3.1)$$

$E_0(J)$ is the energy of the rotation around the z axis. The coefficients a_{ij} depend on the value of the angular momentum J . Let the z axis be stationary for $J = J_0$, i.e., $a_{10}(J_0) = a_{01}(J_0) = 0$. In such a case we can confine ourselves to quadratic terms in ξ and η in the expansion (3.1). Under the J variation the local behaviour of $E(\xi, \eta)$ does not change qualitatively and the system still has the stationary rotation axis which can move, however, with respect to its position at $J = J_0$. This is a regular variation of the precession axis.

The critical point⁵ J_c (if it exists) is defined by both the stationary condition and the equation $a_{11}^2(J_c) - 4a_{02}(J_c)a_{20}(J_c) = 0$ (the vanishing of the Hessian). The cubic terms of the expansion (3.1) are to be taken into account in the neighbourhood of the critical point. The expression (3.1) can be transformed by a nonlinear transformation to a canonical form of a catastrophe function of a fold type [17]. It has the form

$$E(\xi, \eta) = E_0(J) - \alpha(J - J_c)\xi + a_{02}\eta^2 + a_{30}\xi^3, \quad (3.2)$$

where the coefficients a_{02} and a_{30} are present at the point J_c .

The study of the surface (3.2) shows that the critical phenomenon considered is connected with the appearance of two stationary rotation axes, stable and unstable. The energy of rotation around these axes is equal to

$$E_{1,2}(J) = E_0(J) \mp \frac{2|\alpha(J - J_c)|^{3/2}}{\sqrt{27|a_{30}|}}, \quad (3.3)$$

and the directions of these axes are close to that of the z axis. The stationary axes arise for $J > J_c$ if α and a_{30} are of the same sign and for $J < J_c$ if they are opposite in sign. In both cases the axes coincide and disappear at J_c . The stability of the stationary axis depends on the sign of a_{02} . For $a_{02} > 0$ the axis with the minimal rotation energy $E_1(J)$ is stable and for $a_{02} < 0$, that with the maximal energy $E_2(J)$

⁵ To be more exact, it is a degenerate critical point in terms of the catastrophe theory.

is stable. The singularity of the second derivative of the rotation energy with respect to J takes place at J_c : $E''_{1,2}(J) \propto \mp |J - J_c|^{-1/2}$.

Figure 1 shows the classical trajectories of the rotational motion to the left and to the right of the critical point. The trajectories in the part of the phase space where the stationary axes arise are shown. All the trajectories are global for $J < J_c$ which is due to the absence of a stationary rotation axis. For $J > J_c$ the local trajectories describe the precession of the vector \mathbf{J} around the stationary axis if their energy E satisfies $E_1 < E < E_0$. The separatrix s passes through the saddle point of the surface (3.2) with the energy $E = E_0(J)$ and separates the local trajectories from the global ones. The separatrix is a global curve and, therefore, this critical phenomenon is not local.

3.2. Critical Phenomena for Local Symmetry Groups C_s , C_2 , and C_{2v}

Let us choose the symmetry plane σ to be the plane xz of the body-fixed frame. Then the g_m functions in the classical rotation energy $E(\theta, \varphi)$ (2.8) are real. Expanding $E(\theta, \varphi)$ for small θ and retaining the terms up to the fourth order of smallness, we have

$$E(\xi, \eta) = E_0(J) + a_{10}\xi + a_{20}\xi^2 + a_{02}\eta^2 + a_{30}\xi^3 + a_{12}\xi\eta^2 + a_{40}\xi^4 + a_{22}\xi^2\eta^2 + a_{04}\eta^4. \quad (3.4)$$

Here $E_0(J)$ is the energy of rotation around the z axis. If the coefficient a_{02} is other than zero for all the J values, the stationary rotation axis (if any exists) changes its orientation in a regular manner and remains in the plane σ . The critical point can arise in this case if both the two coefficients a_{10} and a_{20} become zero. This critical phenomenon has been discussed earlier. It is connected with the appearance of two stationary rotation axes lying in the σ plane.

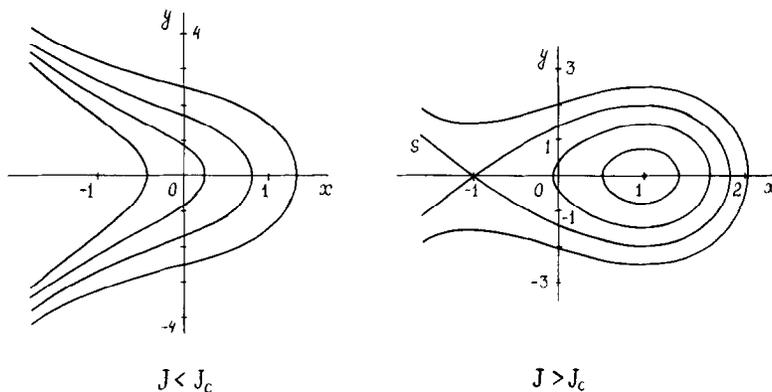


FIG. 1. The classical trajectories close to the north pole of the phase sphere for the critical phenomenon corresponding to the local symmetry group C_1 . The positive values of the coefficients a_{02} , and a_{30} in the expression (3.2) are chosen.

The critical point J_c , defined by $a_{02}(J_c) = 0$, is a new one. Let us transform the expression (3.4) for this case. We rotate the body-fixed frame to align the z axis with the stationary rotation axis. Then, using a nonlinear coordinate transformation, we reduce the expansion (3.4) in the neighbourhood of J_c to the form

$$E(\xi, \eta) = E_0(J) - \alpha(J - J_c) \eta^2 + a_{20} \xi^2 + a_{04} \eta^4, \quad (3.5)$$

where the coefficients a_{20} and a_{04} are taken at J_c . It is not difficult to show that the critical phenomena for the local symmetry groups C_2 and C_{2v} are characterized by the same energy surface (3.5).

There are two types of critical phenomena depending on the relative signs of the coefficients a_{20} and a_{04} in the expression (3.5). If a_{20} and a_{04} have opposite signs, the critical phenomenon is reduced to a change of the stability of the stationary rotation axis. The rotation axis z , stable for $J < J_c$, becomes unstable for $J > J_c$ if α and a_{20} are of the same sign. The stability changes in an inverse order if α and a_{40} are of the same sign. The appearance or disappearance of the stable rotation axis is accompanied by a simultaneous appearance or disappearance of two equivalent unstable axes lying in the yz plane symmetric to the z axis and close to it. These axes correspond to the saddle points A and A' on the surface (3.5) with the energy

$$E_1(J) = E_0(J) - \frac{\alpha^2(J - J_c)^2}{4a_{04}}. \quad (3.6)$$

The separatrix s goes through the points A and A' (see Fig. 2). Classical trajectories are shown in Fig. 2 for the system close to the critical point J_c . It follows from the figure that this critical phenomenon is not local and is not accompanied by the symmetry breaking for the classical rotation.

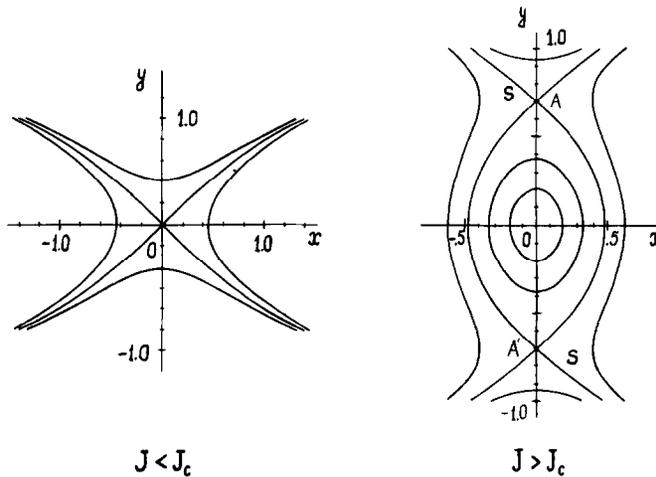


FIG. 2. The classical trajectories for the nonlocal critical phenomenon of the C_{2v} symmetry ($\alpha < 0$, $a_{20} > 0$, $a_{04} < 0$).

If the coefficients a_{20} and a_{04} have the same sign, the critical phenomenon results in the variation of the direction and number of the stationary rotation axes. Instead of the z axis, there arise two equivalent stationary rotation axes lying in the yz plane symmetric to the z axis. The energy of rotation around these equivalent axes is given by the expression (3.6). The system of classical trajectories changes as follows in passing the critical point J_c . If α , a_{20} , and a_{04} all are of the same sign, the z -axis rotation with the energy $E_0(J)$ goes over into the rotation around one of the equivalent axes with the energy $E_1(J)$ for $J > J_c$. If the sign of α is opposite to those of a_{20} and a_{04} , the transition occurs in the inverse order. In both cases the invariance of the classical solution with respect to the σ or C_2 symmetry elements is violated. Another particular feature of the considered critical phenomenon is the discontinuity of the second derivative of the maximal or minimal rotation energy with respect to J at J_c ,

$$\Delta E''(J_c) = E_1''(J_c) - E_0''(J_c) = -\alpha^2/2a_{04}. \quad (3.7)$$

The character of the critical phenomenon can be determined by considering the family of classical trajectories of the rotational motion in the phase space. Figure 3 shows these trajectories close to the north pole of the phase sphere to the left and to the right of the critical point J_c for positive values of the coefficients α , a_{20} , a_{04} . The trajectories describe the precession of the vector \mathbf{J} around the z axis with the energy $E > E_0$ for $J < J_c$. For $J > J_c$ the precession takes place around one of the two equivalent axes specified by the orientation $\mathbf{k}(\theta_0, \pi/2)$ and $\mathbf{k}'(\theta_0, 3\pi/2)$, where $\theta_0^2 = \alpha(J - J_c)/2a_{04}$, and by the energy $E_1 < E < E_0$. The energy $E_0(J)$ corresponds to the saddle point of the surface (3.5) and to the separatrix s which separates the

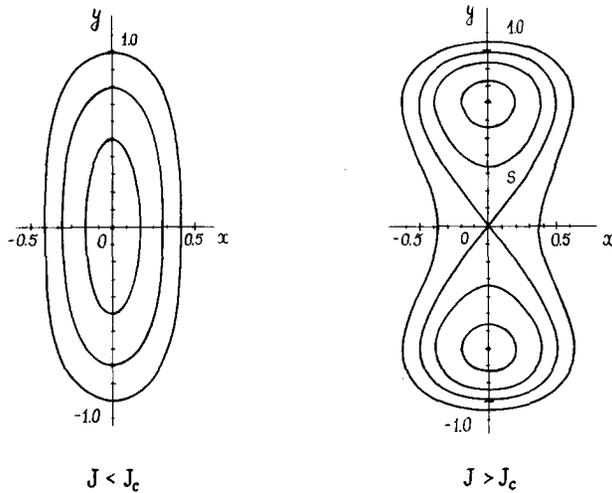


FIG. 3. The classical trajectories for the local critical phenomenon of the C_{2v} symmetry ($\alpha > 0$, $a_{20} > 0$, $a_{04} > 0$).

local trajectories of the precessional motion from the global ones. The localization of the separatrix near the critical point J_c is evidence for a *local critical phenomenon* occurring in a limited region of the phase space.

Now let us consider a quantum treatment of this local critical phenomenon. For simplicity, we use the effective rotational Hamiltonian (2.4) for the local symmetry group C_{2v} ,

$$H_{\text{eff}} = g_0(\mathbf{J}^2, J_z^2) + \frac{1}{2}J_+^2 g_2(\mathbf{J}^2, J_z) + \frac{1}{2}g_2(\mathbf{J}^2, J_z) J_-^2 + \frac{1}{2}J_+^4 g_4(\mathbf{J}^2, J_z) + \frac{1}{2}g_4(\mathbf{J}^2, J_z) J_-^4 + \dots \quad (3.8)$$

The set of classical trajectories in the phase space shown in Fig. 3 is associated with quantum states ν of the rotational multiplet which satisfy the condition

$$\langle J_\nu | J^2 - J_z^2 | J_\nu \rangle / J^2 \ll 1. \quad (3.9)$$

We shall call them *the lowest states of the rotational multiplet* although, in fact, they are the lowest only when the maximal moment of inertia corresponds to the z axis. To describe these states, one can use the approximate Hamiltonian resulting from (3.8) by expanding the g_0 , g_2 , and g_4 functions in series in terms of the small value $(J_z^2 - J^2)/J^2$. The approximate Hamiltonian possesses all the symmetry properties of the initial one and has the form

$$H_{C_{2v}} = E_0(J) + a_1(J) \frac{J_z^2 - J^2}{J^2} + a_2 \left(\frac{J_z^2 - J^2}{J^2} \right)^2 + b_1 \frac{J_+^2 + J_-^2}{J^2} + \frac{b_2}{2J^4} ([J_z^2 - J^2, J_+^2]_+ + [J_z^2 - J^2, J_-^2]_+) + c_1 \frac{J_+^4 + J_-^4}{J^4}, \quad (3.10)$$

where

$$\begin{aligned} a_1(J) &= J^2 g_0'(\mathbf{J}^2, J^2) \approx -2b_1 + \alpha(J - J_c), \\ a_2 &= \frac{1}{2}J_c^4 g_0''(\mathbf{J}_c^2, J_c^2), \\ b_1 &= \frac{1}{2}J_c^2 g_2(\mathbf{J}_c^2, J_c), \quad b_2 = \frac{1}{4}J_c^3 g_2'(\mathbf{J}_c^2, J_c), \\ c_1 &= \frac{1}{2}J_c^4 g_4(\mathbf{J}_c^2, J_c). \end{aligned} \quad (3.11)$$

Its regular part $E_0(J) = g_0(\mathbf{J}^2, J^2)$ is the energy of the classical rotation around the axis z . Appendix B shows that the terms included in (3.10) are sufficient for the description of the lowest levels of the rotational multiplet in the transition region. This means that the Hamiltonian (3.10), depending on six coefficients J_c , α , a_2 , b_1 , b_2 , c_1 , specified by the internal structure of the system, is universal for critical phenomena in the case of the C_{2v} local symmetry.

We use approximate solutions for the Hamiltonian (3.10) to study the changes in the rotational motion in passing the critical point. The boson representation of the angular momentum operators in the body-fixed frame is appropriate for this pur-

pose (see Appendix A). For $J < J_c$ the axis z is stable and the lowest levels of the Hamiltonian (3.10) correspond to the precession of the vector \mathbf{J} around this axis. These levels are accurately reproduced by the harmonic approximation in which the effective rotational Hamiltonian has the form of (A.3) with the coefficients of (B.5). In such an approximation the lowest levels of the rotational multiplet can be characterized by a quantum number M of the angular momentum projection on the z axis of the body-fixed frame. The energy of these states is given, according to (A.5), by the expression

$$E_{JM} = E_0(J) + a_1(J) \frac{2J-1}{J^2} + \omega_z \left(J - |M| + \frac{1}{2} \right), \quad M = \pm J, \pm(J-1), \dots, \quad (3.12)$$

where the precession frequency is approximately equal to

$$\omega_z \approx \frac{4}{J} \sqrt{b_1 \alpha (J - J_c)}. \quad (3.13)$$

The states are doubly degenerate with respect to the sign of the projection M .⁶ The lowest level corresponds to the state with $|M| = J$, which corresponds, in its turn, to the rotation of the system around the z axis with the energy $E_0(J)$ in the classical limit ($J \rightarrow \infty$).

The frequency (3.13) becomes imaginary for $J > J_c$. It indicates the instability of the precession around the z axis. As a result, two equivalent precession axes \mathbf{k} and \mathbf{k}' arise. Let us consider, first, the precession of the vector \mathbf{J} around the first axis. The precession axis should coincide with the z axis to use the harmonic approximation. The required transformation of the H_{C_2} Hamiltonian is given in Appendix B. In the harmonic approximation the Hamiltonian (3.10) is reduced to the form of (A.3) with coefficients given by (B.12), which can be written as

$$\begin{aligned} P &= \frac{\sqrt{2J(2J-1)}}{2J^2} \left\{ 2b_1 - \frac{4b_2}{J^2} (J-1) + \left[a_1 + 2b_1 - \frac{a_2}{J^2} (2J^2 - 3J + 2) \right. \right. \\ &\quad \left. \left. - \frac{b_2}{J^2} (6J^2 - 11J + 5) - \frac{6c_1}{J^2} (J-1)(2J-3) \right] \sin^2 \theta_0 \right\}, \\ Q &= 0, \\ S &= \frac{2J-1}{J^2} \left\{ -a_1 + \frac{a_2}{J^2} (2J-1) + \left[-a_1 - 2b_1 + \frac{a_2}{J^2} (4J^2 - 8J + 5) \right. \right. \\ &\quad \left. \left. + \frac{b_2}{J^2} (6J^2 - 11J + 5) \right] \sin^2 \theta_0 \right\}. \end{aligned} \quad (3.14)$$

⁶ The degeneracy is the consequence of the symmetry of the Hamiltonian (3.10) with respect to the inversion. In real molecular spectra this symmetry results in a doublet structure including the D_2 -symmetry levels A and B_1 for even M and the B_2 and B_3 levels for odd M . There is only one totally symmetric state A instead of the doublet in the rotational spectra of deformed nuclei and molecules consisting of nuclei with zero spins. The doublet splitting is small compared to the energy gap between levels for the local critical phenomena. We shall neglect it assuming each level of the rotational multiplet to be doubly degenerate.

According to (B.14), the angle θ_0 specifying the orientation of the precession axis \mathbf{k} is given by

$$\theta_0^2 \approx \sin^2 \theta_0 = \frac{\alpha(J - J_c)}{2(a_2 + 2b_2 + 2c_1)}. \quad (3.15)$$

The energy of the lowest energy levels of the rotational multiplet for $J > J_c$ is characterized approximately by the quantum number K of the angular momentum projection on the precession axis \mathbf{k} ,

$$E_{JK} = E_1(J) - S/2 + \omega_k(J - |K| + 1/2), \quad K = \pm J, \pm(J - 1), \dots, \quad (3.16)$$

where

$$E_1(J) = E_0(J) - \frac{1}{4J^3} (J - 1)(2J - 1)(2J - 3)(a_2 + 2b_2 + 2c_1) \sin^4 \theta_0 \quad (3.17)$$

is reduced in the classical limit to the energy (3.6) of the rotation around the \mathbf{k} axis. The precession frequency is given by

$$\omega_k \approx \frac{4}{J} \sqrt{2b_1 \alpha(J - J_c)} \quad (3.18)$$

for sufficiently small θ_0 .

The wavefunction of the lowest level of the rotational multiplet with $K = J$ for the precession around the \mathbf{k} axis can be calculated from (A.10) using the rotation (B.10). It takes the form

$$\begin{aligned} \varphi_{J,J}(\mathbf{k}, q) &= R(\pi/2, \theta_0, -\pi/2) \varphi_{J,J}(q) \\ &= \sqrt{\frac{2b_1}{\pi\alpha(J - J_c)}} \exp \left\{ -\sqrt{\frac{b_1}{2\alpha(J - J_c)}} (q - \theta_0 \sqrt{J})^2 \right\}, \end{aligned} \quad (3.19)$$

where q is the dimensionless coordinate for the oscillation motion. The wavefunction $\varphi_{J,J}(\mathbf{k}', q)$ for the precession around the axis can be calculated analogously. It differs from (3.19) in the sign of the angle θ_0 . The functions $\varphi(\mathbf{k})$ and $\varphi(\mathbf{k}')$, corresponding to the same energy (3.16), describe the states of the H_{C_2} Hamiltonian with a broken C_2 symmetry. The operator of this symmetry element transforms $\varphi(\mathbf{k})$ into $\varphi(\mathbf{k}')$ and vice versa. It should be noted that the broken symmetry is a consequence of the harmonic approximation.

C_2 invariant combinations can be constructed using $\varphi(\mathbf{k})$ and $\varphi(\mathbf{k}')$ as a basis:

$$\varphi_{J,J,\tau}(q) = \frac{1}{\sqrt{2(1 + \tau R)}} \{ \varphi_{J,J}(\mathbf{k}, q) + \tau \varphi_{J,J}(\mathbf{k}', q) \}. \quad (3.20)$$

Here $\tau = \pm 1$ are eigenvalues of the symmetry element C_2 . $R = \exp\{-J\theta_0^2 \sqrt{2b_1/\alpha(J - J_c)}\}$ is an overlap integral for $\varphi_{J,J}(\mathbf{k})$ and $\varphi_{J,J}(\mathbf{k}')$. The symmetrized

functions (3.20) enable us to estimate the splitting energy ΔE of the opposite parity energy levels. We obtain $\Delta E \propto \exp(-\delta(J - J_c))$ with $\delta \approx 1$ by averaging the $H_{C_{2v}}$ Hamiltonian over these functions. Thus, the energy splitting of the opposite parity levels in the rotational multiplet becomes exponentially small for sufficiently large $(J - J_c)$.

The harmonic approximation becomes inappropriate in the vicinity of the critical point J_c . An exact numerical solution of $H_{C_{2v}}$ (3.10) for some J values close to J_c is required to follow the rearrangement of the lowest energy levels in the rotational multiplet. It is natural to perform the diagonalization of this Hamiltonian on the basis $|J, M\rangle$ of the J_z eigenfunctions. The eigenstates of $H_{C_{2v}}$ are classified according to the irreducible representations A_1, A_2, B_1, B_2 of the group C_{2v} [18], which is a local symmetry group of this Hamiltonian. The type of representation depends on the quantum number M in the expansion of the $H_{C_{2v}}$ eigenfunctions in terms of the $|J, M\rangle$ functions. The results of the numerical diagonalization of the $H_{C_{2v}}$ Hamiltonian for some particular set of parameters are given in Fig. 4. It shows the lowest energy level dependence on the quantum number J . These levels form a sequence of the $A_1 + A_2$ doublets for even M and the $B_1 + B_2$ doublets for odd M at $J < J_c$. The inversion splitting of the doublets is not shown due to its smallness. As J approaches J_c , the doublets $A_1 + A_2$ and $B_1 + B_2$ also come closer, forming for

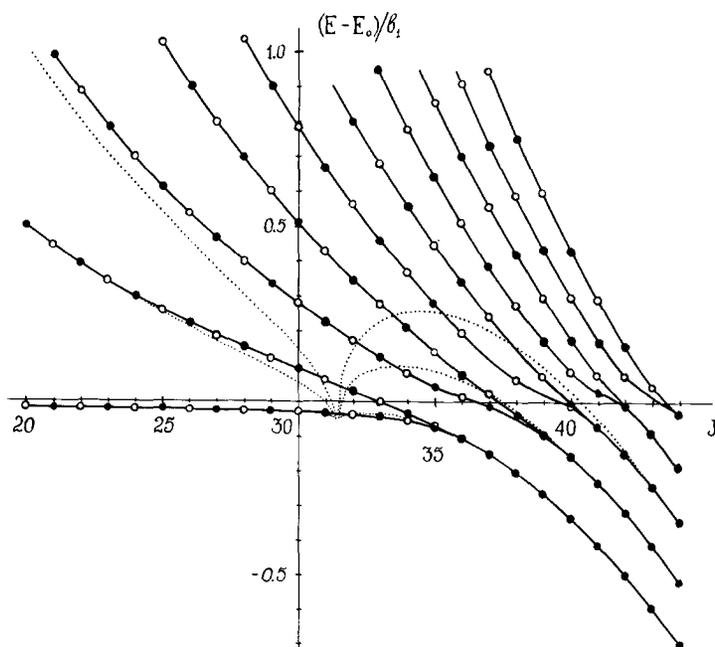


FIG. 4. The lowest levels of the rotational multiplet in the transition region for the local critical phenomenon of the C_{2v} symmetry. The parameters of the $H_{C_{2v}}$ Hamiltonian: $J_c = 30$; $\alpha/b_1 = 0.3$; $b_2/b_1 = -1.0$; $a_2/b_1 = 7.0$; $c_1/b_1 = 0.5$. (O) $A_1 + A_2$ doublets; (●) $B_1 + B_2$ doublets; (···) the harmonic approximation.

$J > J_c$ a four-fold cluster $A_1 + A_2 + B_1 + B_2$ which corresponds to a delocalized precession around two equivalent axes. The lowest energy levels calculated using (3.12) and (3.16) in the harmonic approximation are shown in the same figure for comparison.

Higher local symmetry groups C_n or C_{nv} ($n \geq 3$) are appropriate for molecular problems and for cluster and quasimolecular states of nuclei. There are two types of associated critical phenomena. From the point of view of their classification it makes no difference whether the z axis is the C_n or the C_{nv} symmetry axis, because the difference between these local energy surfaces is not essential for these two cases. For the case of simplicity we shall consider the local symmetry group C_{nv} . The rotational energy surface close to the z axis can be obtained by the expansion of (2.8) in series in terms of the small value θ . The condition of the appearance of the critical phenomena is the zero value of the coefficient before θ^2 at $J = J_c$. The dependence which is different for various local symmetries defines only the number of equivalent axes but not the type of the critical phenomena.

3.3. Critical Phenomena for Local Symmetry Groups C_3 and C_{3v}

The rotation energy surface for the local symmetry group C_{3v} close to the critical point J_c has the form

$$E(\theta, \varphi) = E_0(J) - \alpha(J - J_c) \theta^2 + 2b\theta^3 \cos 3\varphi, \quad (3.21)$$

where $E_0(J)$ is the energy of rotation around the stationary z axis; α , b are constants. A critical phenomenon consists in the change of the stability type of the rotation axis. If $\alpha > 0$, the axis z with the maximal moment of inertia⁷ (minimal rotation energy E_0) for $J < J_c$ is transformed into an axis with the minimal moment of inertia (maximal rotation energy E_0) for $J > J_c$. The transformation takes place in the reverse order for $\alpha < 0$. The z axis transformation is accompanied by a reorientation of the three unstable rotation axis in the neighbourhood of $\theta = 0$ rotated through an angle of 120° with respect to each other. They are associated with three saddle points on the surface (3.21) with the rotation energy $E_1(J) = E_0(J) + \alpha^3(J_c - J)^3/27b^2$.

The classical trajectories close to the north pole of the phase sphere are shown in Fig. 5. The local trajectories are separated from the global ones by separatrices s , being themselves global curves, passing through the saddle points of the surface (3.21) with the energy E_1 .⁸ It is clear from the figure that the precession motion of the vector \mathbf{J} around the z axis (point 0) is local if the system is far from J_c . The axis z becomes unstable at the very critical point J_c because the separatrices pass through the point 0 and the local trajectories disappear. Thus, the critical

⁷ We speak about a local characteristic of the moment of inertia for the z -axis rotation.

⁸ The rotation energy surface (3.21) is identical to the potential energy surface of the Henon-Heiles model system [19] which is widely used to study a chaotic motion.

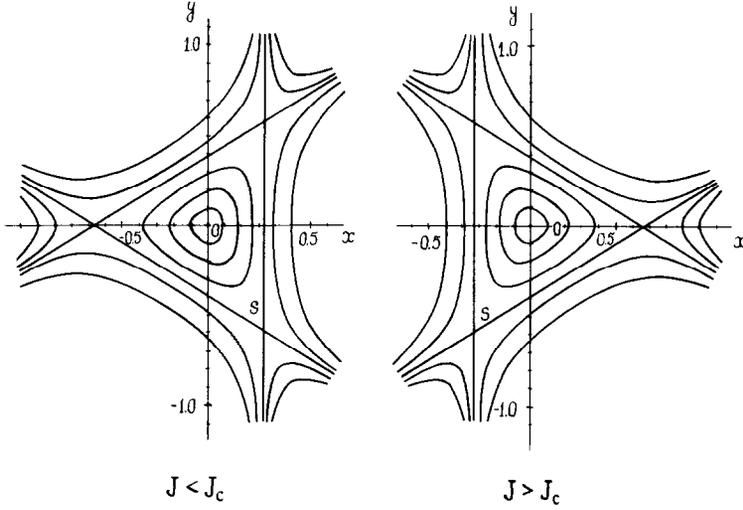


FIG. 5. The classical trajectories for the critical phenomenon of the C_{3v} symmetry.

phenomenon is not local close to J_c . It is necessary to include the terms with the operators J_{\pm}^6 , J_{\pm}^9 , etc. in the Hamiltonian H_{eff} ,

$$H_{\text{eff}} = g_0(\mathbf{J}^2, J_z^2) + \frac{1}{2} J_+^3 g_3(\mathbf{J}^2, J_z) + \frac{1}{2} g_3(\mathbf{J}^2, J_z) J_-^3 + \dots \quad (3.22)$$

for an appropriate quantum description.

Let us consider a quantum problem assuming the parameter α in (3.22) to be sufficiently large in its absolute value. In such a case the discrete character of the quantum number J enables us to exclude the essentially nonlocal region and to use the first terms of the expansion of H_{eff} (3.22) in $(J_z^2 - J^2)/J^2$. The so-obtained Hamiltonian

$$H_{C_{3v}} = E_0(J) + \alpha(J - J_c) \frac{J_z^2 - J^2}{J^2} + \frac{b}{2J^4} ([J_+^3, J_z]_+ + [J_-^3, J_z]_+), \quad (3.23)$$

where

$$\begin{aligned} J^2 g'_0(\mathbf{J}^2, J^2) &= \alpha(J - J_c), \\ b &= \frac{1}{2} J_c^3 g_3(\mathbf{J}_c^2, J_c), \end{aligned} \quad (3.24)$$

is adequate for the lowest energy levels of the rotational multiplet. For these levels the second term in $H_{C_{3v}}$ is more important than the third. The Hamiltonian (3.23) retains the symmetry properties of the initial Hamiltonian (3.22).

It is sufficient to take into account only the two first terms of the $H_{C_{3v}}$ Hamiltonian to describe the precession motion in the harmonic approximation. The precession energy equals

$$E_{JM} = E_0(J) - \frac{2\alpha}{J} (J - J_c)(J - |M|), \quad M = \pm J, \pm(J-1), \dots \quad (3.25)$$

The corresponding eigenfunction coincides with that of the J_z operator. The same functions are used to obtain the exact solutions of the Hamiltonian (3.23). These solutions are classified according to the irreducible representations A_1 , A_2 , E of the C_{3v} group [18]. The type of representation is connected with the sequence of the quantum number M in the expansion of the $H_{C_{3v}}$ eigenfunctions in terms of the $|J, M\rangle$ functions. Accordingly, there appear three sequences of the quantum numbers J ($3n, 3n+1, 3n+2$) with different orders of the lowest energy levels in the rotational multiplet. Figure 6 shows the ratio of the lowest level energy to the precession frequency $E_{J, \pm(J-1)} - E_0(J)$ (3.25). The regular part of the energy $E_0(J)$ is taken to be a zero point. To the left and to the right of the critical point the lowest levels form a system of doublets $A_1 + A_2$ for $M = 3n$, and a system of doubly degenerate levels of the E type for $M = 3n+1, 3n+2$. Figure 6 clearly shows that the critical phenomenon manifests itself by a decrease in the number of equidistant levels corresponding to the precession of the vector \mathbf{J} in approaching the critical point J_c and by its increase in going away from it. The inversion of the energy level structure takes place in passing through the critical point.

3.4. Critical Phenomena for Local Symmetry Groups C_4 and C_{4v}

The classical rotation energy surface in the neighbourhood of the z axis and close to the critical point J_c has the following form for the local symmetry group C_{4v} ,

$$E(\theta, \varphi) = E_0(J) - \alpha(J - J_c) \theta^2 + (a + 2b \cos 4\varphi) \theta^4. \quad (3.26)$$

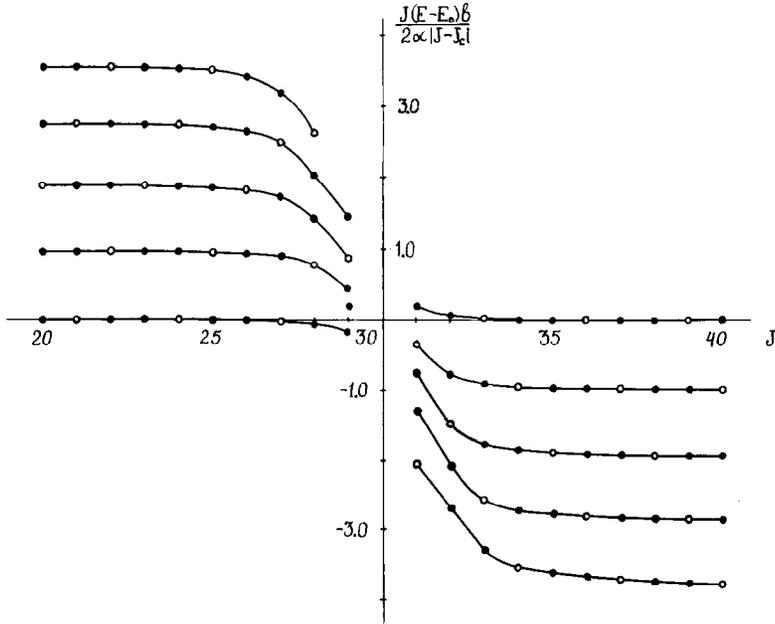


FIG. 6. The lowest levels of the rotational multiplet in the transition region for the critical phenomenon of the C_{3v} symmetry ($J_c = 30$; $\alpha/b = 0.8$ in the Hamiltonian (3.23)). (O) $A_1 + A_2$ doublets; (●) doubly degenerate levels of the E type.

Here $E_0(J)$ is the energy of the rotation around the stationary axis z ; α , a , b are constants and, in general, one may assume $b > 0$. Two types of critical phenomena are possible depending on relative values of a and b .

If $|a| < 2b$, the critical phenomenon is not local and, analogously to that of the C_{3v} symmetry, corresponds to a change of the stability type of the rotation axis. The difference is as follows. The change of stability is associated with the reorientation of four equivalent unstable rotation axes with the energy E_1 or E_2 ,

$$E_{1,2}(J) = E_0(J) - \frac{\alpha^2(J - J_c)^2}{4(a \mp 2b)}, \quad (3.27)$$

where E_0 is the maximal or minimal energy of rotation around the z axis.

The critical phenomenon is more complicated for $|a| > 2b$. In such a case four stable equivalent axes rotated by 90° with respect to one another arise or disappear together. The z axis remains stable but changes its type of stability at the critical point J_c . If $a > 2b$, at $\alpha > 0$ the minimal rotation energy $E_0(J)$ about the z axis for $J < J_c$ changes into the maximal one for $J > J_c$. This variation is accompanied by an appearance of four additional equivalent stable rotation axes $\mathbf{k}_i(\theta_0, \pi(2i - 1)/4)$, $i = 1, 2, 3, 4$; $\theta_0^2 = \alpha(J - J_c)/2(a - 2b)$ with the energy $E_1(J)$. At $\alpha < 0$ the transition takes places in the reverse order with increasing J . If $a < -2b$, the same transitions occur with the small difference of an interchange of the minimal and maximal rotation energies. Four unstable equivalent axes arise simultaneously with the stable ones in all cases. These unstable axes are rotated by 45° about the z axis with respect to the stable axes. They correspond to the saddle points of the surface (3.26) with the energy $E_2(J)$ for $a > 2b$ and $E_1(J)$ for $a < -2b$.

The classical trajectories near the north pole of the phase sphere are shown in Fig. 7 for the case of $a > 2b$ and $\alpha > 0$. The closed trajectories with the energy $E > E_0$ correspond to the precession of the \mathbf{J} vector around the z axis (the point 0)

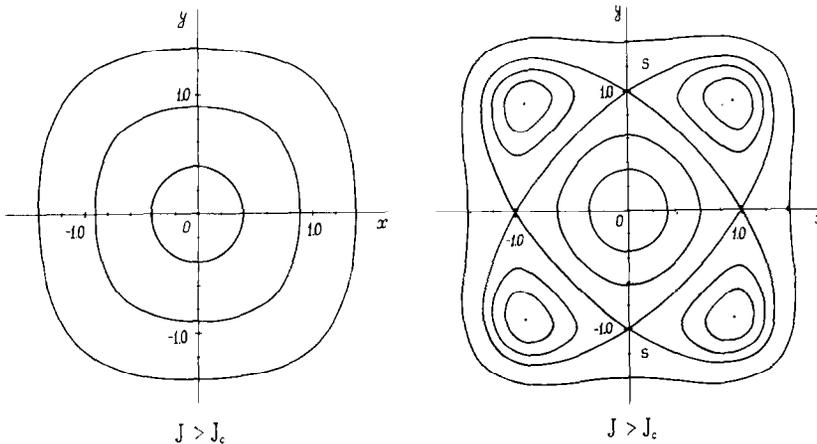


FIG. 7. The classical trajectories for the local critical phenomenon of the C_{4v} symmetry ($\alpha > 0$, $a/b = 8.0$).

for $J < J_c$. The precessions around each of the four stable axes \mathbf{k}_i with the energy $E_1 < E < E_2$ arise for $J > J_c$ along with the precession around the z axis with the energy $E_2 < E < E_0$. The separatrix s passing through these four saddle points of the surface (3.26) separates trajectories of these precessional motions. It also separates the local precessional trajectories from the global ones. The family of phase trajectories is typical of the local critical phenomenon. It is characterized by a breaking of the classical rotation invariance with respect to the C_4 symmetry element and by a jump discontinuity at J_c of the second derivative with respect to J of the minimal (E_1) or maximal (E_2) rotation energy,

$$E''(J_c) = E''_{1,2}(J_c) - E''_0(J_c) = -\frac{\alpha^2}{2(a \mp 2b)}. \quad (3.28)$$

The local character of this critical phenomenon enables us to obtain a universal Hamiltonian from H_{eff} (2.4) for the lowest energy levels of the rotational multiplet (see Appendix B),

$$H_{C_{3v}} = E_0(J) + a_1(J) \frac{J_z^2 - J^2}{J^2} + a_2 \left(\frac{J_z^2 - J^2}{J^2} \right)^2 + b_1 \frac{J_+^4 + J_-^4}{J^4}, \quad (3.29)$$

where

$$\begin{aligned} a_1(J) &= J^2 g'_0(\mathbf{J}^2, J^2) = \alpha(J - J_c), \\ a_2 &= \frac{1}{2} J_c^2 g''_0(\mathbf{J}_c^2, J_c^2); \quad b_1 = \frac{1}{2} J_c^2 g_4(\mathbf{J}_c^2, J_c). \end{aligned} \quad (3.30)$$

The regular part $E_0(J) = g_0(\mathbf{J}^2, J^2)$ is the energy of the rotation around the z axis.

Consider now the variation of the precession motion in passing through the critical point J_c for $a > 2b$ and $\alpha > 0$. The axis z is stable both to the left and to the right of J_c . The precession of the \mathbf{J} vector around this axis is described by the harmonic approximation Hamiltonian (A.3) whose parameters

$$P = Q = 0; \quad S = -\alpha(J - J_c) \frac{2J - 1}{J^2} + a_2 \left(\frac{2J - 1}{J^2} \right)^2 \quad (3.31)$$

can be found easily from $H_{C_{4v}}$. The energy of the lowest levels of the rotational multiplet is given by

$$E_{J,M} = E_0(J) + \frac{2J - 1}{J^2} \left\{ \alpha(J_c - J) + a_2 \frac{2J - 1}{J^2} \right\} (J - |M|). \quad (3.32)$$

The precession around the z axis with the aximal moment of inertia is transformed into that with the minimal moment in passing through the critical point.

Four equivalent precession axes arise for $J > J_c$. Let us consider the \mathbf{J} -vector precession around the $\mathbf{k}_1(\theta_0, \pi/4)$ axis. To realize the harmonic approximation we express the Hamiltonian $H_{C_{4v}}$ in terms of the spherical tensors (2.3) and perform the

rotation R (B.10) in the body-fixed frame through angles $\alpha = \pi/4$, $\beta = \theta_0$, $\gamma = 0$. In passing from the transformed Hamiltonian $RH_{C_{4v}}R^{-1}$ to the harmonic approximation Hamiltonian (A.3) we get

$$\begin{aligned}
 P &= \frac{\sqrt{2J(2J-1)}}{2J^2} \left\{ -\alpha(J-J_c) + \frac{a}{J^2}(2J^2-3J+2) \right. \\
 &\quad \left. - \frac{6b}{J^2}(2J-3)(J-1) \right\} \sin^2 \theta_0, \\
 Q &= 0, \\
 S &= \frac{2J-1}{J^2} \left\{ -\alpha(J-J_c) + \frac{a}{J^2}(2J-1) \right. \\
 &\quad \left. + \left[-\alpha(J-J_c) + \frac{2a}{7J^2}(14J^2-43J+26) \right] \sin^2 \theta_0 \right\}, \\
 \sin^2 \theta_0 &= \frac{\alpha(J-J_c) - a(2J-1)/J^2}{(J-1)(2J-3)(a-2b)} J^2.
 \end{aligned} \tag{3.33}$$

The energy of the lowest levels is given in this approximation by

$$E_{J,K} = E_1(J) - S/2 + \omega(J - |K| + 1/2), \quad K = \pm J, \pm(J-1), \dots, \tag{3.34}$$

where

$$E_1(J) = E_0(J) - \frac{a-2b}{4J^3} (2J-1)(2J-3)J(J-1) \sin^4 \theta_0 \tag{3.35}$$

is the energy of the rotation around the \mathbf{k}_1 axis, and K is the angular momentum projection on this axis. The precession frequency is given for a sufficiently small θ_0 by

$$\omega = \frac{8\alpha}{J} (J-J_c) \sqrt{b/(a-2b)}, \quad J > J_c. \tag{3.36}$$

The harmonic approximation with the broken symmetry (3.34) can be improved by using delocalized and properly C_{4v} -symmetrized wavefunctions.

The modification of the precession motion results in a rearrangement of the lowest energy levels of the rotational multiplet. This rearrangement can be followed by using an exact numerical treatment of the $H_{C_{4v}}$ Hamiltonian. We classify the eigenstates of $H_{C_{4v}}$ by irreducible representations A_1, A_2, B_1, B_2, E of the C_{4v} group [18]. Figure 8 shows the ratio of the lowest level energy to the precession frequency around the z axis for $J < J_c$. For $J < J_c$ the lowest part of the rotational multiplet forms a nearly equally spaced system of doublets $A_1 + A_2$ ($M = 4n$), $B_1 + B_2$ ($M = 4n + 2$) and doubly degenerate E type levels ($M = 4n + 1, 4n + 3$).

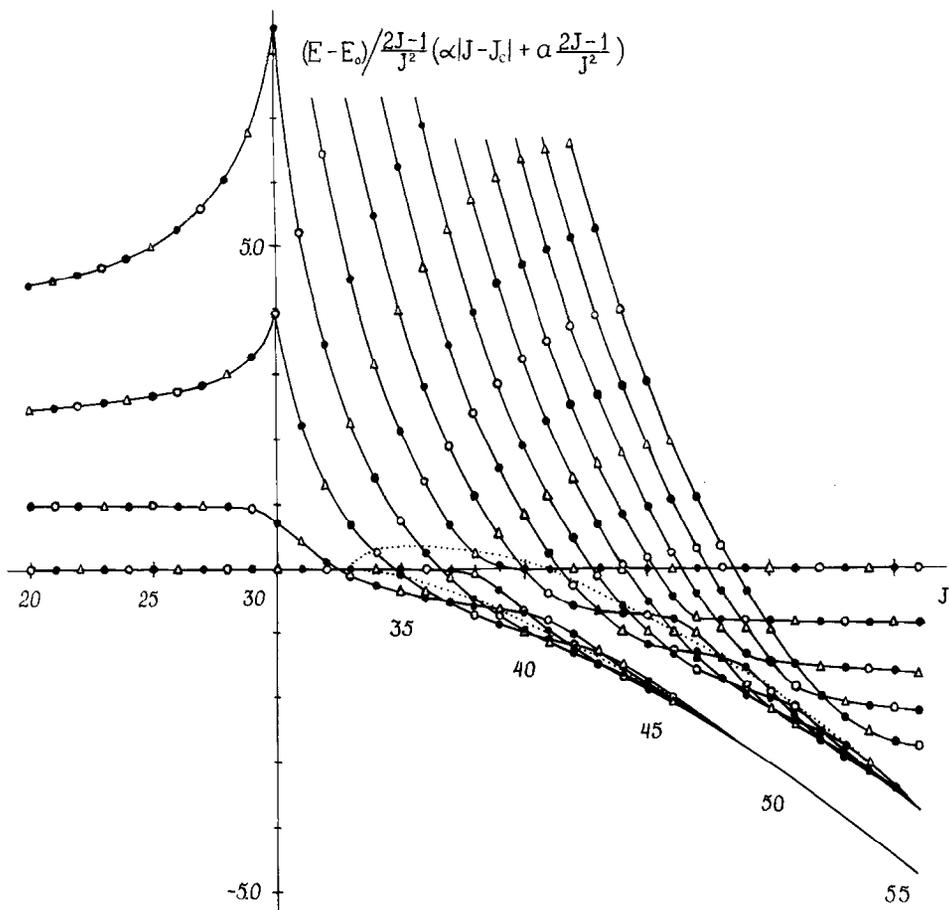


FIG. 8. The lowest levels of the rotational multiplet in the transition region for the local critical phenomenon of the C_{4v} symmetry. The parameters of the $H_{C_{4v}}$ Hamiltonian: $J_c = 30$; $\alpha/b = 0.18$; $a/b = 8.0$. (○) $A_1 + A_2$ doublets; (●) doubly degenerate levels of the E type; (△) $B_1 + B_2$ doublets; (⋯) the harmonic approximation.

Under increase in J these levels either come closer forming an eight-fold degenerate cluster $A_1 + A_2 + B_1 + B_2 + 2E$ (a delocalized precession around four equivalent axes) or rearrange to form the initial structure (the precession around the z axis). The results of the lowest energy level calculations for $J > J_c$ in the harmonic approximation (3.34) are shown in the same figure for comparison.

3.5. Critical Phenomena for Local Symmetry Groups C_n and C_{nv} , $n \geq 5$

High symmetry elements C_n ($n \geq 5$) are rather rare. They are available only for heavy molecules which usually have a spectroscopically unresolved rotational structure. Nevertheless, we consider the critical phenomena for the local symmetry groups C_{nv} ($n \geq 5$) for completeness. The rotational energy surface in the

neighbourhood of the z axis and close to the critical point J_c can be written in the form

$$E(\theta, \varphi) = E_0(J) - \alpha(J - J_c) \theta^2 + a\theta^4 + 2b\theta^n \cos n\varphi. \quad (3.37)$$

The last term in this expression is small compared to $a\theta^4$. Thus, there is only one type of critical phenomenon for all the groups considered. This critical phenomenon is the same as that for the C_{4v} group in the case of $|a| > 2b$. The difference is that there exist n equivalent axes instead of four for the surface (3.37).

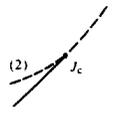
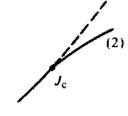
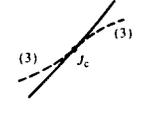
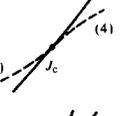
4. CONCLUSION

All the critical phenomena for the purely rotational motion are presented in Table I. A graphical representation of the dependence of the classical rotation energy E on the angular momentum J in the neighbourhood of the critical point J_c is shown in Table I for positive values of coefficients specifying the energy surface. The dashed line corresponds to the energy of rotation around the unstable axis; the solid line, around the stable one. The solid line is associated with the rotation around the maximal inertia moment axis if it is lower than the dashed line in energy. If it lies above the dashed line, it corresponds to the rotation around the minimal inertia moment axis. A numeral in parentheses at the line denotes the number of equivalent rotation axes.

All the critical phenomena considered can be called elementary. This means that they are associated with the going to zero of *only one* coefficient of the local rotational Hamiltonian at the critical point J_c . More complicated cases, which correspond to the going to zero of several or even an infinite number of coefficients simultaneously, are possible. In the last case a groove with an indifferent equilibrium is formed on the energy surface and the corresponding critical phenomenon resulting in the rotation of the \mathbf{J} -vector through a finite angle with respect to the body-fixed frame is analogous to a first-order phase transition [5].

There are two local critical phenomena among the five types of elementary ones considered. In the classical limit the local critical phenomena are characterized by the degeneracy (equivalent rotation axes), the breaking of the local group \mathfrak{G} symmetry, and the discontinuity of the second derivative of the rotation energy with respect to J in the J_c point. These local critical phenomena are similar to the second-order phase transitions. The classical picture is only an illustration for such isolated quantum systems as molecules and atomic nuclei. The local critical phenomena in the rotational spectra can be seen by the rearrangement of the rotational multiplet structure, i.e., by the appearance of energy level clusters corresponding to the delocalized precession of the vector \mathbf{J} around equivalent axes. The $(J - J_c)$ increase results in the exponential decrease in the intracluster splitting. However, the precession is not localized on one axis and the intracluster states have definite symmetry with respect to the group \mathfrak{G} . Thus, the spontaneously broken

TABLE I
Types of Critical Phenomena for a Nondegenerate Isolated Rotational Band

Local symmetry group \mathfrak{G}	Energy surface close to the z axis of the body-fixed frame	Graphical representation of the $E(J)$ dependence	Singularity in the critical point J_c
C_1	$E(\xi, \eta) = E_0(J) - \alpha(J - J_c) \xi + a_{02} \eta^2 + a_{30} \xi^3$		$E''(J) \sim -(J - J_c)^{-1/2}$
C_5 C_{2v}, C_{2r}	$E(\xi, \eta) = E_0(J) - \alpha(J - J_c) \eta^2 + a_{20} \xi^2 + a_{04} \eta^4$		—
C_3, C_{3v}	$E(\theta, \varphi) = E_0(J) - \alpha(J - J_c) \theta^2 + 2b\theta^3 \cos 3\varphi$		$\Delta E''(J_c) = -\frac{\alpha^2}{2a_{04}}$
C_4, C_{4v}	$E(\theta, \varphi) = E_0(J) - \alpha(J - J_c) \theta^2 + (a + 2b \cos 4\varphi) \theta^4$		—
C_n, C_{nv} $n \geq 5$	$E(\theta, \varphi) = E_0(J) - \alpha(J - J_c) \theta^2 + a\theta^4 + 2b\theta^n \cos n\varphi$		$\Delta E''(J_c) = -\frac{\alpha^2}{2(a - 2b)}$

symmetry [20, 21] is not appropriate for the critical phenomena. The Hamiltonian and its eigenfunctions remain invariant with respect to the local symmetry group \mathfrak{G} . This is a principal difference between the critical phenomena and the phase transitions in macroscopic systems.

For sufficiently large J an arbitrarily small perturbation, nonsymmetric with respect to \mathfrak{G} , transforms the system from a symmetric delocalized state to a nonsymmetric localized one which corresponds to the classical picture. This state is nonstationary but its decay time may be large enough (due to a small tunneling through the barrier separating equivalent axes) for it to be treated as really existing. An example of such a transition for an inversion doublet in the XY_3 type molecules

under the influence of the interaction with the environment is discussed in [22]. The similarity between the local critical phenomena and the second-order phase transitions manifests itself in the universal nature of the collective motion close to the critical point. For the phase transitions this universality means that a detailed structure of the Hamiltonian of the macroscopic system is not essential on the scale of long-wave fluctuations responsible for the phase transition [23]. The universal character of the local critical phenomena is due to the fact that it occurs in a limited region of the collective motion phase space. Accordingly, the collective Hamiltonian in the vicinity of the critical point does not depend on the internal structure of the system up to numerical values of its coefficients.

The universal behaviour is of practical importance for the description of the rotational spectra of molecules and atomic nuclei. It allows us to replace the power expansion at $J=0$ which is clearly inadequate for high J by an expansion at J_c . Until now such a possibility has not been studied in either nuclear or molecular spectroscopy.

APPENDIX A: HARMONIC APPROXIMATION FOR QUANTUM PRECESSION

We use the boson representation proposed by Marshalek [24] for the angular momentum operators to study the energy levels of the rotational multiplet. We shall consider the angular momentum operators in the body-fixed frame

$$J_z = J - b^+ b, \quad J_+ = J_- = b^+ \sqrt{2J - b^+ b}, \quad (\text{A.1})$$

which act in the space of wavefunctions

$$\varphi_{J,v} = \sum_{M=-J}^J a_M^{(v)} \frac{(b^+)^{J-M}}{\sqrt{(J-M)!}} |0\rangle \quad (\text{A.2})$$

corresponding to the state v of an isolated rotational multiplet. $|0\rangle$ is a vacuum state of the boson operators b^+ , b .

Let us consider the precession motion around the z axis. We expand the Hamiltonian H_{eff} (2.4) in terms of boson operators b^+ and b employing the formulae (A.1) and one of the methods described in Ref. [25]. The general form of the Hamiltonian in the harmonic approximation is

$$H = E_0(J) + S b^+ b + (P + iQ) b^+ b^+ + (P - iQ) b b, \quad (\text{A.3})$$

where the coefficients E_0 , P , Q , S depend on the parameters of the Hamiltonian (2.4) and on the quantum number J . The harmonic approximation describes the states which can be approximately characterized by the quantum number M of the angular momentum projection on the z axis of the body-fixed frame.

The Hamiltonian (A.3) can be diagonalized by a linear canonical transformation

$$b = u\beta + v\beta^+, \quad |u|^2 - |v|^2 = 1 \quad (\text{A.4})$$

with new boson operators β^+ and β . The energy of the levels corresponding to the precession of the vector \mathbf{J} around the z axis is given by

$$E_{J,M} = E_0(J) - \frac{1}{2}S + \frac{S}{|S|} \sqrt{S^2 - 4P^2 - 4Q^2} (J - |M| + 1/2),$$

$$M = \pm J, \pm(J-1), \dots \quad (\text{A.5})$$

The condition $S^2 > 4(P^2 + Q^2)$ is necessary for the states with $M = \pm J$ to be stable and the corresponding axis to be that of the stable rotation. The critical value J_c (for which $S^2 = 4(P^2 + Q^2)$) is the transition point from the states with energy (A.5) to those corresponding to the precession of \mathbf{J} around some other stable rotation axis. The harmonic approximation is adequate if the following condition is satisfied: $|J - J_c| \gg J_c^{-2/3}$ [10].

The wavefunction of the Hamiltonian (A.3) for the state $|M| = J$ has the form

$$\varphi_{J,\pm J} = \frac{1}{\sqrt{|u|}} \exp\left(\frac{v}{2u^*} b^+ b^+\right) |0\rangle. \quad (\text{A.6})$$

The coordinate representation proves to be useful for studying the precession around equivalent axes. For this purpose we introduce a dimensionless coordinate q ($|q| < \infty$) according to the relation

$$b^+ = \frac{1}{\sqrt{2}} \left(q - \frac{d}{dq}\right), \quad b = \frac{1}{\sqrt{2}} \left(q + \frac{d}{dq}\right). \quad (\text{A.7})$$

We put (A.7) into the equation $H\varphi_{J,M} = E\varphi_{J,M}$ with the Hamiltonian (A.3) and transform the so-obtained differential equation by the substitution

$$\varphi_{J,M}(q) = \psi(q) \exp\left(-i \frac{Q}{S-2P} q^2\right) \quad (\text{A.8})$$

to the form

$$-\frac{1}{2}(S-2P) \frac{d^2\psi}{dq^2} + \frac{S^2 - 4P^2 - 4Q^2}{2(S-2P)} q^2 \psi = (E - E_0 + S/2) \psi. \quad (\text{A.9})$$

This equation can describe small precession near the equilibrium, $q = 0$, if $(S + 2P)$ and $(S - 2P)$ have the same sign, and $S^2 - 4P^2 > 4Q^2$. In the coordinate representation the wavefunction of the $M = J$ state has the form

$$\varphi_{J,\pm J}(q) = (f/\pi)^{1/4} \exp\left\{-\frac{1}{2}(f + ig) q^2\right\}, \quad (\text{A.10})$$

where

$$f = \frac{(S^2 - 4P^2 - 4Q^2)^{1/2}}{S - 2P}, \quad g = \frac{Q}{S - 2P}. \quad (\text{A.11})$$

Thus, the linear canonical transformation (A.4) changes the mass, force constant, and phase of the wavefunction of the oscillatory motion.

APPENDIX B:
PROOF OF UNIVERSAL CHARACTER OF
LOCAL CRITICAL PHENOMENON HAMILTONIANS

The Hamiltonian describing the lowest energy levels of the rotational multiplet will be called universal if it depends on a finite number of constants. The universal Hamiltonian contains a finite number of expansion terms of the effective rotational Hamiltonian (2.4) with the expansion parameter (3.9). The universality is inherent in the Hamiltonian of local critical phenomena only.

Let the effective Hamiltonian (2.4) be written in the form

$$H_{\text{eff}} = H^{(4)} + H^{(6)} + H^{(8)} + \dots, \quad (\text{B.1})$$

where $H^{(k)}$ contains the operators J_α with their power not exceeding k . For the critical phenomena with the C_{2v} and C_{4v} symmetries the $H^{(4)}$ terms are given by (3.10) and (3.29), correspondingly, and the $H^{(6)}$ terms equal

$$\begin{aligned} H_{C_{2v}}^{(6)} = & a_3 \left(\frac{J_z^2 - J^2}{J^2} \right)^2 + \frac{b_3}{2J^6} ([J_z^2 - J^2, J_+^2]_+ + [(J_z^2 - J^2)^2, J_-^2]_+) \\ & + \frac{c_2}{2J^6} ([J_z^2 - J^2, J_+^4]_+ + [J_z^2 - J^2, J_-^2]_+) + \frac{d_1}{J^6} (J_+^6 + J_-^6), \end{aligned} \quad (\text{B.2})$$

$$H_{C_{4v}}^{(6)} = a_3 \left(\frac{J_z^2 - J^2}{J^2} \right)^3 + \frac{b_2}{2J^6} ([J_z^2 - J^2, J_+^4]_+ + [J_z^2 - J^2, J_-^4]_+). \quad (\text{B.3})$$

The coefficients E_0 , a_i , b_i , etc., can be expressed in terms of derivatives of the g_m functions and have the same order of magnitude (see Eqs. (3.11) and (3.30)). We prove that in the transition region the term $H^{(4)}$ is the leading term of the expansion (B.1). This very term is a universal rotational Hamiltonian. To prove it, we use the harmonic approximation where the Hamiltonian (B.1) has the form (A.3) with the coefficients

$$\begin{aligned} E &= E_0 + E^{(4)} + E^{(6)} + E^{(8)} + \dots, \\ S &= S^{(4)} + S^{(6)} + S^{(8)} + \dots, \\ Q &= 0, \\ P &= P^{(4)} + P^{(6)} + P^{(8)} + \dots, \end{aligned} \quad (\text{B.4})$$

written in the form of an expansion in such a way that $E^{(k)}$, $S^{(k)}$, and $P^{(k)}$ correspond to the term $H^{(k)}$.

Consider at first the precession of the vector \mathbf{J} around the z axis for J and J_c . Straightforward calculations yield the following expressions for the coefficients of the $H_{C_{2v}}$ Hamiltonian,

$$\begin{aligned}
 E^{(4)} &= E^{(6)} = \dots = 0 \\
 S^{(4)} &= -a_1 \frac{2J-1}{J^2} + a_2 \left(\frac{2J-1}{J^2} \right)^2, \\
 S^{(6)} &= -a_3 \left(\frac{2J-1}{J^2} \right)^3, \\
 P^{(4)} &= \left(\frac{b_1}{J^2} - \frac{b_2(J-1)}{J^4} \right) \sqrt{2J(2J-1)}, \\
 P^{(6)} &= 8b_3 \left(\frac{J-1}{J^3} \right)^2 \sqrt{2J(2J-1)}, \dots
 \end{aligned} \tag{B.5}$$

For the $H_{C_{4v}}$ Hamiltonian $P^{(k)}=0$ and all the other coefficients are the same as those for $H_{C_{2v}}$. Thus the addition of the succeeding terms of the expansion (B.1) to $H^{(4)}$ modifies the results of the harmonic approximation by contributions not higher than J^{-1} . The additional terms increase the anharmonicity of the precession motion which is essential only for higher states of the rotational multiplet. However, these terms are not important for the lowest levels of the rotational multiplet.

The rotation of the body-fixed frame is necessary to describe the precession of the vector \mathbf{J} around one of the equivalent axes whose direction differs from that of the z -axis (the region $J > J_c$). The required transformation of the $H_{C_{2v}}$ and $H_{C_{4v}}$ Hamiltonians can be performed most easily by expressing them in terms of the spherical tensor operators (2.3) in the form

$$H_{\text{eff}} = E_0(J) + \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{lm} T_{lm}, \tag{B.6}$$

where according to (B.1)

$$A_{lm} = A_{l,-m} = A_{lm}^{(4)} + A_{lm}^{(6)} + A_{lm}^{(8)} + \dots \tag{B.7}$$

For the $H_{C_{2v}}$ Hamiltonian we have

$$\begin{aligned}
 A_{00}^{(4)} &= -\frac{2J-1}{3J} a_1 + \frac{a_2}{15J^3} (2J-1)(4J^2+1), \\
 A_{20}^{(4)} &= \frac{\sqrt{6}}{3J^2} \left[a_1 - \frac{a_2}{7J^2} (8J^2 - 6J + 5) \right], \\
 A_{22}^{(4)} &= \frac{2}{J^2} \left[b_1 - \frac{b_2}{7J^2} (6J^2 - J + 5) \right],
 \end{aligned} \tag{B.8}$$

$$\begin{aligned}
A_{40}^{(4)} &= \frac{2\sqrt{70}}{35J^4} a_2, & A_{42}^{(4)} &= \frac{2b_2}{\sqrt{7}J^4}, & A_{44}^{(4)} &= \frac{4c_1}{J^6}; \\
A_{00}^{(6)} &= -\frac{a_3}{105J^5} (2J-1)(24J^4+6J^2+5), \\
A_{20}^{(6)} &= \frac{\sqrt{6}a_3}{21J^6} (8J^4-8J^3+10J^2-10J+7), \\
A_{22}^{(6)} &= \frac{2b_3}{21J^6} (16J^4-4J^3-16J^2+13J-177), & (B.9) \\
A_{40}^{(6)} &= -\frac{2\sqrt{70}a_3}{385J^6} (18J^2-15J+35), \\
A_{42}^{(6)} &= -\frac{2b_3}{11\sqrt{7}J^6} (16J^2-6J-41), \\
A_{44}^{(6)} &= -\frac{4c_2}{11J^6} (10J^2-J-38), & A_{60}^{(6)} &= \frac{4a_3}{\sqrt{231}J^6}, \\
A_{62}^{(6)} &= \frac{8b_3}{3\sqrt{55}J^6}, & A_{64}^{(6)} &= \frac{\sqrt{32}c_2}{\sqrt{33}J^6}, & A_{66}^{(6)} &= \frac{8d_1}{J^6}, \dots
\end{aligned}$$

We rotate the body-fixed frame by the angles α , β , and γ to align the z axis with one of the equivalent precession axes. The operator of this rotation

$$R(\alpha, \beta, \gamma) = \exp(i\gamma J_z) \exp(i\beta J_y) \exp(i\alpha J_z) \quad (B.10)$$

transforms the effective Hamiltonian (B.6) into the form

$$\begin{aligned}
RH_{\text{eff}}R^{-1} &= E_0(J) + \sum_{l=0}^{\infty} \sum_{m, m'} A_{lm} D_{mm'}^{(l)}(-\alpha, -\beta, -\gamma) T_{lm} \\
&= \sum_m H_m, & (B.11)
\end{aligned}$$

where $D_{mm'}^{(l)}$ is the Wigner function in the definition by Edmonds [26]. The operators H_m can be expressed in terms of linear combinations of the spherical tensors T_{2m} , T_{4m} , etc. In the harmonic approximation the rotation of the body-fixed frame is equivalent to translation of the origin. Thus, one must reduce to zero the expression $H_{-1} = H_{+1}^+$ proportional b^+ , to describe the precession around one of the equivalent axes. This requirement enables us to define the rotation angles β , α , γ . From the remaining terms it is sufficient to take into account the terms H_m with $m=0, \pm 2$ which yield the Hamiltonian (A.3) with the coefficients (B.4). To study

the convergence properties of the series for E , S , and P , we calculate two initial terms for each of them. For the Hamiltonian $H_{c_{2\epsilon}}$ the results are

$$\begin{aligned}
 E^{(4)} &= (2J-1) \left\{ -\frac{1}{2J} (a_1 + 2b_1) + \frac{a_2}{2J^3} (2J-1) + \frac{2b_2}{J^3} (J-1) \right. \\
 &\quad \left. + \frac{1}{4J^3} (a_2 + 2b_2 + 2c_1)(J-1)(2J-3) \sin^2 \beta \right\} \sin^2 \beta, \\
 S^{(4)} &= (2J-1) \left\{ \frac{a_1}{J^2} + \frac{a_2}{J^4} (2J-1) + \frac{3}{2J^2} (a_1 + 2b_1) \sin^2 \beta \right. \\
 &\quad \left. + \frac{1}{2J^4} (2J-5)[a_2(4J-3) + 6b_2(J-1)] \sin^2 \beta \right. \\
 &\quad \left. - \frac{5}{2J^4} (a_2 + 2b_2 + 2c_1)(J-1)(2J-3) \sin^4 \beta \right\}, \tag{B.12}
 \end{aligned}$$

$$\begin{aligned}
 P^{(4)} &= \sqrt{2J(2J-1)} \left\{ \frac{b_1}{J^2} - \frac{2b_2}{J^4} (J-1) - \frac{1}{4J^2} (a_1 + 2b_1) \sin^2 \beta \right. \\
 &\quad \left. - \frac{1}{4J^4} [a_2(4J^2 - 12J + 7) + 2b_2(J-1)(6J-11) + 12c_1(J-1)(2J-3)] \sin^2 \beta \right. \\
 &\quad \left. + \frac{3}{4J^4} (a_2 + 2b_2 + 2c_1)(J-1)(2J-3) \sin^4 \beta \right\},
 \end{aligned}$$

$$\begin{aligned}
 E^{(6)} &= (2J-1) \left\{ -\frac{a_3}{2J^5} (2J-1)^2 - \frac{8b_3}{J^4} (J-2) \right. \\
 &\quad \left. - \frac{1}{4J^5} (J-1)(2J-3)[a_3(6J-5) + 2b_3(6J-11) + 8c_2(J-2)] \sin^2 \beta \right. \\
 &\quad \left. - \frac{1}{8J^5} (J-1)(J-2)(2J-3)(2J-5)(a_3 + 2b_3 + 2c_2 + 2d_1) \sin^4 \beta \right\} \sin^2 \beta,
 \end{aligned}$$

$$\begin{aligned}
 S^{(6)} &= \frac{2J-1}{J^6} \left\{ -a_3(2J-1)^2 - \frac{a_3}{2} (48J^3 - 172J^2 + 184J - 63) \sin^2 \beta \right. \\
 &\quad \left. - 3b_3(12J^3 - 60J^2 + 89J - 77) \sin^2 \beta - (J-1)(2J-3) \right. \\
 &\quad \times \left[\frac{a_3}{4} (3J-20)(6J-7) + b_3(8J^2 - 66J + 95) + \frac{5}{2} c_2(J-2)(2J-13) \right] \sin^4 \beta \\
 &\quad \left. + \frac{21}{8} (a_3 + 2b_3 + 2c_2 + 2d_1)(J-1)(J-2)(2J-3)(2J-5) \sin^6 \beta \right\}, \tag{B.13}
 \end{aligned}$$

$$\begin{aligned}
P^{(6)} = & \frac{1}{J^6} \sqrt{2J(2J-1)} \left\{ 8b_3 J(J-2) + \frac{1}{4} [a_3(24J^3 - 84J^2 + 90J - 31) \right. \\
& + 8b_3(36J^3 - 164J^2 + 235J - 99) + 48c_2(J-1)(J-2)(2J-3)] \sin^2 \beta \\
& + \frac{1}{4} (J-1)(2J-3) [3a_3(2J^2 - 15J + 15) + b_3(14J^2 - 99J + 136) \\
& + 15d_1(J-2)(2J-5)] \sin^4 \beta \\
& \left. - \frac{15}{8} (4a_3 + b_3 + c_2 + d_1)(J-1)(J-2)(2J-3)(2J-5) \sin^6 \beta \right\}.
\end{aligned}$$

The angle β of the body-fixed frame rotation included in the above formulae can be found from the equation

$$\begin{aligned}
& \frac{1}{2J^2} (a_1 + 2b_1) - \frac{a_2}{2J^4} (2J-1) - \frac{2b_2}{J^4} (J-1) + \frac{a_3}{2J^6} (2J-1) + \frac{8b_3}{J^5} (J-2) \\
& - \frac{1}{2J^4} (J-1)(2J-3) \left\{ a_2 + 2b_2 + 2c_1 - \frac{a_3}{2J^2} (6J-5) - \frac{b_3}{J^2} (6J+11) \right. \\
& \left. - \frac{4c_2}{J^2} (J-1) \right\} \sin^2 \beta + \frac{1}{36J^6} (12a_3 + b_3 + 12c_1 - 12d_1) \\
& \times (J-1)(J-2)(2J-1)(2J-3) \sin^4 \beta + \dots = 0. \tag{B.14}
\end{aligned}$$

The two other rotation angles equal $\alpha = -\gamma = \pi/2$. Similar expressions may be obtained for the $H_{C_{4v}}$ Hamiltonian.

The analysis of the expressions (B.12), (B.13), and (B.14) shows that there are two small parameters J^{-1} and $\sin^2 \beta \propto (J - J_c)/J_c$ in the series (B.4) for $J > J_c$. The terms leading in these parameters are present only in $E^{(4)}$, $P^{(4)}$, and $S^{(4)}$. Thus, the term $H^{(4)}$ in the expansion (B.1) is sufficient for the description of the lowest energy levels of the rotational multiplet close to the critical point J_c . Strictly speaking, the harmonic approximation used above to prove universal character is not valuable in the vicinity of the critical point. Nevertheless, the parameter $(J - J_c)/J_c$ is small in this region and the contribution from the terms $H^{(k)}$ with $k \geq 6$ into the effective rotational Hamiltonian is negligible.

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