# Quantum Bifurcations

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## Article Outline



## Glossary

**Classical limit** The classical limit is the classical mechanical problem which can be constructed from a given quantum problem by some limiting procedure. During such a construction the classical limiting manifold should be defined which plays the role of classical phase space. As soon as quantum mechanics is more general than classical mechanics, going to the classical limit from a quantum problem is much more reasonable than discussing possible quantizations of classical theories [73].

**Energy-momentum map** In classical mechanics for any problem which allows the existence of several integrals of motion (typically energy and other integrals often named as momenta) the Energy-Momentum (EM) map gives the correspondence between the phase space of the initial problem and the space of values of all independent integrals of motion. The energy-momentum map introduces the natural foliation of the classical phase space into common levels of values of energy and momenta [13,34]. The image of the EM map is the region of the space of possible values of integrals of motion which includes regular and critical values. The quantum analog of the image of the energy-momentum map is the joint spectrum of mutually commuting quantum observables.

**Joint spectrum** For each quantum problem a maximal set of mutually commuting observables can be introduced [16]. A set of quantum wave functions which are mutual eigenfunctions of all these operators exists. Each such eigenfunction is characterized by eigenvalues of all mutually commuting operators. The representation of mutual eigenvalues of $n$ commuting operators in the $n$-dimensional space gives the geometrical visualization of the joint spectrum.

**Monodromy** In general, the monodromy characterizes the evolution of some object after it makes a close path around something. In classical Hamiltonian dynamics the Hamiltonian monodromy describes for completely integrable systems the evolution of the first homology group of the regular fiber of the energy-momentum map after a close path in the regular part of the base space [13].

For a corresponding quantum problem the quantum monodromy describes the modification of the local structure of the joint spectrum after its propagation along a close path going through a regular region of the lattice.

**Quantum bifurcation** Qualitative modification of the joint spectrum of the mutually commuting observables under the variation of some external (or internal) parameters and associated in the classical limit with the classical bifurcation is named quantum bifurcation [59]. In other words the quantum bifurcation is the manifestation of the classical bifurcation presented in the classical dynamic system in the quantum version of the same system.

**Quantum-classical correspondence** Starting from any quantum problem the natural question consists of defining the corresponding classical limit, i. e. the classical dynamic variables forming the classical phase space and the associated symplectic structure. Whereas in simplest quantum problems defined in terms of standard position and momentum operators with commutation relation $[q_i, p_j] = i\hbar\delta_{ij}$, $[q_i, q_j] = [p_i, p_j] = 0$ $(i, j = 1 \ldots n)$ the classical limit phase space is the $2n$-dimensional Euclidean space with standard symplectic structure on it, the topology of the classical limit manifold in many other important for physical applications cases can be rather non-trivial [73,86].

**Quantum phase transition** Qualitative modifications of the ground state of a quantum system occurring under the variation of some external parameters at zero temperature are named quantum phase transitions [65]. For finite particle systems the quantum phase transition can be considered as a quantum bifurcation [60].

**Spontaneous symmetry breaking** Qualitative modification of the system of quantum states caused by perturbation which has the same symmetry as the initial problem. Local symmetry of solutions decreases but the number of solutions increases. In the energy spectra of finite particle systems the spontaneous symmetry breaking produces an increase of the "quasidegeneracy", i. e. formation of clusters of quasi-degenerate levels whose multiplicity can be much higher than the dimension of the irreducible representations of the global symmetry group [51].

**Symmetry breaking** Qualitative changes in the properties (dynamical behavior, and in particular in the joint spectrum) of quantum systems which are due to modifications of the global symmetry of the problem caused by external (less symmetrical than original problem) perturbation can be described as symmetry breaking effects. Typical effects consist of splitting of degenerate energy levels classified initially according to irreducible representation of the initial symmetry group into less degenerate groups classified according to irreducible representation of the subgroup (the symmetry group of the perturbation) [47].

## Definition of the Subject

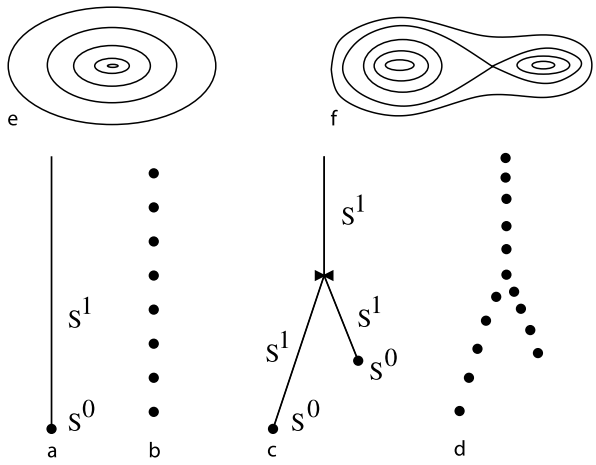
Quantum bifurcations (QB) are qualitative phenomena occurring in quantum systems under the variation of some internal or external parameters. In order to make this definition a little more precise we add the additional requirement: The qualitative modification of the "behavior" of a quantum system can be described as QB if it consists of the manifestation for the quantum system of the classical bifurcation presented in classical dynamic systems which is the classical analog of the initial quantum system. Quantum bifurcations are typical elementary steps leading from the simplest in some way effective Hamiltonian to more complicated ones under the variation of external or internal parameters. As internal parameters one may consider the values of exact or approximate integrals of motion. The construction of an effective Hamiltonian is typically based on the averaging and/or reduction procedure which results in the appearance of "good" quantum numbers (or approximate integrals of motion). The role of external parameters can be played by forces of external champs, phenomenological constants in the effective Hamiltonians, particle masses, etc. In order to limit the very broad field of qualitative changes and of possible quantum bifurcations in particular, we restrict ourselves mainly to quantum systems whose classical limit is associated with compact phase space and is nearly integrable. This means that for quantum problems the set of mutually commuting observables can be constructed within a reasonable physical approximation almost everywhere at least locally.

Quantum bifurcations are supposed to be universal phenomena which appear in generic families of quantum systems and explain how relatively simple behavior becomes complicated under the variation of some physical parameters. To know these elementary bricks responsible for increasing complexity of quantum systems under control parameter modifications is extremely important in order to make the extrapolation to regimes unaccessible to experimental study.

## Introduction

In order to better understand the manifestations of quantum bifurcations and their significance for concrete physical systems we start with the description of several simple model physical problems which exhibit in some sense the simplest (but nevertheless) generic behavior. Let us start with the harmonic oscillator. A one-dimensional harmonic oscillator has an equidistant system of eigenvalues. All eigenvalues can be labeled by consecutive integer quantum numbers which have the natural interpretation in terms of the number of zeros of eigenfunctions. The classical limit manifold (classical phase space) is a standard Euclidean 2-dimensional space with natural variables $\{p, q\}$. The classical Hamiltonian for the harmonic oscillator is an example of a Morse-type function which has only one stationary point $p = q = 0$ and all non-zero energy levels of the Hamiltonian are topological circles. If now we deform slightly the Hamiltonian in such a way that its classical phase portrait remains topologically the same, the spectrum of the quantum problem changes but it can be globally described as a regular sequence of states numbered consecutively by one integer and such description remains valid for any mass parameter value. Note, that for this problem increasing mass means increasing quantum state density and approaching classical behavior (classical limit).

More serious modification of the harmonic oscillator can lead, for example, to creation of new stationary points of the Hamiltonian. In classical theory this phenomenon is known as fold bifurcation or fold catastrophe [3,31]. The phase portrait of the classical problem changes qualitatively. As a function of energy the constant level set of the Hamiltonian has different topological structure (one circle, two circles, figure eight, circle and a point, or simply point). The quantum version of the same problem shows the existence of three different sequences




**Quantum Bifurcations, Figure 1**
**Classical and quantum bifurcations for a one degree-of-freedom system. Situations before (a,b,e) and after (c,d,f) the bifurcation are shown. a Energy map for harmonic oscillator-type system. Inverse images of each point are indicated. b Quantum state lattice for harmonic oscillator-type system. c Energy map after the bifurcation. Inverse images of each point are indicated. d Quantum state lattice after bifurcation represented as composed of three regular parts glued together. e Phase portrait for harmonic oscillator-type system. Inverse images are $S^1$ (generic inverse image) and $S^0$ (inverse image for minimal energy value). f Phase portrait after bifurcation**

of states which become clearly visible in the limit of the high density of states which can be reached by increasing the mass value parameter [42]. Such qualitative modification of the energy spectrum of the 1D-quantum Hamiltonian gives the simplest example of the phenomenon which can be described as a quantum bifurcation. Figure 1 shows a schematic representation of quantum bifurcations for a model system with one degree-of-freedom in parallel in quantum and classical mechanics.

After looking for one simple example we can formulate a more general question which concerns the appearance in more general quantum systems of qualitative phenomena which can be characterized as quantum bifurcations.

## Simplest Effective Hamiltonians

We turn now to several models which describe some specific classes of relatively simple real physical quantum systems formed by a finite number of particles (atoms, molecules, ...). Spectra of such quantum objects are studied nowadays with very high accuracy and this allows us to compare the behavior predicted by quantum bifurcations with the precise information about energy level structure found, for example, from high-resolution molecular spectroscopy.

Typically, the intra-molecular dynamics can be split into electronic, vibrational, and rotational ones due to important differences in characteristic energy excitations or in time scales. The most classical is the rotational motion and probably due to that the quantum bifurcations as a counterpart to classical bifurcations were first studied for purely rotational problems [59,61].

Effective rotational Hamiltonians describe the internal structure of rotational multiplets formed by isolated finite particle systems (atoms, molecules, nuclei) [35]. For many molecular systems in the ground electronic state any electronic and vibrational excitations are much more energy consuming as compared with rotational excitations. Thus, to study the molecular rotation the simplest physical assumption is to suppose that all electronic and all vibrational degrees-of-freedom are frozen. This means that a set of quantum numbers is given which have the sense of approximate integrals of motion specifying the character of vibrational and electronic motions in terms of these "good" quantum numbers. At the same time for a free molecule in the absence of any external fields due to isotropy of the space the total angular momentum $J$ and its projection $J_z$ on the laboratory fixed frame are strict integrals of motion. Consequently, to describe the rotational motion for fixed values of $J$ and $J_z$ it is sufficient to analyze the effective problem with only one degree-of-freedom. The dimension of classical phase space in this case equals two and the two classical conjugate variables are: the projection of the total angular momentum on the body fixed frame and conjugate angle variable. The classical phase space is topologically a two-dimensional sphere, $S^2$. There is a one-to-one correspondence between the points on a sphere and the orientation of the angular momentum in the body-fixed frame. Such a representation gives a clear visualization of a classical rotational Hamiltonian as a function defined over a sphere [35,49].

In quantum mechanics the rotation of molecules is traditionally described in terms of an effective rotational Hamiltonian which is constructed as a series in rotational operators $J_x$, $J_y$, $J_z$, the components of the total angular momentum $\mathbf{J}$. In a suitably chosen molecular fixed frame the effective Hamiltonian has the form

$$H_{\text{eff}} = AJ_x^2 + BJ_y^2 + CJ_z^2 + \sum c_{\alpha\beta\gamma} J_x^\alpha J_y^\beta J_z^\gamma + \cdots , \quad (1)$$

where $A$, $B$, $C$ and $c_{\alpha\beta\gamma}$ are constants. To relate quantum and classical pictures we note that $\mathbf{J}^2$ and energy are integrals of Euler's equations of motion for dynamic variables $J_x$, $J_y$, $J_z$. The phase space of the classical rotational problem with constant $|\mathbf{J}|$ is $S^2$, the two-dimensional sphere, and it can be parametrized with spherical

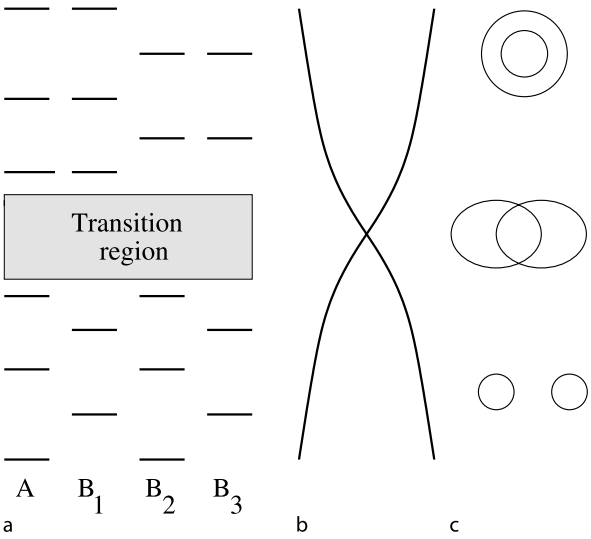
angles $(\theta, \phi)$ in such a way that the points on $S^2$ define the orientation of **J**, i. e. the position of the axis and the direction of rotation. To get the classical interpretation of the quantum Hamiltonian we introduce the classical analogs of the operators $J_x, J_y, J_z$

$$\mathbf{J} \longrightarrow \begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} \sqrt{J(J+1)} \qquad (2)$$

and consider the rotational energy as a function of the dynamical variables $(\theta, \phi)$ and the parameter $J$.

Thus, for an effective rotational Hamiltonian the corresponding classical symbol is a function $E_J(\theta, \phi)$ defined over $S^2$ and named usually the rotational energy surface [35].

Taking into account the symmetry imposed by the initial problem and the topology of the phase space the simplest rotational Hamiltonian can be constructed. In classical mechanics the simplest Hamiltonian can be defined (using Morse theory [55,88]) as a Hamiltonian function with the minimal possible number of non-degenerate stationary points compatible with the symmetry group action of the classical phase space. Morse theory in the presence of symmetry (or equivariant Morse theory) implies important restrictions on the number of minima, maxima, and saddle points. In the absence of symmetry the simplest Morse type function on the $S^2$ phase space has one minimum and one maximum, as a consequence of Morse inequalities. In the presence of non-trivial symmetry group action the minimal number of stationary points on the sphere increases. For example, many asymmetric top molecules (possessing three different moment of inertia of the equilibrium configuration) have $D_{2h}$ symmetry group [47]. This group includes rotations over $\pi$ around $\{x, y, z\}$ axes, reflections in $\{xy, yz, zx\}$ planes and inversion as symmetry operations. Any $D_{2h}$ invariant function on the sphere has at least six stationary points (two equivalent minima, two equivalent maxima, and two equivalent saddle points). This means that in quantum mechanics the asymmetric top has eigenvalues which form two regular sequences of quasi-degenerate doublets with the transition region between them. The correspondence between the quantum spectrum and the structure of the energy map for the classical problem is shown in Fig. 2. Highly symmetrical molecules which have cubic symmetry, for example, can be described by a simplest Morse-type Hamiltonian with 26 stationary points (6 and 8 minima/maxima and 12 saddle points). As a consequence, the corresponding quantum Hamiltonian shows the presence of six-fold and eight-fold quasi-degenerate clusters of rotational levels.




**Quantum Bifurcations, Figure 2**
**a Schematic representation of the energy level structure for asymmetric top molecule. *Vertical axis* corresponds to energy variation. Quantum levels are classified by the symmetry group of the asymmetric top. Two fold clusters at two ends of the rotational multiplet are formed by states with different symmetry. b Foliation of the classical phase space ($S^2$ sphere) by constant levels of the Hamiltonian given in the form of its Reeb graph. Each *point* corresponds to a connected component of the constant level set of the Hamiltonian (energy). c Geometric representation of the constant energy sections**

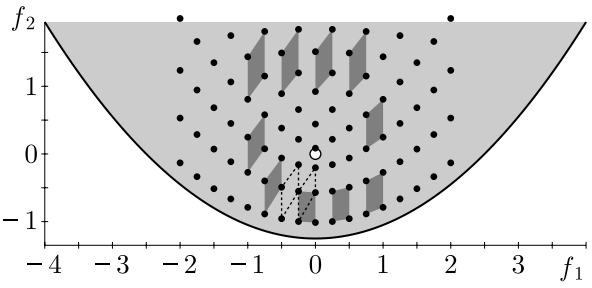
As soon as the simplest classical Hamiltonian is characterized by the appropriate system of stationary points the whole region of possible classical energy values (in the case of dynamical systems with only one degree-of-freedom the energy-momentum map becomes simply the energy map) appears to be split into different regions corresponding to different dynamical regimes, i. e. to different regions of the phase portrait foliated by topologically non-equivalent systems of classical trajectories. Accordingly, the energy spectrum of the corresponding quantum Hamiltonian can be qualitatively described as formed by regular sequences of states within each region of the classical energy map.

Quantum bifurcations are universal phenomena which lead to a new organization of the energy spectrum into qualitatively different regions in accordance with corresponding qualitative modifications of the classical energy-momentum map under the variation of some control parameter.

## Simplest Hamiltonians for Two Degree-of-Freedom Systems

When the quantum system has two or larger number of degrees-of-freedom the simplest dynamical regimes often correspond in classical mechanics to a quasi-regular dynamics which can be reasonably well approximated by an integrable model. The integrable model in classical mechanics can be constructed by normalizing the Hamiltonian and by passing to so-called normal forms [2,49]. The quantum counterpart of normalization is the construction of a mutually commuting set of operators which should not be mistaken with quantization of systems in normal form. Corresponding eigenvalues can be used as "good" quantum numbers to label quantum states. A joint spectrum of mutually commuting operators corresponds to the image of the energy-momentum map for the classical completely integrable dynamical problem. In this context the question about quantum bifurcations first of all leads to the question about qualitative classification of the joint spectra of mutually commuting operators. To answer this question we need to start with the qualitative description of foliations of the total phase space of the classical problem by common levels of integrals of motion which are mutually in involution [2,7]. One needs to distinguish the regular and the singular values of the energy-momentum map. For Hamiltonian systems the inverse images of the regular values are regular tori (one or several) [2]. A lot of different singularities are possible. In classical mechanics different levels of the classifications are studied in detail [7]. The diagram which represents the image of the classical EM map together with its stratification into regular and critical values is named the bifurcation diagram. The origin of such a name is due to the fact that the values of integrals of motion can be considered as control parameters for the phase portraits (inverse images of the EM map) of the reduced systems.

For quantum problems the analog of the classical stratification of the EM map for integrable systems is the splitting of the joint spectrum of several commuting observables into regions formed by regular lattices of joint eigenvalues. Any local simply connected neighborhood of a regular point of the lattice can be deformed into part of the regular $Z^n$ lattice of integers. This means that local quantum numbers can be consistently introduced to label states of the joint spectrum. If the regular region is not simply connected it still can be characterized locally by a set of "good" quantum numbers. At the same time this is impossible globally. Likewise in classical mechanics the Hamiltonian monodromy is the simplest obstruction to the existence of the global action-angle variables [17,57], in




**Quantum Bifurcations, Figure 3**
**Joint spectrum of two commuting operators together with the image of the classical EM map for the resonant 1 : (−1) oscillator given by (3). Quantum monodromy is seen as a result of transportation of the elementary cell of the quantum lattice along a close path through a non simply connected region of the regular part of the image of the EM map. Taken from [58]**

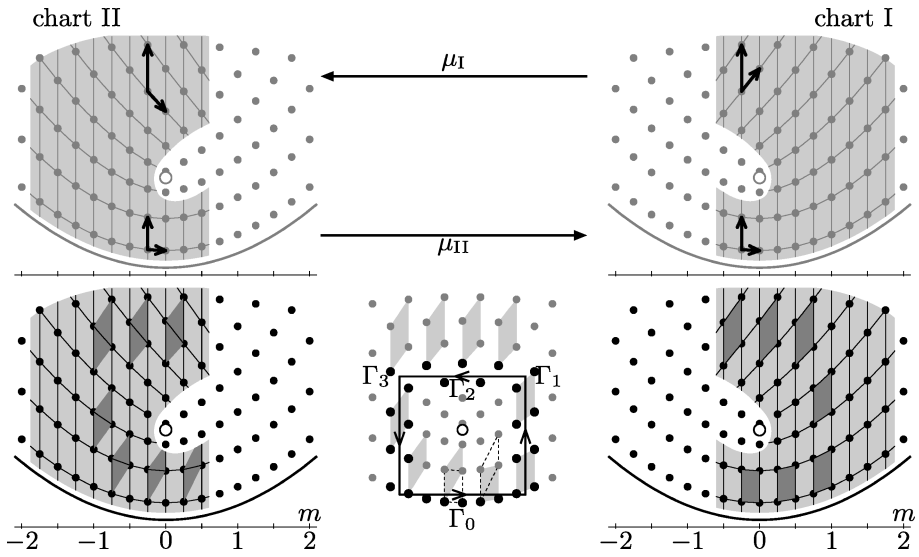
quantum mechanics the analog notion of quantum monodromy [14,33,68,80] characterizes the global non-triviality of the regular part of the lattice of joint eigenvalues. Figure 3 demonstrates the effect of the presence of a classical singularity (isolated focus-focus point) on the global properties of the quantum lattice formed by joint eigenvalues of two commuting operators for a simple problem with two degrees-of-freedom, which is essentially the $1 : (-1)$ resonant oscillator [58]. Two integrals of motions in this example are chosen as

$$f_1 = \frac{1}{2}\left(p_1^2 + q_1^2\right) - \frac{1}{2}\left(p_2^2 + q_2^2\right), \tag{3}$$

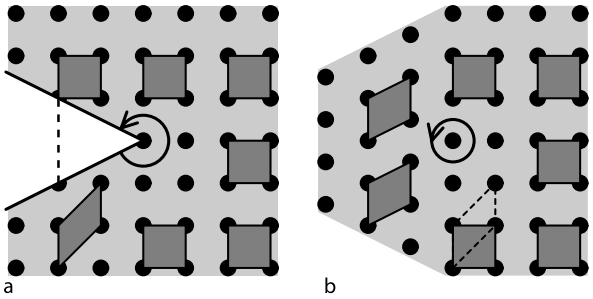
$$f_2 = p_1 q_2 + p_2 q_1 + \frac{1}{4}\left(p_1^2 + q_1^2 + p_2^2 + q_2^2\right)^2. \tag{4}$$

Locally in any simply connected region which does not include the classical singularity of the EM map situated at $f_1 = f_2 = 0$, the joint spectrum can be smoothly deformed to the regular $Z^2$ lattice [58,89]. Such lattices are shown, for example, in Fig. 4. If somebody wants to use only one chart to label states, it is necessary to take care in respect of the multivaluedness of such a representation. There are two possibilities:

(i) One makes a cut and maps the quantum lattice to a regular $Z^2$ lattice with an appropriate solid angle removed from it (see Fig. 5 [58,68,89]). Points on the boundary of such a cut should be identified and a special matching rule explaining how to cross the path should be introduced. Similar constructions are quite popular in solid state physics in order to represent defects of lattices, like dislocations, disclinations, etc. We just note that the "monodromy defect" introduced




**Quantum Bifurcations, Figure 4**
**Two chart atlas which covers the quantum lattice of the 1 : (−1) resonant oscillator system represented in Fig. 3. *Top plots* show the choice of basis cells and the gluing map between the charts. *Bottom plots* show the transport of the elementary cell (*dark gray quadrangles*) in each chart. *Central bottom panel* shows close path $\Gamma$ and its quantum realization (*black dots*) leading to non-trivial monodromy (compare with Fig. 3). Taken from [58]**



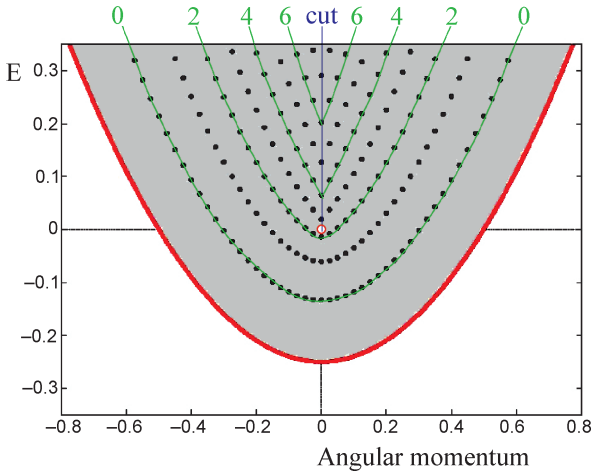

**Quantum Bifurcations, Figure 5**
**Construction of the 1 : (−1) lattice defect starting from the regular $Z^2$ lattice. The solid angle is removed from the regular $Z^2$ lattice and points on the so-obtained boundary are identified by vertical shifting. *Dark gray quadrangles* show the evolution of an elementary lattice cell along a closed path around the defect point. Taken from [58]**

in such a way is different from standard construction for dislocation and disclination defects [45,50]. The inverse procedure of the construction of the "monodromy defect" [89] from a regular lattice is represented in Fig. 5. Let us note that the width of the solid angle removed depends on the direction of the cut and the direction of the cut itself can be chosen in an ambiguous way.

(ii) An alternative possibility is to make a cut in such a way that the width of the removed angle becomes equal to zero. For focus-focus singularities one such direction always exists and is named an eigenray by Symington [75]. The same construction is used in some physical papers [10,11,84]. The inconvenience of such a procedure is the appearance of discontinuity of the slope of the constant action (quantum number) line at the cut, whereas the values of actions themselves are continued (see Fig. 6). This gives the wrong impression that this eigenray is associated with some special non-regular behavior of the initial problem, whereas there is no singularity except at one focus-focus point.

## Bifurcations and Symmetry

The general mathematical answer about the possible qualitative modifications of a system of stationary points of functions depending on some control parameters can be found in bifurcation (or catastrophe) theory [3,31,32]. It is important that the answer depends on the number of control parameters and on the symmetry. Very simple classification of possible typical bifurcations of stationary points of a one-parameter family of functions under presence of symmetry can be formulated for dynamical systems with one degree-of-freedom. The situation is particularly simple because the phase space is two-dimensional and the complete list of local symmetry groups (which are




**Quantum Bifurcations, Figure 6**

**Representation of the quantum joint spectrum for the "Mexican hat" potential $V(r) = ar^4 - br^2$ with the "cut" along the eigenray. For such a cut the left and the right limits at the cut give the same values of actions (good quantum numbers) but the lines of constant values of actions exhibit a "kink" at the cut (the discontinuity of the first derivative)**

the stabilizers of stationary points) includes only 2D-point groups [83]. It should be noted that the global symmetry of the problem can be larger than the local symmetry of the bifurcating stationary points. In such a case the bifurcations occur simultaneously for all points forming one orbit of the global symmetry group [51,52]. We describe briefly here (see Table 1) the classification of the bifurcations of stationary points in the presence of symmetry for families of functions depending on one parameter and associated quantum bifurcations [59,61]. Their notation includes the local symmetry group and several additional indexes which specify creation/annihilation of stationary points and the local or non-local character of the bifurcation. The list of possible bifurcations includes:

$C_1^{\pm}$ A non-symmetrical non-local bifurcation resulting in the appearance (+) or disappearance (−) of a stable-unstable pair of stationary points with the trivial local symmetry $C_1$. In the quantum problem this bifurcation is associated with the appearance or disappearance of a new regular sequence of states glued at its end with the intermediate part of another regular sequence of quantum states [42,77].

$C_2^{L\pm}$ A local bifurcation with the broken $C_2$ local symmetry. This bifurcation results either in appearance of a triple of points (two equivalent stable points with $C_1$ local symmetry and one unstable point with $C_2$ local symmetry) instead of one stable point with $C_2$ symmetry, or in inverse transformation. The number of stationary points in this bifurcation increases or decreases by two. For the quantum problem the result is the transformation of a local part of a regular sequence of states into one sequence of quasi-degenerate doublets.

$C_2^{N\pm}$ A non-local bifurcation with the broken $C_2$ local symmetry. This bifurcation results in appearance (+) or disappearance (−) of two new unstable points with broken $C_2$ symmetry and simultaneous transformation of the initially stable (for +) or unstable (for −) stationary point into an unstable/stable one. The number of stationary points in this bifurcation increases or decreases by two. For the quantum problem this means the appearance of a new regular sequence of states near the separatrix between two different regular regions.

$C_n^N$ $(n = 3, 4)$ A non-local bifurcation corresponding to passage of $n$ unstable stationary points through a stable stationary point with $C_n$ local symmetry which is accompanied with the minimum ↔ maximum change for a stable point with the $C_n$ local symmetry. The number of stationary points remains the same. For the quantum problem this bifurcation corresponds to transformation of the increased sequence of energy levels into a decreased sequence.

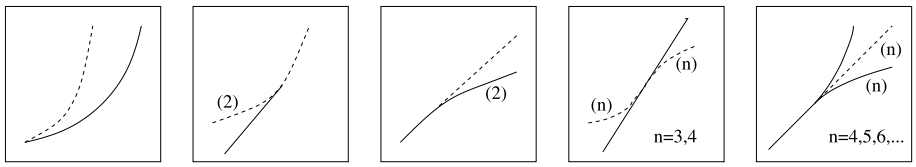
$C_n^{L\pm}$ $(n \geq 4)$ A local bifurcation which results in appearance (+) or disappearance (−) of $n$ stable and $n$ unstable stationary points with the broken $C_n$ symmetry and a simultaneous minimum ↔ maximum change of a stable point with the $C_n$ local symmetry. The number of stationary points increases or decreases by $2n$. In the quantum problem after bifurcation a new sequence of $n$-times quasi-degenerate levels appears/disappears.

Universal quantum Hamiltonians which describe the qualitative modification of the quantum energy level system around the bifurcation point are given in [59,61].

The presence of symmetry makes it much easier to observe the manifestation of quantum bifurcations. Modification of the local symmetry of stable stationary points results in the modification of the cluster structure of energy levels, i. e. the number and the symmetry types of energy level forming quasi-degenerate groups of levels. This phenomenon is essentially the spontaneous breaking of symmetry [51]. Several concrete molecular systems which show the presence of quantum bifurcations in rotational structure under rotational excitation are cited in Table 2. Many other examples can be found in [9,23,59,67,71,87,88,91,92] and references therein. In purely vibrational problems breaking dynamical $SU(N)$ symmetry of the isotrope harmonic oscillator till finite

**Quantum Bifurcations, Table 1**

**Bifurcations in the presence of symmetry. *Solid lines* denote stable stationary points. *Dashed lines* denote unstable stationary points. *Numbers in parenthesis* indicate the multiplicity of stationary points**




$C_1^{\pm}$ $C_2^{N\pm}$ $C_2^{L\pm}$ $C_n^N,\ n=3,4$ $C_n^{L\pm},\ n\geq 4$

**Quantum Bifurcations, Table 2**

**Molecular examples of quantum bifurcations in the rotational structure of individual vibrational components under the variation of the absolute value of angular momentum, *J*. $J_c$ is the critical value corresponding to bifurcation**

| Molecule | Component | $J_c$ | Bifurcation type |
|---|---|---|---|
| $SiH_4$ | $\nu_2(+)$ | 12 | $C_2^{N+}$ |
| $SnH_4$ | $\nu_2(-)$ | 10 | $C_2^{N+}, C_3^N, C_4^N, C_2^{N-}$ |
| $CF_4$ | $\nu_2(+)$ | 50 | $C_4^{L+}$ |
| $H_2Se$ | $\|0\rangle$ | 20 | $C_2^{L+}$ |

symmetry group results in formation of so-called nonlinear normal modes [23,54] or quasimodes [1], or local modes [9,25,38,39,43,46,48]. In the case of two degrees-of-freedom the analysis of the vibrational problem can be reduced to the analysis of the problem similar to the rotational one [35,66] and all the results about possible types of bifurcations found for rotational problems remain valid in the case of intra-molecular vibrational dynamics.

## Imperfect Bifurcations

According to general results the possible types of bifurcations which are generically present (and persist under small deformations) in a family of dynamical systems strictly depend on the number of control parameters. In the absence of symmetry only one bifurcation of stationary points is present for a one-parameter family of Morse-type functions, namely the formation (annihilation) of two new stationary points. This corresponds to saddle-node bifurcation for one degree-of-freedom Hamiltonian systems. The presence of symmetry increases significantly the number of possible bifurcations even for families with only one parameter [31,32]. From the physical point-of-view it is quite natural to study the effect of symmetry breaking on the symmetry allowed bifurcation. Decreasing symmetry naturally results in the modification of the allowed types of bifurcations but at the same time it is quite clear that at sufficient slight symmetry breaking perturbation the resulting behavior of the system should be rather close to the behavior of the original system with higher symmetry.

In the case of a small violation of symmetry the so-called "imperfect bifurcations" can be observed. Imperfect bifurcations, which are well known in the classical theory of bifurcations [32] consist of the appearance of stationary points in the neighborhood of another stationary point which does not change its stability. In some way one can say that imperfect bifurcation mimics generic bifurcation in the presence of higher symmetry by the special organization of several bifurcations which are generic in the presence of lower symmetry. Naturally quantum bifurcations follow the same behavior under the symmetry breaking as classical ones. Very simple and quite natural examples of imperfect quantum bifurcations were demonstrated on the example of the rotational structure modifications under increasing angular momentum [90]. The idea of appearance of imperfect bifurcations is as follows. Let us suppose that some symmetrical molecule demonstrates under the variation of angular momentum a quantum rotational bifurcation allowed by symmetry. The origin of this bifurcation is due, say, to centrifugal distortion effects which depend strongly on $J$ but are not very sensitive to small variation of masses even in the case of symmetry breaking isotopic substitution. In such a case a slight modification of the masses of one or several equivalent atoms breaks the symmetry and this symmetry violation can be made very weak due to the small ratio $\Delta M/M$ under isotope substitution. In classical theory the effect of symmetry breaking can be easily seen through the variation of the position of stationary points with control parameter. For example, instead of a pitchfork bifurcation which is typical for $C_2$ local symmetry, we get for the unsymmetrical problem (after slight breaking of $C_2$ symmetry) a smooth evolution of the position of one stationary point and the appearance of two new stationary points in fold catastrophe (see Fig. 7). In associated quantum bifurcations the most important effect is the splitting of clusters. But one should be careful with this interpretation because in quantum mechanics of finite particle systems the clusters are always split

due to quantum mechanical tunneling between different equivalent regions of localization of quantum wave functions. Intercluster splitting increases rapidly approaching the region of classical separatrix. The behavior of quantum tunneling was studied extensively in relation to the quantum breathers problem [6,29]. Systematic application of quasi-classical methods to reproduce quantum energy level structure near the singularities of the energy-momentum maps where exponentially small corrections are important is possible but requires special efforts (see for example [12]) and we will not touch upon this problem here.

## Organization of Bifurcations

The analysis of the quantum bifurcations in concrete examples of rotating molecules have shown that in some cases the molecule undergoes several consecutive qualitative changes which can be interpreted as a sequence of bifurcations which sometimes cannot even be separated into elementary bifurcations for the real scale of the control parameter [88]. One can imagine in principle that successive bifurcations lead to quantum chaos in analogy with classical dynamical systems where the typical scenario for the transition to chaos is through a sequence of bifurcations. Otherwise, the molecular examples were described with effective Hamiltonians depending only on one degree-of-freedom and the result of the sequence of bifurcations was just the crossover of the rotational multiplets [64]. In some sense such a sequence of bifurcations can be interpreted as an imperfect bifurcation assuming initially higher dynamical symmetry, like the continuous $SO(3)$ group.

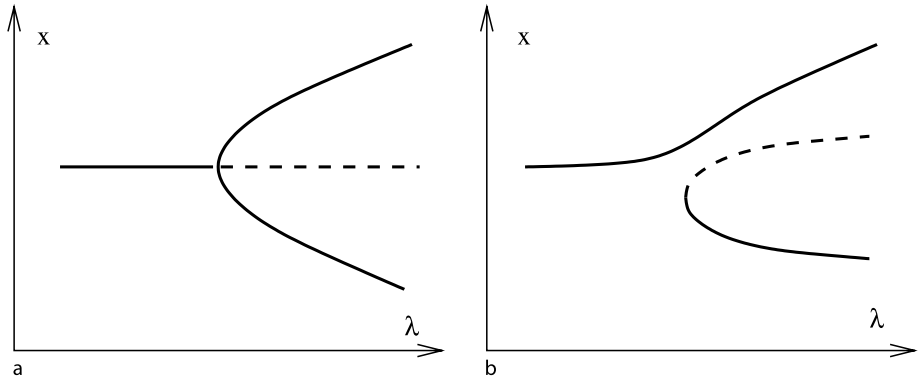
Later, a similar crossover phenomenon was found in a quite different quantum problem, like the hydrogen atom in external fields [24,53,72]. The general idea of such organization of bifurcations is based on the existence of two different limiting cases of dynamical regimes for the same physical quantum system (often under presence of the same symmetry group) which are qualitatively different. For example, the number of stationary points, or their stability differs. If $H_1$ and $H_2$ are two corresponding effective Hamiltonians, the natural question is: Is it possible to transform $H_1$ into $H_2$ by a generic perturbation depending on only one parameter? And if so, what is the minimal number of bifurcations to go through?

The simplest quantum system for which such a question becomes extremely natural is the hydrogen atom in the presence of external static electric ($F$) and magnetic ($G$) fields. Two natural limits – the Stark effect in the electric field and Zeeman effect in the magnetic field – show quite different qualitative structure even in the extremely low field limit [15,20,63,72,78]. Keeping a small field one can go from one (Stark) limit to another (Zeeman) and this transformation naturally goes through qualitatively different regimes [24,53]. In spite of the fact that the hydrogen atom (even without spin and relativistic corrections) is only a three degree-of-freedom system, the complete description of qualitatively different regimes in a small field limit is still not done and remains an open problem [24].

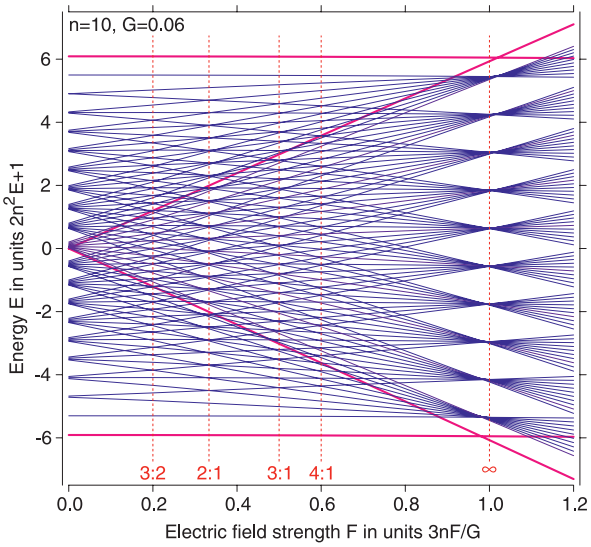
An example of clearly seen qualitative modifications of the quantum energy level system of the hydrogen atom under the variation of $F/G$ ratio of the strengths of two parallel electric and magnetic fields is shown in Fig. 8. The calculations are done for a two degree-of-freedom system after the normalization with respect to the global action. In quantum mechanics language this means that only energy levels which belong to the same $n$-shell of the hydrogen atom are treated and the interaction with other $n'$ shells is taken into account only effectively. The limiting classical phase space for this effective problem is the four-dimensional space $S^2 \times S^2$, which is the direct product of two two-dimensional spheres. In the presence of axial symmetry this problem is completely integrable and the Hamiltonian and the angular momentum provide a complete set of mutually commuting operators. Energies of stationary points of classical Hamiltonian limit are shown on the same Fig. 8 along with quantum levels. When one of the characteristic frequencies goes through zero, the so-called collapse phenomena occurs. Some other non-trivial resonance relations between two frequencies are also indicated. These resonances correspond to special organization of quantum energy levels. At the same time it is not necessary here to go to joint spectrum representation in order to see the reorganization of stationary points of the Hamiltonian function on $S^2 \times S^2$ phase space under the variation of the external control parameter $F/G$. A more detailed treatment of qualitative features of the energy level systems for the hydrogen atom in low fields is given in [15,20,24].

## Bifurcation Diagrams for Two Degree-of-Freedom Integrable Systems

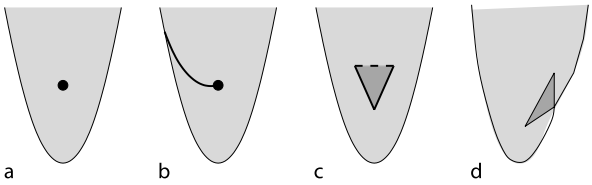
Let us consider now the two degree-of-freedom integrable system with compact phase space as a bit more complex but still reasonably simple problem. Many examples of such systems possess EM maps with the stratification of the image formed by the regular part surrounded by the singular boundary. The most naturally arising examples of classical phase spaces, like $S^2 \times S^2$, $CP^2$, are of that type. All internal points on the image of the EM map are regular in these cases. In practice, real physical problems, even




**Quantum Bifurcations, Figure 7**
**Imperfect bifurcations. a Position *x* of stationary points as a function of control parameter λ during a pitchfork bifurcation in the presence of $C_2$ local symmetry. b Modifications induced by small symmetry perturbation of lower symmetry. *Solid line*: Stable stationary points. *Dashed lines*: Unstable stationary points**




**Quantum Bifurcations, Figure 8**
**Reorganization of the internal structure of the *n*-multiplet of the hydrogen atom in small parallel electric and magnetic fields. Energies of stationary points of the classical Hamiltonian (*red solid lines*) are shown together with quantum energy levels (*blue solid lines*). The figure is done for $n = 10$ (there are $n^2 = 100$ energy levels forming this multiplet). As the ratio *F*/*G* of electric *F* and magnetic *G* fields varies this two degree-of-freedom system goes through different zones associated with special resonance relations between two characteristic frequencies (shown by *vertical dashed lines*). Taken from [24]**




**Quantum Bifurcations, Figure 9**
**Typical images of the energy momentum map for completely integrable Hamiltonian systems with two degrees-of-freedom in the case of: a integer monodromy, b fractional monodromy, c non-local monodromy, and d bidromy. Values in the *light shaded area* lift to single 2-tori; values in the *dark shaded area* lift to two 2-tori. Taken from [69]**

after necessary simplifications and approximations lead to more complicated models. Some examples of fragments of images of the EM map with internal singular points are shown in Fig. 9. In classical mechanics the inverse images of critical values are singular tori of different kinds. Some of them are represented in Fig. 10. Inverse images of critical points situated on the boundary of the EM image have lower dimension. They can be one-dimensional tori ($S^1$-circles), or zero-dimensional (points).

The natural question now is to describe typical generic modifications of the Hamiltonian which lead to qualitative modifications of the EM map image in classical mechanics and to associated modifications of the joint spectrum in quantum mechanics.

The simplest classical bifurcation leading to modification of the image of the EM map is the Hamiltonian Hopf bifurcation [79]. It is associated with the following modification of the image of the EM map. The critical value of the EM map situated on the boundary leaves the boundary and enters an internal domain of regular values (see Fig. 11)CE2. As a consequence, the toric fibration over the closed path surrounding an isolated singularity is non-trivial. Its non-triviality can be characterized by the Ham-



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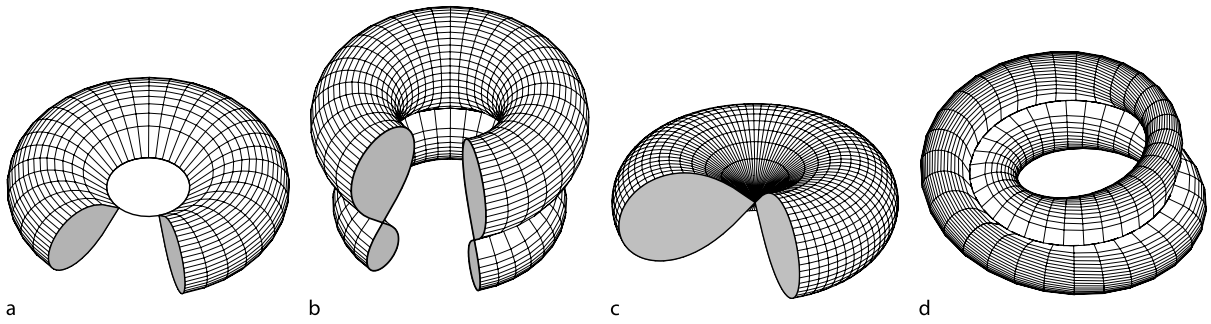
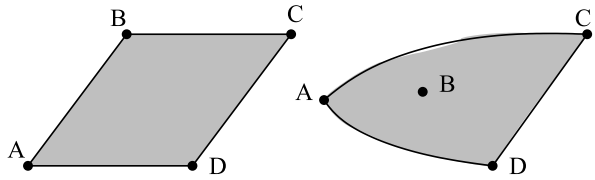



**Quantum Bifurcations, Figure 10**

**Two-dimensional singular fibers in the case of integrable Hamiltonian systems with two degrees-of-freedom (*left* to *right*): singular torus, bitorus, pinched and curled tori. Singular torus corresponds to critical values in Fig. 9c, d (ends of bitoris line). Bitorus corresponds to critical values in Fig. 9c, d, which belong to singular line (fusion of two components). Pinched torus corresponds to isolated focus-focus singularity in Fig. 9a. Curled torus is associated with critical values at singular line in Fig. 9b (fractional monodromy). Taken from [69]**




**Quantum Bifurcations, Figure 11**

**Qualitative modification of the image of the EM map due to Hamiltonian Hopf bifurcation. *Left*: Simplest integrable toric fibration over $S^2 \times S^2$ classical phase space. *A*, *B*, *C*, *D*: Critical values corresponding to singular $S^0$ fibers. Regular points on the boundary correspond to $S^1$ fibers. Regular internal points: Regular $T^2$ fibers. *Right*: Appearance of an isolated critical value inside the field of regular values. Critical value *B* corresponds to pinched torus shown in Fig. 10**

iltonian monodromy which describes the mapping from the fundamental group of the base space into the first homology group of the regular fiber [18]. A typical pattern of the joint spectrum around such a classical singularity is shown in Fig. 3. The joint spectrum manifests the presence of quantum monodromy. Its interpretation in terms of regular lattices is given in Figs. 4 and 5.

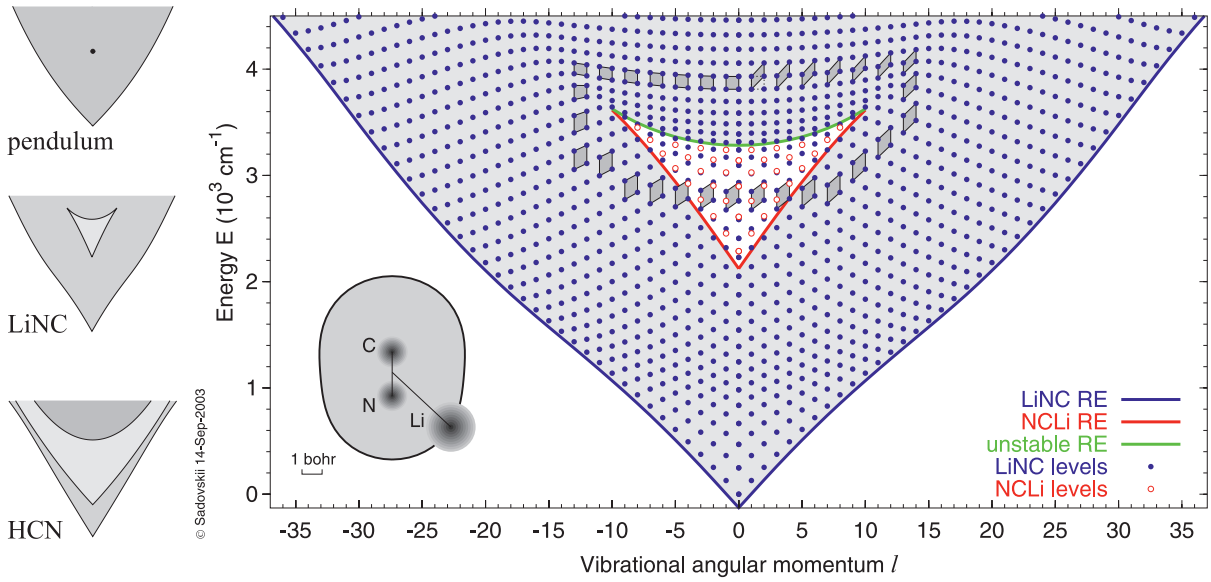
Taking into account additional terms of higher order it is possible to distinguish different types of Hamiltonian Hopf bifurcations usually named as subcritical and supercritical [19,79]. New qualitative modification, for example, corresponds to transformation of an isolated singular value of the EM map into an "island", i. e. the region of the EM image filled by points whose inverse images consist of two connected components. Integrable approximation for vibrational motion in the LiCN molecule shows the presence of such an island associated with the non-local quantum monodromy (see Fig. 12) [40]. The monodromy naturally coincides with the quantum monodromy of isolated focus-focus singularity which deforms continuously into the island monodromy. It is interesting to note that in molecule HCN which is rather similar to LiCN, the region with two components in the inverse image of the EM map exists also but the monodromy cannot be defined due to impossibility to go around the island [22].

In the quantum problem the presence of "standard" quantum monodromy in the joint spectrum of two mutually commuting observables can be seen through the mapping of a locally regular part of the joint spectrum lattice to an idealized $Z^2$ lattice. Existence of local actions for the classical problem which are defined almost everywhere and the multivaluedness of global actions from one side and the quantum-classical correspondence from another side allow the interpretation of the joint spectrum with quantum monodromy as a regular lattice with an isolated defect.

Recently, the generalization of the notion of quantum (and classical) monodromy was suggested [21,58]. For quantum problems the idea is based on the possibility to study instead of the complete lattice formed by the joint spectrum only a sub-lattice of finite index. Such a transformation allows one to eliminate certain "weak line singularities" presented in the image of the EM map. The resulting monodromy is named "fractional monodromy" because for the elementary cell in the regular region the formal transformation after a propagation along a close path crossing "weak line singularities" turns out to be represented in a form of a matrix with fractional coefficients.

An example of quantum fractional monodromy can be given with a $1:(-2)$ resonant oscillator system possessing two integrals of motion $f_1, f_2$ in involution:

$$f_1 = \frac{\omega}{2}\left(p_1^2 + q_1^2\right) - \frac{2\omega}{2}\left(p_2^2 + q_2^2\right) + R_1(q,p)\,, \qquad (5)$$




**Quantum Bifurcations, Figure 12**

**Quantum joint spectrum for the quantum model problem with two degrees-of-freedom describing two vibrations in the LiCN molecule. The non-local quantum monodromy is shown by the evolution of the elementary cell of the quantum lattice around the singular line associated with gluing of two regular lattices corresponding in molecular language to two different isomers, LiCN and LiNC. Classical limit (*left*) shows the possible deformation of isolated focus-focus singularity for pendulum to non-local island singularity for LiNC model. In contrast to LiCN, the HCN model has an infinite island which cannot be surrounded by a close path. Taken from [40]**

$$f_2 = \mathrm{Im}\left[(q_1 + ip_1)^2(q_2 + ip_2)\right] + R_2(q, p)\,. \qquad (6)$$

The corresponding joint spectrum for the quantum problem is shown in Fig. 13. It can be represented as a regular $Z^2$ lattice with a solid angle removed (see Fig. 14). The main difference with the standard integer monodromy representation is due to the fact that even after gluing two sides of the cut we get the one-dimensional singular stratum which can be neglected only after going to a sub-lattice (to a sub-lattice of index 2 for 1 : 2 fractional singularity).

Another kind of generalization of the monodromy notion is related to the appearance of multi-component inverse images for the EM maps. We have already mentioned such a possibility with the appearance of non-local monodromy and Hamiltonian Hopf bifurcations (see Fig. 12). But in this case two components of the inverse image belong to different regular domains and cannot be joined by a path going only through regular values. Another possibility is suggested in [69,70] and is explained schematically in Fig. 15. This figure shows that the arrangement of fibers can be done in such a way that one connected component can be deformed into another connected component along a path which goes only through regular tori. The existence of a quantum joint spectrum corresponding to such a classical picture was demonstrated on the example of a very well-known model problem with three degrees-of-freedom: Three resonant oscillators with 1 : 1 : 2 resonance, axial symmetry and with small detuning between double degenerate and non-degenerate modes [30,70]. The specific behavior of the joint spectrum for this model can be characterized as self-overlapping of a regular lattice. The possibility to propagate the initially chosen cell through a regular lattice from the region of self-overlapping of lattice back to the same region but to another component was named "bidromy". More complicated construction for the same problem allows us to introduce the "bipath" notion. The bipath starts at a regular point of the EM image, and crosses the singular line by splitting itself into two components CE3. Each component belongs to its proper lattice in the self-overlapping region. Two components of the path can go back through the regular region only and fuse together. The behavior of quantum cells along a bipath is shown in Fig. 16. Providing a rigorous mathematical description of such a construction is still an open problem. Although the original problem has three degrees-of-freedom, it is possible to construct a model system with two degrees-of-freedom and with similar properties.



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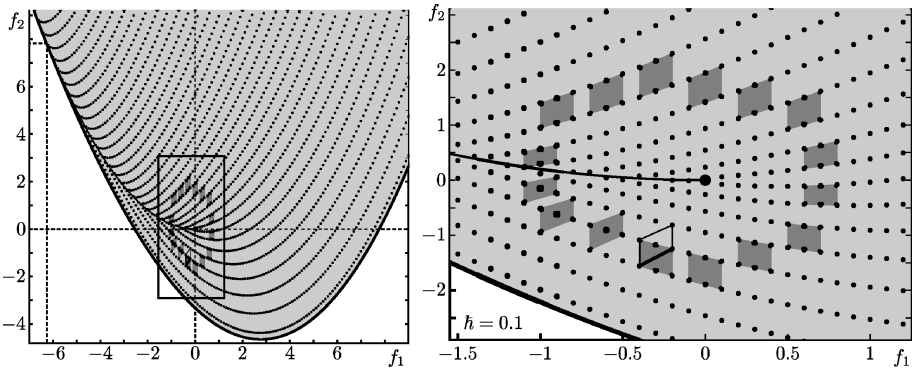
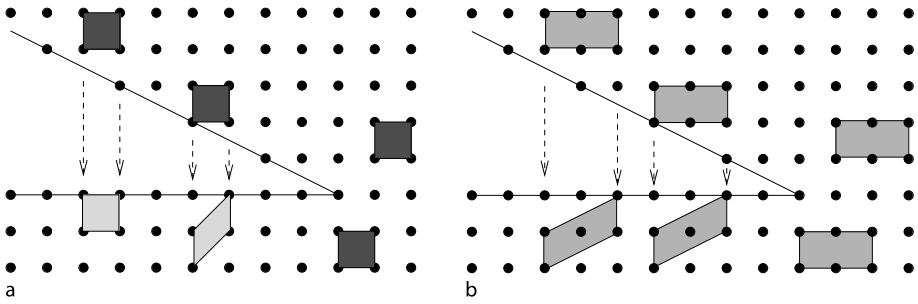
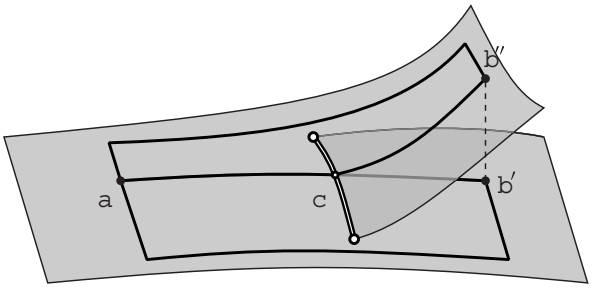



**Quantum Bifurcations, Figure 13**
**Joint quantum spectrum for two-dimensional non-linear 1 : (−2) resonant oscillator (5). The singular line is formed by critical values whose inverse images are curled tori shown in Fig. 10. In order to get the unambiguous result of the propagation of the cell of the quantum lattice along a closed path crossing the singular line, the elementary cell is doubled. Taken from [58]**




**Quantum Bifurcations, Figure 14**
**Representation of a lattice with 1 : 2 rational defect by cutting and gluing. *Left*: The elementary cell goes through cut in an ambiguous way. The result depends on the place where the cell crosses the cut. *Right*: Double cell crosses the cut in an unambiguous way. Taken from [58]**




**Quantum Bifurcations, Figure 15**
**Schematic representation of the inverse images for a problem with bidromy in the form of the unfolded surface. Each connected component of the inverse image is represented as a *single point*. The path $b' - a - b''$ starts and ends at the same point of the space of possible values of integrals of motion but it starts at one connected component and ends at another one. At the same time the path goes only through regular tori. Taken from [70]**

## Bifurcations of "Quantum Bifurcation Diagrams"

We want now to stress some differences in the role of internal and external control parameters. From one point-of-view a quantum problem, which corresponds in the classical limit to a multidimensional integrable classical model, possesses a joint spectrum qualitatively described by a "quantum bifurcation diagram". This diagram shows that the joint spectrum is formed from several parts of regular lattices through a cutting and gluing procedure. Going from one regular region to another is possible by crossing singular lines. The parameter defined along such a path can be treated as an internal control parameter. It is essentially a function of values of integrals of motion. To cross the singular line is equivalent to passing CE5 the quantum bifurcation for a family of reduced systems with a smaller number of degrees of freedom.

On the other side we can ask the following more general question. What kinds of generic modifications of "bi-

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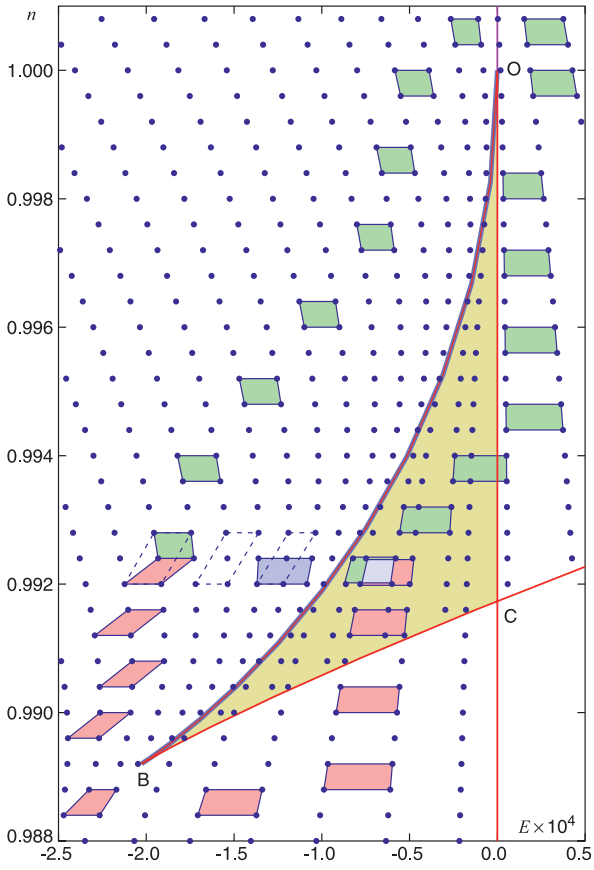


**Quantum Bifurcations, Figure 16**
**Joint quantum spectrum for problem with bidromy. Quantum states are given by two numbers (energy, *E*, and polyad number, *n*) which are the eigenvalues of two mutually commuting operators. Inside the *OAB* curvilinear triangle two regular lattices are clearly seen. One can be continued smoothly through the *OC* boundary whereas another continues CE4 through the *BC* boundary. This means that the regular part of the whole lattice can be considered as a one self-overlapping regular lattice. The figure suggests also the possibility to define the propagation of a double cell along a "bipath" through the singular line *BO* which leads to splitting of the cell into two elementary cells fusing at the end into one cell defining in such a way the "bidromy" transformation associated with a bipath. Taken from [70]**

furcation diagrams" are possible for a family of integrable systems depending on some external parameters? Hamiltonian Hopf bifurcation leading to the appearance of a new isolated singular value and as a consequence appearance of monodromy is just one of the possible effects of this kind. Another possibility is the transformation of an isolated focus-focus singular value into the island associated with the presence of a second connected component of the inverse image of the EM map. It is also possible that such an island is born within the regular region of the EM map. In such a case naturally the monodromy transformation associated with a closed path surrounding the so-obtained island should be trivial (identity).

The boundary of the image of the EM map can also undergo transformation which results in the appearance of the region with two components in the inverse image but, in contrast to the previous example of the appearance of an island, these two components can be smoothly deformed one onto CE6 another along a continuous path going only through regular values of the EM map. Examples of all such modifications were studied on simple models inspired by concrete quantum molecular systems like the H atom, $CO_2$, LiCN molecules and so on [24,30,40].

## Semi-Quantum Limit and Reorganization of Quantum Bands

Up to now we have discussed the qualitative modifications of internal structures of certain groups of quantum levels which are typically named bands. Their appearance is physically quite clear in the adiabatic approximation. The existence of fast and slow classical motions manifests itself in quantum mechanics through the formation of so-called energy bands. The big energy difference between energies of different bands correspond to fast classical variables whereas small energy differences between energy levels belonging to the same band correspond to classical slow variables. Typical bands in simple quantum systems correspond to vibrational structure of different electronic states, rotational structure of different vibrational states, etc.

If now we have a quantum problem which shows the presence of bands in its energy spectrum, the natural generalization consists of putting this quantum system in a family, depending on one (or several) control parameters. What are the generic qualitative modifications which can be observed within such a family of systems when control parameters vary? Apart from qualitative modifications of the internal structure of individual bands which can be treated as the earlier discussed quantum bifurcations, another qualitative phenomenon is possible, namely the redistribution of energy levels between bands or more generally, the reorganization of bands under the variation of some control parameters [8,26,28,62,68]. In fact this phenomenon is very often observed in both the numerical simulations and the real experiments with molecular systems exhibiting bands. A typical example of molecular rovibrational energy levels classified according to their energy and angular momentum is shown in Fig. 17. It is important to note that the number of energy levels in bands before and after their "intersection" changes.



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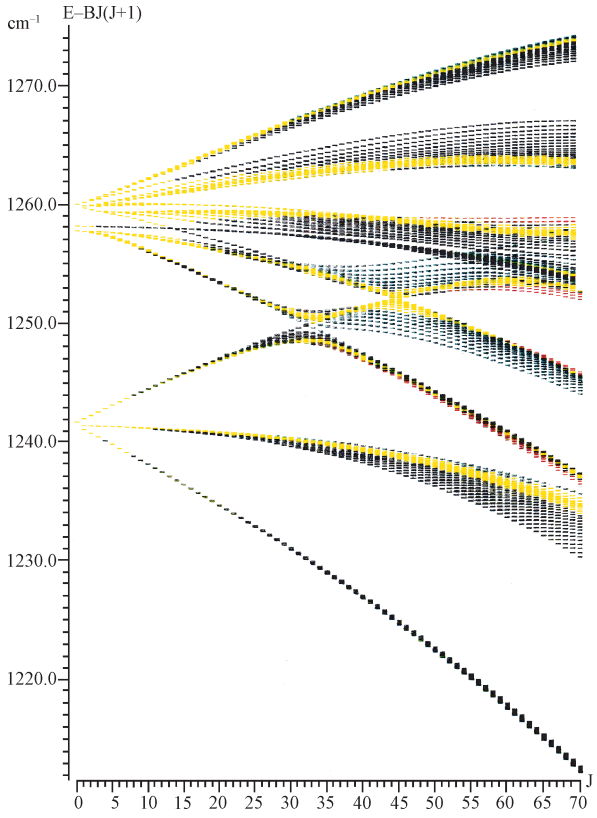



**Quantum Bifurcations, Figure 17**

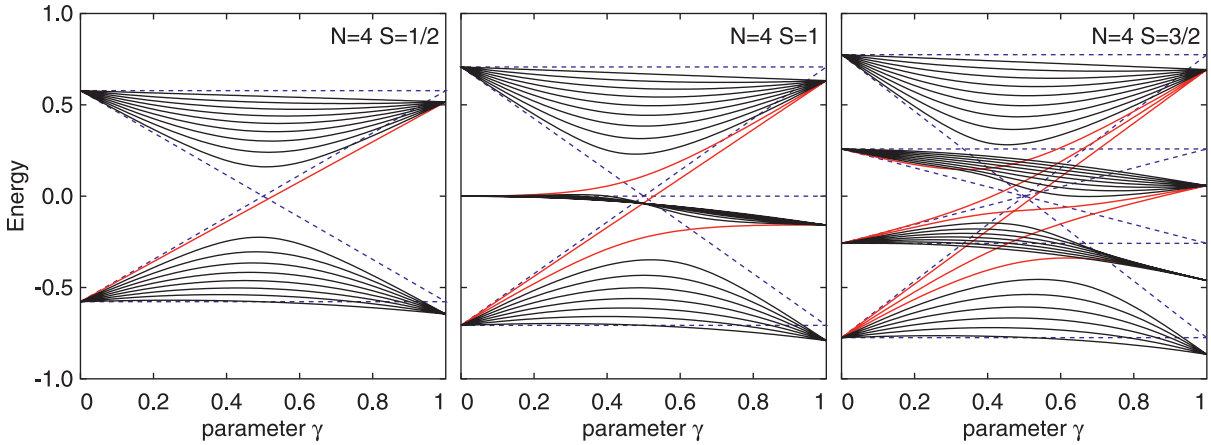
**System of rovibrational energy levels of $^{13}CF_4$ molecule represented schematically in $E$, $J$ coordinates. The number of energy levels in each clearly seen band is $2J + 1 + \delta$, where $\delta$ is a small integer which remains constant for isolated bands and changes at band intersections. In the semi-quantum model $\delta$ is interpreted as the first Chern class, characterizing the non-triviality of the vector bundle formed by eigenfunctions of the "fast" subsystem over the classical phase space of the "slow" subsystem [27]**

The same phenomenon of the redistribution of energy levels between energy bands can be understood by the example of a much simpler quantum system of two coupled angular momenta, say orbital angular momentum and spin in the presence of a magnetic field interacting only with spin [62,68].

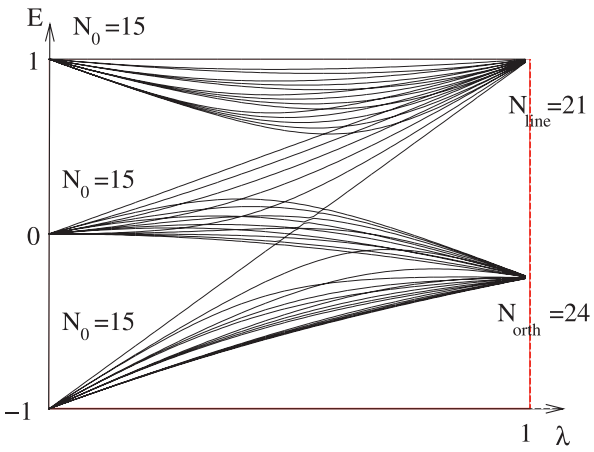
$$H = \frac{1-\gamma}{\mathbf{S}} S_z + \frac{\gamma}{\mathbf{NS}} (\mathbf{N}\cdot\mathbf{S}) , \quad 0 \le \gamma \le 1 . \qquad (7)$$

The Hamiltonian for such a system can be represented in the form of a one-parameter family (7) having two natural limits corresponding to uncoupled and coupled angular momenta. The interpolation of eigenvalues between these two limits is shown in Fig. 18 for different values of spin quantum number, $S = 1/2, 1, 3/2$. The quantum number of orbital momentum is taken to be $N = 4$. Although this value is not much larger than the $S$ values, the existence of bands and their reorganization under the variation of the external parameter $\gamma$ is clearly seen in the figure.

Although the detailed description of this reorganization of bands will take us rather far away from the principal subject it is important to note that in the simplest situations there exists a very close relation between the redistribution phenomenon and the Hamiltonian Hopf bifurcations leading to the appearance of Hamiltonian monodromy [81]. In the semi-quantum limit when part of the dynamical variables are treated as purely classical and all the rest as quantum, the description of the complete system naturally leads to a fiber bundle construction [27]. The role of the base space is taken by the classical phase space for classical variables. A set of quantum wave-functions associated with one point of the base space forms a complex fiber. As a whole the so-obtained vector bundle with complex fibers can be topologically characterized by its rank and Chern classes [56]. Chern classes are related to the number of quantum states in bands formed due to quantum character of the total problem with respect to "classical" variables. Modification of the number of states in bands can occur only at band contact and is associated with the modification of Chern classes of the corresponding fiber bundle [26]. The simplest situation takes place when the number of degrees of freedom associated with classical variables is one. In this case only one topological invariant – the first Chern class is sufficient to characterize the non-triviality of the fiber bundle and the difference in Chern classes is equal to the number of energy levels redistributed between corresponding bands. Moreover, in the generic situation (in the absence of symmetry) the typical behavior consists of the redistribution of only one energy level between two bands. The generic phenomena become more complicated with increasing the number of degrees of freedom for the classical part of variables. The model problem with two slow degrees of freedom (described in classical limit by the $CP^2$ phase space) and three quantum states was studied in [28]. A new qualitative phenomenon was found, namely, the modification of the number of bands due to formation of topologically coupled bands. Figure 19 shows the evolution of the system of energy levels along with the variation of control parameter $\lambda$. Three quantum bands (at $\lambda = 0$) transform into two bands (in the $\lambda = 1$) limit. One of these bands has rank one, i. e. it is associated with one quantum state. Another has rank two. It is associated with two quantum states. Both bands have non-trivial topology (non-trivial Chern classes). Moreover, it is quite important that the newly formed topologically coupled band of rank two can




**Quantum Bifurcations, Figure 18**
**Rearrangement of energy levels between bands for model Hamiltonian (7) with two, three, or four states for "fast" variable. Quantum energy levels are shown by *solid lines*. Classical energies of stationary points for energy surfaces are shown by *dashed lines*. Taken from [68]**




**Quantum Bifurcations, Figure 19**
**Rearrangement of three bands into two topologically non-trivially coupled bands. Example of a model with three electronic states and vibrational structure of polyads formed by three quasi-degenerate modes. At $\lambda = 0$ three bands have each the same number of states, namely 15. In the classical limit each initial band has rank one and trivial topology. At $\lambda = 1$ there are only two bands. One of them has rank 2 and non-trivial first and second Chern classes. Taken from [28]**

be split into two bands of rank one only if a coupling with the third band is introduced.

The corresponding qualitative modifications of quantum spectra can be considered as natural generalizations of quantum bifurcations and probably should be treated as topological bifurcations. Thus, the description of possible "elementary" rearrangements of energy bands is a direct consequence of topological restrictions imposed by a fiber bundle structure of the studied problem.

It is interesting to mention here the general mathematical problem of finding proper equivalence or better to say correspondence between some construction made over real numbers and their generalizations to complex numbers and quaternions. This paradigm of complexification and quaternization was discussed by Arnold [4,5] on many different examples. The closest to the present subject is the example of complexification of the Wigner–Neumann non-crossing rule resulting in a quantum Hall effect (in physical terms). In fact, the mathematical basis of the quantum Hall effect is exactly the same fiber bundle construction which explains the redistribution of energy levels between bands in the above-mentioned simple quantum mechanical model.

## Multiple Resonances and Quantum State Density

Rearrangement of quantum energy states between bands is presented in the previous section as an example of a generic qualitative phenomenon occurring under variation of a control parameter. One possible realization of bands is the sequence of vibrational polyads formed by a system of resonant vibrational modes indexed by the polyad quantum number. In the classical picture this construction corresponds to the system of oscillators reduced with respect to the global action. The reduced classical phase space is in such a case the weighted projective space. In the case of particular $1 : 1 : \ldots : 1$ resonance the corresponding reduced phase space is a normal complex projec-

tive space $CP^n$. The specific resonance conditions impose for a quantum problem specific conditions on the numbers of quantum states in polyads. In the simplest case of harmonic oscillators with $n_1 : n_2 : \ldots : n_k$ resonance the numbers of states in polyads are given by the generating function

$$g = \frac{1}{(1-t^{n_1})(1-t^{n_2})\cdots(1-t^{n_k})} = \sum_N C_N\, t^N\,, \quad (8)$$

where $N$ is the polyad quantum number. Numbers $C_N$ are integers for integer $N$ values, but they can be extended to arbitrary $N$ values and represented in the form of a quasi-polynomial, i.e, a polynomial in $N$ with coefficients being a periodic function whose CE7 period equals the least common multiplier of $n_i, i = 1, \ldots, k$. Moreover, the coefficients of the polynomial can be expressed in terms of so-called Todd polynomials which indicates the possibility of topological interpretation of such information [52,88].

## Physical Applications and Generalizations

The most clearly seen physical applications of quantum bifurcations is the qualitative modification of the rotational multiplet structure under rotational excitation, i. e. under the variation of the absolute value of the angular momentum. This is related first of all with the experimental possibility to study high $J$ multiplets (which are quite close to the classical limit but nevertheless manifest their quantum structure) and to the possibility to use symmetry arguments, which allow one to distinguish clusters of states before and after bifurcation just by counting the number of states in the cluster, which depends on the order of group of stabilizer. Nuclear rotation is another natural example of quantum rotational bifurcations [60]. Again the interest in corresponding qualitative modifications is due to the fact that rotational bands are extremely well studied up to very high $J$ values. But in contrast to molecular physics examples, in nuclear physics it mostly happens that only ground states (for each value of $J$) are known. Thus, one speaks more often about qualitative changes of the ground state (in the absence of temperature) named quantum phase transitions [65].

Internal structure of vibrational polyads is less evident for experimental verifications of quantum bifurcations, but it gives many topologically non-trivial examples of classical phase spaces on which the families of Hamiltonians depending on parameters are defined [25,30,38, 41,44,46,66,76,77,85]. The main difficulty here is the small number of quantum states in polyads accessible to experimental observations. But this problem is extremely interesting from the point-of-view of extrapolation of theoretical results to the region of higher energy (or higher polyad quantum numbers) which is responsible as a rule for many chemical intra-molecular processes. Certain molecules, like $CO_2$, or acetylene ($C_2H_2$) are extremely well studied and a lot of highly accurate data exist. At the same time the qualitative understanding of the organization of excited states even in these molecules is not yet completed and new qualitative phenomena are just starting to be discovered.

Among other physically interesting systems it is necessary to mention model problems suggested to study the behavior of Bose condensates or quantum qubits [36,37, 74,82]. These models have a mathematical form which is quite similar to rotational and vibrational models. At the same time their physical origin and the interpretation of results is quite different. This is not an exception. For example, the model Hamiltonian corresponding in the classical limit to a Hamiltonian function defined over $S^2$ classical phase space is relevant to rotational dynamics, description of internal structure of vibrational polyads formed by two (quasi)degenerate modes, in particular to so-called local-normal mode transition in molecules, interaction of electromagnetic field with a two-level system, the Lipkin–Meshkov–Glick model in nuclear physics, entanglement of qubits, etc.

## Future Directions

To date many new qualitative phenomena have been suggested and observed in experimental and numerical studies due to intensive collaboration between mathematicians working in dynamical system theory, classical mechanics, complex geometry, topology, etc., and molecular physicists using qualitative mathematical tools to classify behavior of quantum systems and to extrapolate this behavior from relatively simple (low energy regions) to more complicated ones (high energy regions). Up to now the main accent was placed on the study of the qualitative features of isolated time-independent molecular systems. Specific patterns formed by energy eigenvalues and by common eigenvalues of several mutually commuting observables were the principal subject of study. Existence of qualitatively different dynamical regimes for time-independent problems at different values of exact or approximate integrals of motion were clearly demonstrated. Many of these new qualitative features and phenomena are supposed to be generic and universal although their rigorous mathematical formulation and description is still absent.

On the other side, the analysis of the time-dependent processes should be developed. This step is essential in order to realize at the level of quantum micro-systems



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the transformations associated with the qualitative modifications of dynamical regimes and to control such time-dependent processes as elementary reactions, information data storage, and so on. From this global perspective the main problem of the future development is to support the adequate mathematical formulation of qualitative methods and to improve our understanding of qualitative modifications occurring in quantum micro-systems in order to use them as real micro-devices.

## Bibliography

### Primary Literature


1. Arnold VI (1972) Modes and quasimodes. Funct Anal Appl 6:94–101
2. Arnold VI (1989) Mathematical methods of classical mechanics. Springer, New York
3. Arnold VI (1992) Catastrophe theory. Springer, TS8
4. Arnold VI (1995) Remarks on eigenvalues and eigenvectors of Hermitian matrices, Berry phase, adiabatic connections and quantum Hall effect. Selecta Math New Ser 1:1–19
5. Arnold VI (2005) Arnold's problems. Springer, TS8
6. Aubry S, Flach S, Kladko K, Olbrich E (1996) Manifestation of classical bifurcation in the spectrum of the integrable quantum dimer. Phys Rev Lett 76:1607–1610
7. Bolsinov AV, Fomenko AT (2004) Integrable Hamiltonian systems. In: TS9 Geometry Topology Classifications. Chapman and Hall/CRC, TS8
8. Brodersen S, Zhilinskiĭ BI (1995) Transfer of clusters between the vibrational components of $CF_4$. J Mol Spectrosc 169:1–17
9. Child MS (2000) In: Jensen P, Bunker PR (eds) Computational molecular spectroscopy, chapter 18. Wiley Interscience, Chichester
10. Child MS (2001) Quantum level structure and nonlinear classical dynamics. J Mol Spectrosc 210:157–165
11. Child MS, Weston T, Tennyson J (1999) Quantum monodromy in the spectrum of $H_2O$ and other systems. Mol Phys 96: 371–379
12. Colin de Verdier Y, Vũ Ngoc S (2003) Singular Bohr–Sommerfeld rules for 2D integrable systems. Ann Ec Norm Sup 36:1–55
13. Cushman RS, Bates L (1997) Global aspects of classical integrable systems. Birkhäuser, Basel
14. Cushman RH, Duistermaat JJ (1988) The quantum mechanical spherical pendulum. Bull Am Math Soc 19:475–479
15. Cushman RH, Sadovskiĭ DA (2000) Monodromy in the hydrogen atom in crossed fields. Physica D 142:166–196
16. Dirac PAM (1982) The principles of quantum mechanics. Oxford University Press, TS8
17. Duistermaat JJ (1980) On global action angle coordinates. Comm Pure Appl Math 33:687–706
18. Duistermaat JJ (1998) The monodromy in the Hamiltonian Hopf bifurcation. Angew Z Math Phys 49:156–161
19. Efstathiou K (2004) Metamorphoses of Hamiltonian systems with symmetry. In: TS9 Lecture Notes in Mathematics, vol 1864. Springer, Heidelberg
20. Efstathiou K, Cushman RH, Sadovskiĭ DA (2004) Hamiltonian Hopf bifurcation of the hydrogen atom in crossed fields. Physica D 194:250–274
21. Efstathiou K, Cushman RH, Sadovskiĭ DA (2007) Fractional monodromy in the 1 : −2 resonance. Adv Math 209:241–273
22. Efstathiou K, Joyeux M, Sadovskiĭ DA (2004) Global bending quantum number and the absence of monodromy in the HCN↔CNH molecule. Phys Rev A 69(3):032504-1–15
23. Efstathiou K, Sadovskiĭ DA, Zhilinskiĭ BI (2004) Analysis of rotation-vibration relative equilibria on the example of a tetrahedral four atom molecule. SIAM J Dyn Syst 3:261–351
24. Efstathiou K, Sadovskiĭ DA, Zhilinskiĭ BI (2007) Classification of perturbations of the hydrogen atom by small static electric and magnetic fields. Proc Roy Soc Lond A 463:1771–1790
25. Ezra GS (1996) Periodic orbit analysis of molecular vibrational spectra: Spectral patterns and dynamical bifurcations in Fermi resonant systems. J Chem Phys 104:26–35
26. Faure F, Zhilinskiĭ BI (2000) Topological Chern indices in molecular spectra. Phys Rev Lett 85:960–963
27. Faure F, Zhilinskiĭ BI (2001) Topological properties of the Born–Oppenheimer approximation and implications for the exact spectrum. Lett Math Phys 55:219–238
28. Faure F, Zhilinskiĭ BI (2002) Topologically coupled energy bands in molecules. Phys Lett A 302:242–252
29. Flach S, Willis CR (1998) Discrete breathers. Phys Rep 295: 181–264
30. Giacobbe A, Cushman RH, Sadovskiĭ DA, Zhilinskiĭ BI (2004) Monodromy of the quantum 1 : 1 : 2 resonant swing spring. J Math Phys 45:5076–5100
31. Gilmore R (1981) Catastrophe theory for scientists and engineers. Wiley, New York
32. Golubitsky M, Schaeffer DG (1984) Singularities and groups in bifurcation theory, vol 1. Springer, Berlin
33. Grondin L, Sadovskiĭ DA, Zhilinskiĭ BI (2002) Monodromy in systems with coupled angular momenta and rearrangement of bands in quantum spectra. Phys Rev A 142:012105-1–15
34. Guillemin V (1994) Moment maps and combinatorial invariants of Hamiltonian $T^n$-spaces. Birkhäuser, Basel
35. Harter W (1988) Computer graphical and semiclassical approaches to molecular rotations and vibrations. Comput Phys Rep 8:319–394
36. Hines AP, McKenzie RH, Milburn GJ (2005) Quantum entanglement and fixed-point bifurcations. Phys Rev A 71:042303-1–9
37. Hou X-W, Chen J-H, Hu B (2005) Entanglement and bifurcation in the integrable dimer. Phys Rev A 71:034302-1–4
38. Joyeux M, Farantos SC, Schinke R (2002) Highly excited motion in molecules: Saddle-node bifurcations and their fingerprints in vibrational spectra. J Phys Chem A 106:5407–5421
39. Joyeux M, Grebenschikov S, Bredenbeck J, Schinke R, Farantos SC (TS10) Intramolecular dynamics along isomerization and dissociation pathways. In: TS9 Geometric Structures of Phase Space in Multidimensional Chaos: A Special Volume of Advances in Chemical Physics, part A, vol 130. TS11, TS8, pp 267–303
40. Joyeux M, Sadovskiĭ DA, Tennyson J (2003) Monodromy of the LiNC/NCLi molecule. Chem Phys Lett 382:439–442
41. Joyeux M, Sugny D, Tyng V, Kellman ME, Ishikawa H, Field RW, Beck C, Schinke R (2000) Semiclassical study of the isomerization states of HCP. J Chem Phys 112:4162–4172
42. Kais GRS, Levine RD (1986) Quantum cusp. Phys Rev A 34: 2442–2452
43. Kellman ME (1995) Algebraic models in spectroscopy. Annu Rev Phys Chem 46:395–422




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44. Kellman ME, Lynch ED (1986) Fermi resonance phase space structure from experimental spectra. J Chem Phys 85:7216–7223
45. Kleman M (1983) Points, lines and walls. Wiley, Chichester
46. Kozin IN, Sadovskií DA, Zhilinskií BI (2005) Assigning vibrational polyads using relative equilibria: Application to ozone. Spectrochim Acta A 61:2867–2885
47. Landau L, Lifschits EM (1981) Quantum mechanics, nonrelativistic theory. Elsevier, TS8
48. Lu Z-M, Kellman ME (1997) Phase space structure of triatomic molecules. J Chem Phys 107:1–15
49. Marsden JE, Ratiu TS (1994) Introduction to mechanics and symmetry. Springer, TS8
50. Mermin ND (1979) The topological theory of defects in ordered media. Rev Mod Phys 51:591–648
51. Michel L (1980) Symmetry defects and broken symmetry, configurations, hidden symmetry. Rev Mod Phys 52:617–651
52. Michel L, Zhilinskií BI (2001) Symmetry, invariants, topology, vol I. Basic tools. Phys Rep 341:11–84
53. Michel L, Zhilinskií BI (2001) Symmetry, invariants, topology, vol III. Rydberg states of atoms and molecules. Basic group theoretical and topological analysis. Phys Rep 341:173–264
54. Montaldi J, Roberts R, Stewart I (1988) Periodic solutions near equilibria of symmetric Hamiltonian systems. Philos Trans Roy Soc Lond A 325:237–293
55. Morse M (1925) Relation between the critical points of a real function of *n* independent variables. Trans Am Math Soc 27:345–396
56. Nakahara M (1990) Geometry, topology and physics. IOP Publishing, Bristol
57. Nekhoroshev NN (1972) Action-angle variables and their generalizations. Trans Moscow Math Soc 26:180–198
58. Nekhoroshev NN, Sadovskií DA, Zhilinskií BI (2006) Fractional Hamiltonian monodromy. Ann Henri Poincaré 7:1099–1211
59. Pavlichenkov I (1993) Bifurcations in quantum rotational spectra. Phys Rep 226:173–279
60. Pavlichenkov I (2006) Quantum bifurcations and quantum phase transitions in rotational spectra. Phys At Nucl 69: 1008–1013
61. Pavlichenkov I, Zhilinskií BI (1988) Critical phenomena in rotational spectra. Ann Phys NY 184:1–32
62. Pavlov-Verevkin VB, Sadovskií DA, Zhilinskií BI (1988) On the dynamical meaning of the diabolic points. Europhys Lett 6:573–578
63. Peters AD, Jaffe C, Gao J, Delos JB (1997) Quantum manifestations of bifurcations of closed orbits in the photodetachment cross section of $H^-$ in parallel fields. Phys Rev A 56:345–355
64. Pierre G, Sadovskií DA, Zhilinskií BI (1989) Organization of quantum bifurcations: Crossover of rovibrational bands in spherical top molecules. Europhys Lett 10:409–414
65. Sachdev S (1999) Quantum phase transitions. Cambridge University Press, TS8
66. Sadovskií DA, Fulton NG, Henderson JR, Tennyson J, Zhilinskií BI (1993) Nonlinear normal modes and local bending vibrations of H3+ and D3+. J Chem Phys 99(2):906–918
67. Sadovskií DA, Zhilinskií BI (1993) Group theoretical and topological analysis of localized vibration-rotation states. Phys Rev A 47(4):2653–2671
68. Sadovskií DA, Zhilinskií BI (1999) Monodromy, diabolic points, and angular momentum coupling. Phys Lett A 256:235–244
69. Sadovskií DA, Zhilinskií BI (2006) Quantum monodromy, its generalizations and molecular manifestations. Mol Phys 104:2595–2615
70. Sadovskií DA, Zhilinskií BI (2007) Hamiltonian systems with detuned 1 : 1 : 2 resonance, manifestations of bidromy. Ann Phys NY 322:164–200
71. Sadovskií DA, Zhilinskií BI, Champion JP, Pierre G (1990) Manifestation of bifurcations and diabolic points in molecular energy spectra. J Chem Phys 92:1523–1537
72. Sadovskií DA, Zhilinskií BI, Michel L (1996) Collapse of the Zeeman structure of the hydrogen atom in an external electric field. Phys Rev A 53:4064–4047
73. Simon B (1980) The classical limit of quantum partition functions. Commun Math Phys 71:247–276
74. Somma R, Ortiz G, Barnum H, Knill E, Viola L (2004) Nature and measure of entanglement in quantum phase transitions. Phys Rev A 70:042311-1–21
75. Symington M (2003) Four dimensions from two in symplectic topology. In: Athens GA (ed) Topology and geometry of manifolds. Proc Symp Pure Math, vol 71. AMS, Providence, pp 153–208
76. Tyng V, Kellman ME (2006) Bending dynamics of acetylene: New modes born in bifurcations of normal modes. J Phys Chem B 119:18859–18871
77. Uwano Y (1999) A quantum saddle-node bifurcation in a resonant perturbed oscillator with four parameters. Rep Math Phys 44:267–274
78. Uzer T (1990) Zeeman effect as an asymmetric top. Phys Rev A 42:5787–5790
79. Van der Meer JC (1985) The Hamiltonian Hopf bifurcation. In: TS9 Lect Notes Math, vol 1160. Springer, New York
80. Vũ Ngoc S (1999) Quantum monodromy in integrable systems. Comm Math Phys 203:465–479
81. Vũ Ngoc S (2007) Moment polytopes for symplectic manifolds with monodromy. Adv Math 208:909–934
82. Wang J, Kais S (2004) Scaling of entanglement at a quantum phase transition for a two-dimensional array of quantum dots. Phys Rev A 70:022301-1-4
83. Weyl H (1952) Symmetry. Princeton University Press, TS8
84. Winnewisser M, Winnewisser B, Medvedev I, De Lucia FC, Ross SC, Bates LM (2006) The hidden kernel of molecular quasi-linearity: Quantum monodromy. J Mol Struct V 798:1–26
85. Xiao L, Kellman ME (1990) Catastrophe map classification of the generalized normal-local transition in Fermi resonance spectra. J Chem Phys 93:5805–5820
86. Zhang W-M, Feng DH, Gilmore R (1990) Coherent states: Theory and some applications. Rev Mod Phys 62:867–927
87. Zhilinskií BI (1996) Topological and symmetry features of intramolecular dynamics through high resolution molecular spectroscopy. Spectrochim Acta A 52:881–900
88. Zhilinskií BI (2001) Symmetry, invariants, and topology, vol II. Symmetry, invariants, and topology in molecular models. Phys Rep 341:85–171
89. Zhilinskií BI (2006) Hamiltonian monodromy as lattice defect. In: Monastyrsky M (ed) Topology in condensed matter. Springer series in solid state sciences, vol 150. Springer, TS8, pp 165–186
90. Zhilinskií BI, Kozin I, Petrov S (1999) Correlation between asymmetric and spherical top: Imperfect quantum bifurcations. Spectrochim Acta A 55:1471–1484

91. Zhilinskií BI, Pavlichenkov IM (1988) Critical phenomenon in the rotational spectra of water molecule. Opt Spectrosc 64:688–690
92. Zhilinskií BI, Petrov SV (1996) Nonlocal bifurcation in the rotational dynamics of an isotope-substituted $A_2A_2^*$ molecule. Opt Spectrosc 81:672–676

## Books and Reviews

Waalkens H, Dullin HR (2001) Quantum monodromy in prolate ellipsoidal billiards. Ann Phys NY 295:81–112