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Topological and symmetry features of intramolecular dynamics through high resolution molecular spectroscopy

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Abstract

A short review of the qualitative approach to the study of the intramolecular dynamics of small quantum systems developed recently by Russian scientists is given. The classification of possible qualitative modifications of dynamic regimes under molecular excitation in the spirit of bifurcation (or catastrophe) theory is proposed and the manifestation of predicted effects in experimental high resolution spectra and in ab initio calculated data is discussed.

Keywords: Intramolecular dynamics; High resolution molecular spectroscopy

1. Introduction

The progress of experimental techniques in high-resolution spectroscopy during last 30 years has resulted in an enormous amount of information concerning spectral transitions in very different spectral regions. Hundreds of thousands of lines are known for some rather simple molecules with a relative accuracy of 10^{-7} to 10^{-10}, even in the IR region. However, very often this information is very detailed for one energy region, especially near the ground state, and almost absent for another. This situation creates two rather different theoretical problems: (i) to supply very accurate theoretical models which give the possibility to interpret existing data with experimental accuracy and interpolate them with high accuracy; (ii) to find generic features appropriate for a rather wide class of molecules or specific family of quantum states which enable one to qualitatively predict the possible different regimes of intramolecular dynamics and types of transitions between them under excitation. It is this qualitative aspect which has been studied over a period of about ten years by the author of this paper in tight collaboration with several groups of Russian scientists [1–33] (for previous reviews see Refs. [2,20,34,35]). This short review summarizes the general approach and gives references to a number of papers initially published in Russian and probably not well known by the western spectroscopic community.

Very often the description of a quantum many particle molecular system is based on the construction of the model Hamiltonian which reproduces only the most interesting parts of the energy spectrum rather than the whole spectrum and

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takes into account only some chosen part of the internal degrees of freedom of the system [36–42]. The choice of the important dynamic variables may be made on the grounds of some experimental knowledge or physical assumptions. Effective quantum Hamiltonians describing rotational multiplets for a given vibrational state (effective rotational Hamiltonian), vibrational structure formed by several modes (effective vibrational Hamiltonian for stretching or bending modes give examples of possible choices), internal structure of molecular Rydberg multiplet (effective one-electron Hamiltonian) give the simplest examples of such model operators. Those degrees of freedom which are not explicitly taken into account are implicitly present in the effective Hamiltonian as extra quantum numbers. They are strict or approximate integrals of motion and may be treated as physically meaningful external parameters under the study of the variation of the effective Hamiltonian when varying these quantum numbers. A more or less standard way to study a quantum system by this approach is to construct a phenomenological Hamiltonian with a reasonable number of parameters which may be fitted to experimental data.

The expansion of the effective Hamiltonian is normally done in terms of operators classified by orders of magnitude and respecting the symmetry of the problem. Usually the classification of different terms by order is not strict at all and may vary considerably from one particular example to another. Thus very often even a small variation of phenomenological parameters may produce drastic changes in the energy level system and in the intramolecular dynamics. At the same time some other large variations of the phenomenological parameters may result in minor changes of some numerical values and do not influence the general patterns of the energy levels or global intramolecular dynamics from the qualitative point of view [37,41,43].

The general idea of the present work is to find out some generic features of the energy spectrum and of internal dynamics of a quantum system which are due to the specific choice of the dynamic variables and to symmetry properties rather than to concrete values of the phenomenological parameters.

To follow this way one important assumption must be made – the simplicity assumption about the form of the effective model Hamiltonian. It seems quite natural that the description of the lowest energy levels can be made with the simplest in some sense Hamiltonian whereas going to higher excitation results in more complicated energy level patterns, intramolecular dynamics and, more generally speaking, to a more complicated Hamiltonian.

To make such a study it is necessary first of all to define the notion of the simplest model Hamiltonian, to indicate what the transition to a more complicated Hamiltonian means and to relate the peculiarities of the effective Hamiltonian to observables for the quantum system, primarily to the energy level patterns.

The comparison between quantum and classical descriptions proved to be very useful for the purposes of qualitative analysis. The qualitative (topological) approach to classical mechanics was started by Poincaré and Lyapunov at the end of the nineteenth century [44–46]. Generalization of their ideas resulted in a much wider branch of science "Dynamic system theory", including applications of bifurcation theory and catastrophe theory to the study of enormously different kinds of scientific problems [47–57].

We are interested in this paper in the development of a qualitative approach to quantum systems. The general scheme of such a qualitative analysis can be formulated as follows [2,3,8, 13,34,35].

(i) For given set of dynamic variables used in a model quantum Hamiltonian, construct the corresponding classical description. This step includes the construction of the classical phase space and the definition of the classical symbol corresponding to the quantum Hamiltonian.

(ii) Definition of the simplest classical Hamiltonian on the classical phase space supposing that the simplicity is related to the minimal number of stationary points of the Hamiltonian defined over the classical phase space. The relation between the numbers and types of stationary points and the topological properties of the classical manifold is given by Morse theory. Hence the simplest Hamiltonian receives the

status of the simplest Morse Hamiltonian in the presence of symmetry.

(iv) Description of possible complications of the Hamiltonian under the variation of some external physical parameters which are assumed to be integrals of motion when constructing the effective Hamiltonian. First bifurcations of stationary points are of primary importance because they lead to a more complicated classical Hamiltonian with larger number of stationary points and to clearly seen qualitative changes in the energy level patterns. Further bifurcations generally result in further complications, but in some situations the presence of symmetry may cause the appearance of sequences of bifurcations, again leading to the simplest Hamiltonian (with the minimal number of stationary points).

(v) Based on the results of the classical analysis, the description of the qualitative features of quantum energy level system and intramolecular dynamics may be carried out.

We shall follow this scheme in this paper and discuss such important qualitative features as energy level clustering, localization of the dynamic behavior, and their qualitative changes under the variation of the strict or approximate integrals of motion taking into account only the topological and symmetry properties rather than concrete numerical values of the phenomenological parameters.

In Section 2 we shall discuss the general scheme taking as examples different effective molecular Hamiltonians. Section 3 is devoted mainly to symmetry considerations, whilst Section 4 gives a description of different generic qualitative features and their changes upon parameter variation. Molecular applications of this approach and its possible future are discussed in the last sections.

2. Dynamic variables and classical phase space

The first important step is the choice of the dynamic variables which are important for the study of a given type of internal motion. This choice must be done before the construction of the Hamiltonian both in classical and in quantum mechanics. Restriction to a small number s of degrees of freedom for a real system possessing generally $S > s$ degrees of freedom may be done without any approximation only when additional integral(s) of motion exist. These additional integrals of motion are generally related to some symmetry (Noether theorem) [47,49,52].

A detailed investigation of the reduction procedure for the classical Hamiltonian for a three body system taking into account strict integrals of motion is given by Abraham and Marsden [47]. For a general mechanical N-particle system no further strict reduction is possible. Nevertheless introduction of additional approximate integrals of motion enables us to reduce further the number of dynamic degrees of freedom. Introduction of any one additional integral of motion decreases the number of degrees of freedom by one.

Let us take as an example an arbitrary isolated N-particle system without spin. It has $3N$ degrees of freedom. Taking into account the conservation of the total momentum of the system (this is the consequence of a translational invariance in three-dimensional space) reduces the problem to $3N-3$ degrees of freedom. Regarding the invariance with respect to rotation (isotropy of space) it is possible to introduce two new integrals of motion – the total angular momentum and its projection on an axis of a laboratory fixed frame. The corresponding reduction procedure results in a formulation of the dynamic problem with a smaller number $(3N-5)$ degrees of freedom. $(3N-5)$ is just the number of rovibrational degrees of freedom for a general N-particle system if the conservation of the total momentum (three projections), absolute value of the angular momentum and its projection on an axis of the laboratory fixed frame is assumed.

While the situation seems to be rather clear in classical mechanics some further justifications are necessary for quantum problems. Introduction of spins of individual particles increases the number of degrees of freedom by one for each elementary non-zero spin. This can be easily understood if spin is considered as a momentum with fixed absolute value. For much more abstract algebraic models which are based on the assumption of a dynamic symmetry and are widely used now in

nuclear and molecular physics [23,58–60] it is possible to introduce dynamic degrees of freedom through the concept of the complete set of commuting observables (for more detail see recent articles by Zhang et al. [61,62].

The choice of dynamic variables is a preliminary step for the construction of the classical limit for the quantum problem. While the classical phase space for a general spinless N-body system is a trivial $6N$-dimensional Euclidean space, the reduction of this phase space by taking into accunt additional integrals of motion may result in a smaller dimension. At the same time the topological properties of the reduced phase space generally become more complicated [47,49,52,63,64].

We shall use below the topological properties of the reduced space to analyze general features of the set of classical trajectories and of the system of quantum energy levels. The procedure of the construction of the classical limit is the reversed one to geometrical quantization widely discussed in the literature [65]. While geometrical quantization is often ambiguous, the construction of the classical limit is a rather well defined procedure even in a general abstract situation. A general procedure for the definition of the classical limit is based on the generalized coherent state method formulated mainly by Gilmore and Perelomov about twenty years ago [60,66,67]. Although most physical applications of this method are quite distant from the molecular problems many results proved to be relevant. The recent review article by Zhang et al. [60] discusses in detail the procedure of the construction of the classical limit, so it is not necessary to reconsider this problem.

To characterize the topological properties of the space we shall use mainly such topological invariants as Betti numbers [63,64,68,69]. These invariants are of particular importance for us due to the possibility of relating them to the number of stationary points of a function defined over the manifold. Such a relation is the subject of the Morse theory [18,34,58,68,70–73] and will be discussed below. In more modern terminology Betti numbers are the ranks of the appropriate homology group. We will not go into detail here and give just a "pedestrian" definition by noting that for an N-dimensional space $N+1$ Betti numbers, $b_0, b_1, \cdots, b_N$ are defined. b_0 is equal to unity if any two points of the manifold are connected by a curve belonging to it. If the manifold consists of k different unconnected parts $b_0 = k$ for this manifold. b_1 is equal to zero if any closed curve lying on the manifold is deformed into a point. $b_1 = 1$ shows that there is a set of closed curves which cannot be deformed into a point, but all could be deformed into the same one-dimensional closed curve. This situation takes place for the cylindrical surface. For the surface of the torus there are two different closed curves which cannot be deformed either to a point or to each other. Thus for this surface $b_1 = 2$. Because further examples and a more formal description may be easily found in any manual on elementary topology we go now to relevant molecular applications.

2.1. Number of degrees of freedom and definition of the phase space

2.1.1. Rotational motion

For a general molecular system all electronic and all vibrational degrees of freedom are supposed to be frozen. This means that a set of (or one) quantum numbers is given which has the sense of additional integrals of motion, specifying the character of the vibronic motion. These integrals of motion usually give the description of electronic and vibrational motions in terms of some good quantum numbers, in particular the numbers of different types of vibrational quanta. The total angular momentum J and its projection on the laboratory fixed frame J_z are strict integrals of motion. Consequently one has finally one degree of freedom to describe the rotational motion for a molecular system in a given electronic and vibrational state [38,47,74–79]. The dimension of the classical limit manifold (classical phase space) in this case equals two. The two classical conjugate variables have the following physical interpretation in terms of action-angle variables: the projection of the total angular momentum on the body fixed frame and conjugate angle variable. The classical phase space is 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 Hamiltonian as a function defined over a sphere [77,79,80].

Very often it is not possible to restrict the value of extra quantum numbers by one set. Because these numbers are only approximate ones it is necessary to consider the coupling between them. In such a case we have to study the rotational motion for a few different values of additional approximate quantum numbers together. Such a situation corresponds to the same number of degrees of greedom and to the same classical phase space S^2, but now instead of an energy function defined over the S^2 manifold we have a matrix. Each element of the matrix is a function defined over the S^2 manifold. The dimensions of the matrix coincide with the number of vibronic states taken into consideration. This matrix generalizes the Hamiltonian function and is called a classical symbol corresponding to the quantum Hamiltonian. It is obvious that the quantum Hamiltonian describing the rotational structure of several vibronic states has a similar matrix structure with the dimensions of the matrix equal to the number of quantum states taken into account [13,14,17,20,22,34].

From the point of view of the classical limit the matrix construction corresponds to the classical limit over the rotational dynamics and to a purely quantum study (at a certain level of approximation) of the vibronic motion.

2.1.2. Vibrational motion

Usually while considering the vibrational motion one assumes the existence of an additional integral of motion (extra quantum number) characterizing the electronic motion. The rotational motion is suppressed either by putting $J=0$ or just by neglecting rotational degrees of freedom with the assumption that the rotational structure is too fine to be discussed together with the much more pronounced vibrational effects. Moreover, even among the vibrational modes it is sometimes very useful to restrict oneself by choosing only some of the possible modes. The natural principle of the separation of the vibrational modes is based on taking into account the resonance relations between them [47,48,81]. The most important is surely the 1:1 resonance due to symmetry or quasi-degeneracy. There are many molecules for which near resonances are to be expected on a rather general footing. For example, near degeneracy of symmetric and antisymmetric stretching vibrations in bent triatomic molecules of type AB_2 takes place if atom B is significantly heavier than atom A and the valence angle is close to $\pi/2$. Similar quasi-degeneracy takes place for three equivalent stretching vibrations in molecules with a C_{3v} or D_{3h} point symmetry group.

Different $n{:}m$ resonances between vibrational modes are also quite typical for molecular systems. 1:2 resonances between non-degenerate or between doubly degenerate and non-degenerate vibrational modes has been studied extensively during the last few years. Tetrahedral AB_4 molecules show an example of more complicated resonances. They have near degeneracies of four stretching modes and five bending modes with 1:2 resonance between them. Thus, taking into account the exact degeneracy of vibrations due to symmetry, this resonance may be described as $\nu_1(A_1){:}\nu_3(F_2){:}\nu_2(E){:}\nu_4(F_2) = 2{:}2{:}1{:}1$.

Thus the numbers of vibrational degrees of freedom which are to be studied simultaneously may vary considerably from molecule to molecule and surely depend on the accuracy needed. The dimension of the phase space is in any case twice the number of degrees of freedom.

2.1.3. Vibrational polyads

If we study the vibrational problem with K quasi-degenerate modes a natural possibility is to introduce an approximate integral of motion associated with the total number of vibrational quanta. This enables us to reduce the number of degrees of freedom by one and the dimensions of the classical phase space by two. Assuming the existence of this extra integral of motion we can study the internal structure of vibrational polyads formed by K quasi-degenerate modes in $(2K-2)$-dimensional phase space which is a subspace of the complete vibrational phase space [7,9–12, 18,27,34,58]. For example, the polyads formed by two quasi-degenerate modes can be described by two-dimensional phase space, but this space will

have a non-trivial topology because it was obtained by imposing additional constraints on the four-dimensional Euclidean phase space of two independent oscillators. Taking into account these constraints the classical phase space becomes topologically equivalent to a two-dimensional sphere [82–95]. Generalization to the $K>2$ mode case requires the introduction of even more complicated $(2K-2)$-dimensional phase spaces [18,58].

2.1.4. Rotational structure of vibrational polyads

If we study the rotational structure of the whole vibrational polyad formed by K quasi-degenerate vibrational modes the total number of degrees of freedom equals K because we have $K-1$ vibrational and one rotational degree of freedom. The total dimensions of the phase space are $2K$ and the phase space itself may be described as a direct product of two dimensional phase space for rotational motion and $(2K-2)$-dimensional phase space for the vibrational polyad structure.

It should be noted that in the case of the rotational structure of vibrational polyads the Hamiltonian is a function over $2K$-dimensional phase space, whereas in the case of rotational structure of several vibrational or vibronic states we have a Hamiltonian matrix defined over $(2K-2)$-dimensional phase space [13,34].

2.1.5. Molecular Rydberg states

An interesting molecuar problem is the study of the internal structure of the so-called Rydberg electronic states [96–115]. Highly excited one-electron states of molecules usually form groups of levels with each group being characterized by the same principal quantum number n. There are n^2 levels and each n-multiplet is completely characterized by two quantum numbers. Thus the corresponding classical limit manifold is four dimensional, while the problem possesses two degrees of freedom. The same result follows immediately from the classical description taking into account the existence of three degrees of freedom for the one electron problem and assuming the presence of one additional integral of motion. The reduction procedure gives four dimensional phase space for any given value of the additional integral of motion (quantum number n in the quantum case). Explicit construction of the phase space shows that from the topological point of view it is the direct product of two-dimensional spheres $S^2 \times S^2$. Thus the Hamiltonian describing the internal structure of molecular one-electron Rydberg states is a function defined over four-dimensional phase space [115].

2.1.6. Rotational structure of molecular Rydberg states

Additional inclusion of the rotational motion of the molecular system in a Rydberg polyad leads to a further increase of the number of degrees of freedom. One rotational and two electronic degrees of freedom correspond to six-dimensional phase space. Again, from the topological point of view, the phase space can be described as a direct product of spaces corresponding to pure rotation and to an electron Rydberg state multiplet. Thus the classical phase space is a direct product of three two-dimensional spheres $S^2 \times S^2 \times S^2$.

2.1.7. Algebraic models

Very often a description of quantum systems is based on the construction of algebraic models, the starting point being the dynamic symmetry group and the representation spanned by the state vectors. To define the number of degrees of freedom in such a case it is necessary to find the complete set of commuting observables which are not a multiple of unity within the given representation space [34,58,60–62,66,67]. The number of operators is just the number of degrees of freedom. Let us take as an example the group $SU(3)$ as the dynamic group and a totally symmetric representation of this group as the representation spanned by the state vectors. In this case it is clear that two labels are sufficient to completely describe the state vectors. (These labels may be taken as indices of the irreducible representations for the $SU(3) \supset SO(3) \supset SO(2)$ chain which is multiplicity free for the degenerate totally symmetric representation of the $SU(3)$ group). Thus, in such

a case we have two degrees of freedom and the corresponding phase space is four-dimensional. More precisely it is the homogeneous space $SU(3)/U(2)$ because $U(2)$ is the maximal stability subgroup for a totally summetric representation of the $SU(3)$ group. This formal example is very interesting from the molecular point of view because it corresponds to the description of vibrational polyads formed by three nearly degenerate vibrational modes [18,58].

2.2. Topological structure of the phase space

2.2.1. Rotational motion

Because the phase space for the rotational problem is a two-dimensional sphere S^2 the corresponding Betti numbers may be found very easly from the geometrical representation taking into account their simple definition given at the beginning of the previous subsection. We have $b_0 = 1$, $b_1 = 0$, $b_2 = 1$.

2.2.2. Vibrational motion

The proper definition of the topological properties of the phase space for purely vibrational problems may be complicated due to some restrictions imposed on the range of internal coordinates in some cases. To avoid such a complication here we suppose that all chosen vibrational coordinates are rectilinear or curviliner independent displacements, each defined on its own interval. In such a case, from the topological point of view, the phase space is a $2K$-dimensional Euclidean space for K vibrational modes. The only non-zero Betti number for this space is $b_0 = 1$. The presence of resonances does not influence either the dimension or the topological properties of the phase space.

2.2.3. Vibrational polyads

In the case of vibrational polyads formed by K quasi-degenerate vibrational modes the phase space is the $(2K-2)$-dimensional homogeneous space $SU(K)/U(K-1)$ [18,60]. This space is, in fact, the so called complex projective space. An explicit realization of the complex projective space may be described as follows. Let us take K complex variables and form the subspace filled by points satisfying the requirement

$$|z_1|^2 + \cdots + |z_K|^2 = 1$$

After that it is necessary to unify in one point all the points whose coordinates differ by a phase, namely $(z_1, \ldots, z_K)$ and $z_1 e^{i\phi}, \ldots, z_K e^{i\phi}$. The resulting image is a complex projective space CP^{N-1} which is locally a $(2K-2)$-dimensional real Euclidean space.

For complex projective space CP^{2K-2}, $b_s = 1$ for $s = 0, 2, 4, \ldots, 2K-2$ and $b_s = 0$ for $s = 1, 3, \ldots, 2K-3$.

2.2.4. Rotational structure of vibrational polyads

The phase space is the direct product $S^2 \times CP^{2K-2}$ of a two-dimensional sphere and of the complex projective space. Betti numbers for the space which is a direct product of two spaces with known Betti numbers may be easily found. If $b_i^{(t)}$ $(t = 1,2)$ are the Betti numbers for the two factors then the Betti numbers for the direct product are

$$b_j = b_0^{(1)} b_j^{(2)} + b_1^{(1)} b_{j-1}^{(2)} + \cdots + b_j^{(1)} b_0^{(2)}$$

One particular example is of primary interest due to the simplicity of the situation – the rotational structure of vibrational polyads formed by two quasi-degenerate modes. The phase space is the direct product of two two-dimensional spheres $S^2 \times S^2$. For this space the Betti numbers are $b_0 = b_4 = 1$, $b_1 = b_3 = 0$, $b_2 = 2$.

2.2.5. Molecular Rydberg states

From the topological point of view the example given above is completely equivalent to the phase space for the molecular Rydberg states. Nevertheless, it does not mean that the dynamic behavior or the symmetry properties should be completely the same.

2.2.6. Rotational structure of molecular Rydberg states

The Betti numbers for the classical limit manifold $S^2 \times S^2 \times S$ are as follows: $b_0 = b_6 = 1$, $b_1 = b_3 = b_5 = 0$, $b_2 = b_4 = 3$.

3. Symmetry considerations

3.1. Group images

Many molecular problems possess some symmetry which normally has to be taken into account by introducing an invariance group of the Hamiltonian [2,38,41,43,116,117]. Let G be the symmetry group of the problem considered. The symmetry group G^* of the effective model Hamiltonian can differ from G. It may be either smaller or larger.

The extension of the symmetry group may be due to additional symmetry operations valid only for the studied degrees of freedom. An example of the extension of the symmetry group is given by purely rotational problems. Because the angular momentum operators are invariant with respect to space inversion, the inversion is always included in the symmetry group of the effective rotational operator.

On the contrary, if the dynamic variables which span the studied space have rather high symmetry, the symmetry group of the Hamiltonian constructed over these chosen variables may be significantly smaller than the initial symmetry group G. In more precise terms the symmetry group of the Hamiltonian is the image of the representation spanned by the dynamic variables [2,12,73,118–120]. The concept of group images was successfully applied by Michel to many different physical problems from solid state to particle physics. It is equally useful for molecular problems. We briefly recall a more formal definition of the group image here.

Let G be a group and Γ its representation spanned by dynamic variables. The kernel of the representation Γ ($\ker \Gamma$) is the invariant subgroup of the initial group G which is mapping to unity in the representation Γ. The image of the group G in the representation Γ is the factor group $G/\ker \Gamma$ which is usually denoted by $\mathrm{Im}_G\Gamma$. Sometimes the group G itself is not important for the construction of the group image. Such a situation takes place, for example, for the scalar representation of any group. Their image is the trivial symmetry group C_1. Extension of the dimension of the space of dynamic variables usually involves variables with different symmetry species. In such a case the image of the group for this larger (and generally reducible) representation eventually becomes equivalent to the initial symmetry group G.

3.2. Group action

The characterization of the phase space or of any other spaces spanned by dynamic variables (the coordinate space, for example) from the point of view of the group images is in some sense a global description. It is useful especially for the purpose of qualitative analysis to give a more detailed symmetry group on the points of the space considered. To do this the action of the symmetry group on the points of the space must be introduced [118,121–123]. The general procedure for the construction of the group action includes the following steps.

Firstly it is necessary to find the local symmetry group for every point of the space considered. The local symmetry group is called the isotropy group and it includes all the operations of the total group which leave the chosen point invariant. Thus the isotropy group H is the subgroup of G^* which strictly speaking is the image of the initial group G of the problem considered. Elements g, $g \in G^*$, $g \notin H$, acting on the chosen point give the system of points called the orbit. All the points belonging to the same orbit are equivalent with respect to symmetry. When defining the orbit it is useful to construct a new object: the space of orbits or the orbifold [124]. An orbifold shows the elementary part of the space which is sufficient for the study because the whole space may be obtained as a result of symmetry operations. The elementary cell in crystallography gives the most well known example of the orbifold construction.

It is possible and very important to introduce the equivalence relation between orbits (i.e. the points of the orbifold). All orbits with the same or with a conjugated isotropy group form one stratum. Different strata may have different dimensions. A zero-dimensional stratum is just a system of isolated individual orbits. A stratum of the highest possible dimensions is called a generic

stratum and naturally has dimensions equal to the dimensions of the orbifold. It should be noted that the dimensions of the orbifold may be equal to or less than the dimensions of the initial space on which the action of the symmetry group is studied. The dimensions of the orbifold are smaller than the dimensions of the initial space if orbits themselves have non-zero dimensions. Such a situation is natural for continuous groups. For the action of finite groups the order of the group o[G], the order of the isotropy subgroup o[H], and the number of points in the orbit m, are related: o[G] = o[H]m.

Below we discuss simple molecular applications of the symmetry properties (mainly the group images and the group actions) which give important qualitative results [1,2,5,6,8,13,17,21, 24,125].

3.3. Effective operator construction by means of integrity basis

A short remark should be made here concerning another possible application of symmetry arguments to the construction of the symmetry adapted phenomenological effective Hamiltonians. A straightforward approach uses the step-by-step coupling procedure of irreducible tensors and different kinds of group theoretical coupling coefficients [116,126]. From the global qualitative geometrical point of view another approach based on the theory of invariants and generating function construction is of ultimate use [12,117,127–129]. The mathematical background was initially formulated at the end of the nineteenth century but actual physical applications, mainly concerned with particles and nuclear physics, started about 20–25 years ago. This approach is still unknown by the majority of theoretical spectroscopists apart from several initial demonstrations.

3.4. Examples

3.4.1. Rotational motion

To find the symmetry group of the effective rotational Hamiltonian it is necessary to take into account the point symmetry of the vibronic state considered and to add the space inversion if it is absent. Thus even for molecules with a static model showing no symmetry, the symmetry of the rotational Hamiltonian is the C_i group. The action of the C_i group on the S^2 phase space for the rotational problem shows that all points have trivial C_1 symmetry and all orbits are formed by two points lying on opposite ends of a diameter of the phase sphere. From the topological point of view the space of orbits is the real projective space RP^2. All the orbits belong to the generic two dimensional stratum.

Symmetry groups for many examples of effective rotational Hamiltonians are given in Refs. [2,34,43,126].

3.4.2. Vibrational motion

Let us consider as an example a purely vibrational problem for two stretching vibrations of an AB_2 molecule with C_{2v} point symmetry group. The dynamic variables which form a four-dimensional phase space are classified according to irreducible representations of C_{2v} as $\Gamma = 2(A_1 + B_1)$. The image of the C_{2v} group in this four-dimensional reducible representation is the C_2 group. To simplify the illustration it is possible to restrict ourselves to two-dimensional coordinate space. All points of this two-dimensional coordinate space under the action of the symmetry group are classified according to their isotropy group either as points with a C_2 local symmetry group or as points with a trivial C_1 symmetry group. All points lying on the q^{A_1} axis have the C_2 isotropy group. Each point itself forms an orbit and we have the one dimensional stratum of points with the C_2 isotropy group. All points with non-zero q^{A_1} coordinates have a trivial isotropy group and a pair of points (q^{A_1}, q^{B_1}) and $(q^{A_1}, -q^{B_1})$ forming one orbit. There is a two-dimensional stratum of orbits with a trivial isotropy group. Thus, we have the stratification of the coordinate space considered, which includes the one-dimensional stratum formed by orbits with the C_2 isotropy group and the two-dimensional stratum formed by orbits with the trivial isotropy group [2,7,9–12,34,83].

A slightly less trivial example is the stratification of the vibrational coordinate space for the

doubly degenerate mode of a tetrahedral AB_4 molecule. The image of the E representation of the T_d group is the D_3 group (or in another notation the C_{3v} group, taking into account that the actions of D_3 and C_{3v} groups on the two-dimensional coordinate space are identical) [2,34].

Sometimes it is necessary to study the action of the symmetry group on more complicated objects than the points of the space. The group action on the set of trajectories defined over the coordinate space gives such an example [2,34,63,130–136]. All the trajectories may be classified according to the isotropy group leaving the trajectory invariant as a whole. It should be emphasized that the trajectory has an orientation and the invariance of the trajectory under the action of the symmetry group means that both the location of the trajectory in space and its orientation are conserved.

3.4.3. Vibrational polyads

To find the symmetry of the effective Hamiltonian describing vibrational polyads it is necessary to construct the image of the symmetry group of the total problem in the representation spanned by the generators of the $SU(N)$ group. Many examples of the construction of the group images for vibrational polyads formed by two and three modes are given by Pavlov-Verevkin and Zhilinskii [9–12,18]. Examples of the group action on the complex projective space may be taken from their papers [18,34]. The simplest case of vibrational polyads formed by two quasi-degenerate modes is similar to a purely rotational problem from the point of view of the stratification under the symmetry action.

3.4.4. Molecular Rydberg states

The detailed analysis of the symmetry group actions on the four-dimensional phase space $S^2 \times S^2$ appropriate for the Rydberg problem is now under study by Zhilinskii and Michel [115]. One short remark can be made here. It is well known now that two qualitatively different types of quantum state are present for the quadratic Zeeman effect (the Soloviev–Herrick quantization) [98,137]. The qualitative topological approach immediately gives, for example, the presence of these two kinds of states – rotational and vibrational (2-dimensional oscillator) for a generic Rydberg Hamiltonian under the $D_{\infty h}$ symmetry assuming that the Hamiltonian is of the simples Morse type.

4. Qualitative features and changes

4.1. Classical symbol

Until now we have discussed the choice of degrees of freedom and the properties of corresponding phase spaces. To study particular features of the classical dynamic problem or patterns in the energy spectrum of the quantum Hamiltonian it is necessary to relate the quantum Hamiltonian and its classical analog.

Generally we have an effective quantum Hamiltonian which depends on several quantum numbers corresponding to classical integrals of motion (either strict or approximate ones). Wavefunctions of the effective Hamiltonian are represented in the coordinate space whose dimensions are equal to the number of degrees of freedom. If we use the classical limit for all degrees of freedom of the effective quantum Hamiltonian, the resulting classical Hamiltonian is just a function defined over the classical limit manifold. The stationary points of this function are of primary interest for the description of qualitative features of classical and quantum problems. More generally it is possible to use the classical limit for only some degrees of freedom. Such a procedure is quite natural if a degree of freedom treated quantum mechanically is assiciated with only a finite number of quantum states. Thus we have as a classical symbol a matrix defined over the classical manifold rather than a simple function. The dimensions of the matrix are equal to the number of quantum states for quantum mechanically treated degrees of freedom. Now the stationary points for each energy surface give the simplest classical solutions.

Sometimes it is possible to take into account only a small number of possible quantum states to simplify the resulting problem. As a whole the concept of the classical symbol instead of the

classical Hamiltonian function is applied to a more general situation (matrix rather than function). At the same time new features arise with the appearance of the matrix symbol. The diagonalization of a classical matrix symbol may result in the formation of "conical intersection points" of different energy surfaces [13,14,20,22,125]. In quantum problems these points are related to a redistribution of energy levels between different branches usually present in the spectra. The introduction of specific topological invariants relating classical and quantum description was recently proposed [14,125]. Further development, especially from the point of view of relations to non-commutative geometry and to the quantum Hall effect in solid state physics, seems very promising [138–141].

The stationary points may be classified according to their indices. The index of a stationary point is the number of negative eigenvalues of the Hessian matrix. The stationary point is non-degenerate if all the eigenvalues of the Hessian matrix differ from zero. Thus the index of minimum equals zero, and the index of maximum equals the dimensions of the space over which the function is defined.

Near each stable stationary point of the Hamiltonian there is a family of classical trajectories which corresponds to quasi-regular classical motion, and a reasonable good approximate description of classical motion and of corresponding quantum states is possible. The good small perturbation parameter responsible for the validity of the approximation is the small deviation from the stable stationary point.

Consequently, the first step in the study of the general Hamiltonian is to find the system of stationary points and to indicate their stability (their indices). Each stable point of the reduced Hamiltonian may be associated with a simple periodic trajectory of a more complete Hamiltonian possessing an additional degree of freedom which was supposed to be an integral of motion under the reduction procedure.

4.2. Periodic orbits and non-linear normal modes

The importance of stationary points of the reduced Hamiltonian and the corresponding periodic solutions of the extended Hamiltonian system with one additional integral of motion is due to the fact that the periodic solutions are present even for the more general perturbed problem which does not possess the strict integral of motion. Near the stable stationary point of the energy surface the Hamiltonian system has at least as many periodic solutions as the number of degrees of freedom. This is the result of the center theorem of Lyapunov [50,52,142,143].

The importance of the periodic solutions is because they can be used as a framework around which the dynamics of a system near equilibrium may be organized [144–147]. The periodic solutions may be associated with the normal mode vibrations corresponding to the harmonic approximation of the Hamiltonian near the stable stationary point.

If we have a degenerate case the situation is quite different. For example, if there is a degeneracy of several vibrational modes, in the harmonic approximation the number of periodic solutions is infinite. This is a consequence of high dynamic symmetry. The anharmonicity breaks the dynamic symmetry of the harmonic oscillator but leaves some invariance group as the symmetry group. If the symmetry is not trivial there exists a set of symmetry equivalent periodic trajectories with periods close to those of the periodic trajectories for the linearized system (the harmonic approximation). The theorem proving the existence of the periodic solution near equilibrium for the resonance system was proved by Weinstein [142] and its generalization to the Hamiltonian systems under the presence of symmetry has been discussed by Stewart and co-workers [144,146,147]. These periodic solutions which exist near the equilibrium and have in the linearization limit the same period as the linearized solutions are called the non-linear normal modes. The number of non-linear normal modes is defined by a symmetry and is related to orders of orbits formed by trajectories with different isotropy group. Some applications

of the non-linear normal mode concept to molecular vibrations have been described in Ref. [145].

4.3. Quantum localization

The stationary points of the reduced classical Hamiltonian may be stable or unstable. For stable stationary points classical trajectories starting in its neighborhood remain localized in the vicinity of the stationary point. For an unstable stationary point there is a separatrix passing through it in the reduced space and the classical trajectories starting in the neighborhood of an unstable stationary point may go far away from it in the reduced space but remain in the neighborhood of the separatrix. In the total unreduced space, slight deviation from the stable periodic trajectory corresponds to the formation of a (generically non-periodic) trajectory localized near the elementary stable periodic trajectory. For unstable periodic trajectories slight deviation from them results in localization only with respect to directions orthogonal to the separatrix [148].

For quantum systems the localization of classical trajectories near the stable ones may be interpreted as the formation of localized quantum states. Such an interpretation is possible, for example, if the discussion of the behavior of quantum system is made in terms of the phase space using the Wigner phase space distribution.

The localization of quantum states near the stable and unstable classical periodic trajectories has been studied mainly by Heller [149]. The importance of the periodic solution for the quantization problem, especially in the chaotic region for classical systems, is the subject of current interest for many authors (see Ref. [50] and references cited therein).

4.4. Morse theory applications

The relation between the topology of a manifold and the system of stationary points of a function defined over it is the subject of Morse theory [68,71,72]. In this paper we limit ourselves to generic smooth functions, or Morse functions, which have only non-degenerate stationary points: a small variation of such a function does not influence the number and the type of stability (Morse indices) of its stationary points. In a similar way we consider generic Hamiltonian functions.

The important result of Morse theory may be formulated in the form of the so-called Morse inequalities which relate the numbers of stationary points of a Morse function defined over the manifold to the topological characteristics of the manifold, or Betti numbers [68,69]. These relations are in fact the generalization of the well known Euler relation of polytopes (see Table 1). Let c_k be a number of stationary points of index k (k is the number of negative eigenvalues of the Hessian matrix at the stationary point), b_k be the kth Betti number of an n-dimensional manifold. Then we have the Euler quality (1), and a set of Morse inequalities (2) for $k < n$

$$c_0 - c_1 + \cdots + (-1)^n c_n = b_0 - b_1 + \cdots + (-1)^n b_n \tag{1}$$

$$\left.\begin{aligned} c_0 &> b_0 \\ c_1 - c_0 &> b_1 - b_0 \\ &\cdots\cdots \\ \sum_{m=0}^{k} (-1)^{k-m} c_m &> \sum_{m=0}^{k} (-1)^{k-m} b_m \end{aligned}\right\} \tag{2}$$

Relations (1) and (2) restrict the possible numbers of different stationary points of a Morse function defined over the manifold. In many cases the lowest possible numbers of stationary points are completely defined by Betti numbers just as $c_i = b_i$. Examples of the simplest systems of stationary points and corresponding Betti numbers for several important manifolds are given Table 2,

Table 1
Euler relation between the number of vertices, edges and faces of a polytope

Polytope	Vertices	Edges	Faces	V−E+F
Cube	8	12	6	2
Icosahedron	12	30	20	2
Dodecahedron	20	30	12	2
Buckminsterfullerene	60	90	32	2
Triangulated torus	9	18	9	0

Table 2
Stationary points of the simplest Morse functions defined on some classical limit manifolds

Manifold	Betti numbers	Stationary points[a]	Σ^b
$S^2 \approx CP_1$	$b_0 = b_2 = 1$, $b_1 = 0$	$c_0 = c_2 = 1$	2
$T_2 = S^1 \times S^1$	$b_0 = b_2 = 1$, $b_1 = 2$	$c_0 = c_2 = 1$, $c_1 = 2$	0
CP_2	$b_0 = b_2 = b_4 = 1$, $b_1 = b_3 = 0$	$c_0 = c_2 = c_4 = 1$	3
$S^2 \times S^2$	$b_0 = b_4 = 1$, $b_2 = 2$, $b_1 = b_3 = 0$	$c_0 = c_4 = 1$, $c_2 = 2$	4

[a] c_k is the number of stationary points of Morse index k.
[b] $\Sigma = \Sigma(-1)^k b_k$ is the Euler characteristic of the manifold (see Eq. (1)).

where we impose no symmetry requirements on the functions defined over the manifolds.

In the presence of symmetry, stationary points of a function defined on the manifold are classified by their local symmetry and belong to various orbits. Furthermore, the points lying on the so-called critical orbits are stationary for any invariant smooth function defined over the manifold. A comprehensive discussion of critical orbits may be found in Refs. [118,119,150]. We remind ourselves that critical orbits are those which are isolated in their strata. In particular, all orbits forming zero-dimensional strata are critical. Therefore in the presence of symmetry all possible sets of stationary points must not only satisfy Morse inequalities (2) and the Euler equation (1) but also include all critical orbits and obey the equivalence relations due to symmetry. Consequently, when calculating possible sets of stationary points, we must consider the number of orbits and their dimensions as defined by the action of the symmetry group.

We use the total number of stationary points of a Morse function to characterize this function by its "level of complexity" [34]. Functions with the lowest total number of stationary points compatible with the symmetry requirements are the simplest ones: their "complexity index" equals zero. Similarly, functions of complexity index unity possess the second lowest possible number of stationary points. In this way we arrive at the classification of all invariant Morse functions by their systems of stationary points. In many physically interesting cases with non-trivial symmetry groups, simplest Morse type functions possess stationary points only on the critical orbits. In general, there are several possible sets with the same total number of stationary points but different types (Morse indices) of points or positions of points on strata.

Simplest Morse type functions defined over an S^2 manifold in the presence of different point group symmetries are listed in Table 3. In fact, up to a trivial change of all stationary point indices from k to $\dim S^2 - k$ ($\dim S^2 = 2$), we have only one qualitative type of Morse function for each invariance group in Table 3.

4.5. Generic changes under external parameter variation

Another important question is about the relations between the Morse type functions characterized by different sets of stationary points, i.e. between the functions of different classes. How can we transform any function from one class into another by changing some parameter(s)? The answer may be found in the bifurcation (or catastrophe) theory [52,143,151–153]. It depends on the number of free parameters for a parameterized set of functions. The simplest situation is to restrict ourselves to one-parametric families of functions which are the most interesting for our molecular applications: we consider an integral of motion as a natural parameter to measure the excitation of the system.

Table 3
Simplest Morse functions defined on S^2 in the presence of symmetry

c_k^a	Group					
	C_2, C_{2v}	D_2	D_3, D_{3h}	D_6	O, O_h	I, I_h
c_0	1	2	2 or 3	2 or 6	6 or 8	12 or 20
c_1	0	2	3	6	12	30
c_2	1	2	3 or 2	6 or 2	8 or 6	20 or 12

[a] c_k is the number of stationary points of Morse index k.

Table 4
Molecular and nuclear examples of qualitative changes in the rotational structure under the variation of the angular momentum J

Molecule	Component	J_i value	Type[a]	Bifurcation(s)	J_f value	Type	Ref.[b]
SiH_4	$\nu_2(+)$	$J<12$	0	C_2^{N+}	$J>12$	1	[13,20]
SnH_4	$\nu_2(-)$	$J<10$	0^f	C_2^{N+}, C_3, C_4^N, C_2^{N-}	$J>12$	0^n	[19,22]
CF_4	$\nu_2(+)$	$J<48$	0	C_4^{L+}	$J=50\cdots53$	2	[26,33]
H_2Se	$\|0\rangle$	$J<20$	0	C_2^{L+}	$J>30$	1	[15,32,154–156]
^{149}Gd	yrast band			C_4			[157]

[a] Only the level of complexity is indicated.
[b] Further details on the qualitative changes in the rotational structure may be found in the references.

Bifurcations of stationary points in the presence of symmetry which are generic under the variation of one parameter can be described by the local symmetry of the point at which the bifurcation takes place along with some additional features: increase (+) or decrease (−) in the number of stationary points, and local (L) or non-local (N) character. By a local bifucation we mean that the qualitative changes of the system of classical trajectories occur only in a small region of the phase space close to the bifurcation point.

More details on bifurcations in the presence of symmetry may be found in Refs. [51,52,72,152,153], a particular application to molecular problems and a discussion of quantum-classical correspondence in Refs. [1,20,34,35]. The classification of generic bifurcations enables us to describe generic qualitative changes of Morse type functions under the variation of some parameter. For any Morse type function with a "complexity level" higher than zero it is possible to indicate its "genealogy"; a sequence of bifurcations, or more generally a number of such sequences, leads to this function. Examples may be found in Refs. [19–22,24,26]. For physical applications we normally assume that the lowest energy levels, the low excited states of the molecule, may be reproduced by an effective Hamiltonian of the simplest Morse type. Excitation, which occurs due to the variation of some integral(s) of motion, causes a sequence of bifurcations which result in a more complicated model Hamiltonian describing more excited quantum energy levels.

5. Final statements and molecular examples

Previous sections mainly summarize the phenomenological description of qualitative features and qualitative changes under parameter variation. One of the most interesting global qualitative statements is the existence of only five types of quantum bifurcations in a purely rotational band under J value variation [1,6,8,35]. These five types of quantum bifurcation were theoretically predicted in Refs. [6] and [8]. Now, manifestations of each type of quantum bifurcation are found either in energy level patterns fitted to high resoltuion experimental data or in extensive numerical calculations of rovibrational energy levels (see Table 4). The same statement about five different qualitative changes is valid for purely vibrational problems with one degree of freedom and even for more complicated cases under some restrictions imposed by the symmetry type (only symmetry groups with two-dimensional irreducible representations should be considered). Another aspect of the qualitative description is the microscopic theory. This means that the type of generic qualitative changes should be predicted using some rather crude initial information about molecular structure and intramolecular potential. An example of such a prediction is the formation of fourfold energy level clusters for AB_2 type non-linear molecules under rotational excitation [15,158,159]. This particular simple example has been discussed over the last few years in many theoretical and experimental papers. Special experiments were performed to verify the formation and presence of fourfold clusters and a number of very accurate numerical rovibrational calculations confirmed

Table 5
Morse functions defined over an S^2 mainfold under the presence of C_2 symmetry: qualitatively different types of vibrational energy surfaces for two stretching modes of a C_{2v} triatomic molecule

Type	C_2^a		2 C_1	Genealogy[b]	Molecular examples [83]
	ss	as			
0^n	Min.	Max.	–		SO_2 ($v \leqslant 5$)
0^i	Max.	Min	–		
1	Sad.	Max.	Min.	O^n C_2^L(ss)	H_2O ($v \geqslant 5$)
1	Min.	Sad.	Max.	O^n C_2^L(as)	
1^i	Sad.	Min.	Max.	O^i C_2^L(ss)	
1^i	Max.	Sad.	Min.	O^i C_2^L(as)	O_3 ($v \geqslant 5$)

[a] ss and as denote C_2-invariant orbits which correspond to symmetric and antisymmetric stretching.
[b] Genealogy indicates the type and the place (the orbit) of the bifurcation leading to a more complicated Morse function from the simplest one.

their presence under rotational excitation [32,154–156].

5.1. Rotational motion

The structure of the energy levels of a quantum rotational Hamiltonian can easily be derived from the possible systems of stationary points of Morse functions defined on S^2 (see examples in Table 3). For example, the existence of sixfold and eightfold rotational clusters is typical for any simplest Morse type Hamiltonian of a spherical top molecule, and not just for a concrete operator $R^{4(4,A_1)}$ (or Ω_4 in an alternative notation), which is often used to describe the rotational structure of an isolated vibrational state of such a molecule in the first approximation [38,39].

In Table 4 we present several examples of bifurcations in the rotational structure which were found recently on the bases of the analysis of experimental high resolution spectra (SiH_4, SnH_4) [13,19,20,22], by extensive numerical calculations (CF_4) [26,33,160,161], or predicted theoretically on the basis of a microscopic model [15] and then confirmed experimentally (H_2Se) [32]. Recently an experimentally found C_4-bifurcation in the rotational band of the ^{149}Gd nucleus confirms the wide applicability of the qualitative approach proposed [157]. Along with elementary bifurcations we provide in Table 4 an example of an "organized" sequence of bifurcations which leads to a crossover of the rotational structure and which is a typical-in-some-sense sequence of bifurcations caused by symmetry [19,21,22,24,26].

5.2. Vibrational motion

To interpret the internal structure of vibrational polyads we use an effective Hamiltonian written in terms of vibrational angular momentum operators which are bilinear components of creation and annihilation operators (a_1^+, a_2^+, a_1, a_2 for two quasi-degenerate vibrational modes [2,7,9,11,162]

$$
\begin{aligned}
J_+ &= (J_-)^+ = a_1^+ a_2 \\
J_2 &= \frac{1}{2i}(J_+ - J_-) = \frac{1}{2}(p_1 q_2 - p_2 q_1) \\
J_1 &= \frac{1}{2}(J_+ + J_-) = \frac{1}{2}(p_1 p_2 + q_1 q_2) \\
J_3 &= \frac{1}{2}(a_1^+ a_1 - a_2^+ a_2) = \frac{1}{4}(p_1^2 - p_2^2 + q_1^2 - q_2^2) \\
J &= 2N = \frac{1}{2}(a_1^+ a_1 + a_2^+ a_2) = \frac{1}{4}(p_1^2 + p_2^2 + q_1^2 + q_2^2)
\end{aligned}
\tag{3}
$$

All qualitatively different classical vibrational Hamiltonian functions, often called vibrational energy surfaces [75,82,85,80], can be easily classified by their sets of stationary points.

Nonlinear AB_2 molecules with the C_{2v} symmetry group give many interesting examples of vibrational polyads formed by stretching overtones. Several examples of qualitatively different vibrational energy surfaces for the case of vibrational polyads formed by two quasi-degenerate modes of nonlinear AB_2 molecules which are summarized in Table 5 (see also Ref. [34]) are taken from a series of works by Kellman [83,84].

The particular example of the bending vibration of a D_{3h} symmetric X_3^+ molecule is quite simple from the theoretical point of view and serves as a concrete illustration of rather abstract results and of a somewhat new interpretation of the intramolecular vibrational dynamics [163–169]. To interpret the internal structure of vibrational polyads formed by overtones of the $v_2(E_g)$ mode of an X_3 molecule we use an effective Hamiltonian written in terms of vibrational angular momentum operators which are the bilinear components of creation and annihilation operators (a_1^+, a_2^+, a_1, a_2) for the doubly degenerate vibrational mode of type E_g (Eq. (3)). Topological (the classical phase space is the S^2 sphere) and symmetry (the group action is equivalent to natural D_3 action on the sphere) arguments show immediately that a simplest D_3 symmetric Hamiltonian has two, non-equivalent by symmetry, localization areas: near two equivalent by symmetry stationary points with C_3 local symmetry, and near the three equivalent by symmetry points which have either C_2 or C_2' local symmetry. A correspondng quantum system has twofold and threefold clusters lying at opposite ends of the vibrational energy polyad. Non-local trajectories pass near the saddle points, the separatrices of the vibrational energy surface, and correspond to delocalized quantum states which lie at intermediate energies and do not form any cluster structure. These predictions found by simple qualitative theory [27,34] were confirmed by extensive numerical calculations of the quantum H_3^+ vibrational problem with direct graphical demonstration of the localization of the quantum wave functions associated with energy levels forming threefold clusters [27].

6. Conclusions

The purpose of the present review has been to summarize briefly the present state of the art and to stimulate further fundamental theoretical studies of new physical phenomena – quantum bifurcations – appropriate for highly excited quantum many-body systems. Quantum bifurcations were recently predicted theoretically and discovered later in molecules and nuclei. Further developments of the theory should demonstrate the universality of quantum bifurcations within the framework of the qualitative methods in science and make it possible to interpret and predict the qualitatively different regimes of dynamic behavior of quantum mechanical systems containing a finite number of particles i.e. molecules, atoms, and nuclei. While the qualitative topological approach to classical dynamics initiated by Poincaré and Lyapunov now exists as a highly developed and sophisticated branch of science (dynamical system theory) similar studies of quantum systems are now just at the beginning, especially from the point of view of demonstrating the existence of bifurcations in quantum systems such as atoms, molecules, and nuclei. It is widely accepted that the dynamic behavior of a finite many-body system, as the excitation energy increases, becomes very complicated due to non-linear interactions between different degrees of freedom. Consequently, it should be possible to speak about a dynamic chaos. However, even before chaos sets in, many qualitatively different regimes can be observed. In the simplest cases, the transition from one regime to another may be interpreted in a way similar to classical bifurcations. The chaotic region, which is extremely intricate, is under study by many different groups of theoreticians and experimentalists. At the same time the intermediate region between the regular lowest quantum states and the chaotic region has not been the field of so much interest. However, we expect that it can serve as a key to open the door into "quantum chaos". Further efforts should be made in the theoretical description of new types of physical phenomena, the prediction of favorable conditions for the experimental observation of

bifurcations and their possible use for selective excitation processes. The most important steps may be formulated as follows:

(1) Abstract theory: phenomenological approach. Advanced qualitative classification of quantum systems with a low number of degrees of freedom taking into account symmetry and topology arguments. Further analysis of interrelations between classical and quantum descriptions mainly for bifurcations of stationary points and periodic trajectories.

(2) Abstract theory: microscopic approach. Formulation and analysis (both numerical and analytical) of non-perturbative models applicable to high rotational and vibrational excitation with correct asymptotic behavior at dissociation energy.

(3) Extensive numerical calculations of rovibrational molecular structure from the potential energy functions (which can be ab initio or obtained by fitting to experimental data).

(4) Application of the theoretical models to concrete rovibrational spectra of molecules. Manifestation of quantum bifurcations under rovibrational excitation. Analysis of bifurcations or more general qualitative changes appropriate for time-dependent processes.

(5) Concrete molecular systems to study: H_3^+, H_3, H_2Se, H_2Te, CF_4, SiH_4, atoms and molecules in Rydberg states under the presence of external fields, clusters of atoms and simple molecules in highly degenerate electronic states, diatomic molecules under high rotational excitation.

Two types of theoretical model, namely phenomenological ones (such as the Landau theory for second order phase transitions) and microscopic ones (relating the form of the intramolecular potential energy function to the bifurcations observed for quantum systems) should be equally developed. Further researches should unify as far as possible the different abstract theoretical models and use the resulting approaches for an extensive numerical analysis of simplified non-linear models of dynamics based on topological and group-theoretical arguments. The final purpose of theoretical predictions is to determine the most favorable experimental conditions for observing the effects. This may be achieved only under a tight collaboration between workers specialized in different areas of physics and chemistry but high resoltuion molecular spectroscopy will undoubtly serve as the most powerful experimental tool.

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