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Qualitative Features of Intra-molecular Dynamics. What can be Learned from Symmetry and Topology?

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Abstract. Mathematical tools which are appropriate for the qualitative analysis of simple molecular quantum systems are briefly introduced and discussed.

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1. Introductions

Quantum molecular systems are well described by the standard nonrelativistic Schrödinger equation whose Hamiltonian includes known interactions between particles. Classical molecular systems are Hamiltonian dynamical systems with a finite (in simple cases, not very large) number of degrees of freedom.

For a given particular system, a description of few low energy quantum states becomes, in some sense, a purely technical problem which can be solved by means of some extensive numerical methods. Considerable progress in such *ab initio* calculations was achieved due to enormous advances in computer facilities. Parallel progress in experimental methods of high-resolution spectroscopy resulted in a huge amount of data on relative positions and intensity of various transitions between energy levels of molecular systems. Typically experimental studies are not restricted to the low energy region. Highly excited states are easily accessible in the experiment and moreover they are very important in intra- and inter-molecular processes.

At the same time, we should immediately note that the density of states increases rapidly with energy and, naturally, the main goal (which is inherited from low energies) to describe all possible molecular states becomes rapidly difficult and even impossible in both numerical or experimental studies.

An alternative approach is to describe the global pattern of excited quantum states from the point of view of qualitative analysis and to study the families of systems rather than individual systems. At the same time, it would be desirable to describe only particular energy regions of the system under study rather than to attempt a complete description valid at any possible energies and external conditions. As soon as dynamics of typical molecular systems always has several very different scales it is also natural to neglect in some cases very fine details (some super-fine or hyperfine structure) and in another cases some large scale modifications. More formally speaking, we will suppose that the system under study is physically approximated by an effective classical model with compact classical phase space. Only part among all possible degrees of freedom is taken into account because very high excitations from one side and super-fine excitations from another side are neglected.

Physical examples can be provided by effective rotational Hamiltonians which describe the rotational structure of isolated vibrational states of a molecule. Such model is based on the approximation which neglects vibrational and electronic excitations (supposing that they are sufficiently large compared with rotational structure) and also neglects the hyperfine structure due, for example, to the nuclear spin (supposing that this structure is too fine compared to the rotational structure).

The main idea of the present paper is to show what kind of mathematical tools can be used to explain different qualitative features of energy spectra of simple molecular systems starting form very restricted information about molecular symmetry and the type of dynamical variables. From the abstract mathematical point of view the group-theoretical and topological methods which will be shortly described and used are certainly well known but unfortunately, their application to molecular systems have remained undeveloped until now (for a recent review, see [1–3]). Modern mathematical tools are tested mainly on high energy physics problems, elementary particles, gravitation, and mesoscopic physics. Here we try to argue that molecular physics also remains the important field where modern mathematical constructions can be applied and tested.

2. Effective Hamiltonians, Bands, Super-bands, Separation of Variables

The traditional description of molecular energy levels distinguishes three distinct structures: rotational, vibrational, and electronic. Typically, electronic excitations ΔE_{el} are higher than vibrational excitations ΔE_{vib}, while the latter are higher than rotational excitations ΔE_{rot}. Their ratio is determined by the Born–Oppenheimer mass parameter $\kappa = (m_e/M_n)^{1/4} \sim 1/10$, where m_e is the electron mass and M_n is the typical mass of a nuclei. Normally

$$\Delta E_{\mathrm{el}} : \Delta E_{\mathrm{vib}} : \Delta E_{\mathrm{rot}} = 1 : \kappa^2 : \kappa^4. \tag{1}$$

The natural physical assumption in this situation is to study, for example, rotational structure of one isolated vibrational and electronic quantum state. Another possi-

bility is to neglect the rotational structure, which is supposed to be too fine, and to analyze vibrational structure of one electronic state. Resonances between different vibrational modes result in a natural additional internal vibrational structure, the so-called vibrational polyad structure. Polyads correspond to the well conserved quantity, the number of vibrational excitation quanta on quasi-degenerate vibrational modes. An even cruder description of energy states allows us to neglect the vibrational structure and to restrict to the analysis of specific electronic excitations, for example Rydberg states of atoms and molecules. All these and many other simple physical assumptions result in the separation of a class of states into subclasses forming energy bands. Each band depends on a specific conserved quantity which in the quantum approach can typically take discrete values but in the classical limit can change continuously. The purpose of the present paper is to describe qualitative features of energy bands in molecular systems using both quantum and classical approaches.

3. Internal Structure of Bands

First we suppose that an isolated energy band exists and can be described by an effective Hamiltonian which is written in terms of effective dynamical variables. The Hamiltonian depends also on physical parameters which specify the energy band considered. We consider three different examples of effective Hamiltonians:

(i) Effective rotational Hamiltonian;
(ii) Effective Hamiltonian for vibrational polyads;
(iii) Effective Hamiltonians for electronic Rydberg multiplets.

Qualitative features of the internal structure of corresponding energy bands are due to the topology of the reduced classical phase space and to the symmetry group action on this space.

3.1. TOPOLOGY OF REDUCED CLASSICAL PHASE SPACES AND MORSE THEORY

In order to study effective quantum Hamiltonians from the classical point of view we should first specify the classical phase space (or the classical limit manifold) for the quantum mechanical model ([4–6]).

The effective rotational Hamiltonian is defined over the two-dimensional classical reduced phase space which is a topological two-dimensional sphere S_2 [11, 12].

The reduced classical phase space for the effective Hamiltonians describing internal structure of vibrational polyads formed by n (quasi-)degenerate vibrations is $n-1$-dimensional complex projective space CP_{n-1} [16]. This is a manifold of real dimension $2n-2$.

The classical limit manifold corresponding to effective Hamiltonians describing internal structure of Rydberg multiplets is a four-dimensional manifold whose topology is $S_2 \times S_2$ [3, 7].

As soon as we know the topology of the reduced classical phase space the simplest application of the Morse theory enables us to predict the minimal possible number of stationary points of the effective Hamiltonians defined over the reduced space. In spite of the fact that the Morse theory application can tell us only the possible minimal number of stationary points for a Morse type function (i.e. function with nondegenerate stationary points) this prediction seems to be quite useful due to another intuitive physical idea: '*the simplicity assumption*'. By the simplicity assumption we mean that at low excitation energy effective Hamiltonians typically belong to the class of the simplest possible Morse-type function (i.e. Morse-type function with the minimal possible number of stationary points compatible with the topology of the reduced phase space). Naturally this is only a general principle which nevertheless helps us to better understand possible energy level patterns and their evolution with energy excitation or variation of another physical parameters. We have an initial point to apply the bifurcation theory and to study the evolution of stationary points for families of effective Hamiltonians depending on one or even several parameters.

For the three examples of reduced phase spaces cited above conditions imposed by topology and Morse theory on the minimal number of stationary points are not very restrictive. For the rotational effective Hamiltonian (S_2 phase space) Morse theory implies the existence of one minimum and one maximum. Corresponding Betti numbers are $b_0 = b_2 = 1, b_1 = 0$ and prediction of one minimum and one maximum for a compact space is trivial. Nevertheless, the same arguments combined with the symmetry considerations have less trivial consequences.

For an effective Rydberg Hamiltonians without additional symmetry Morse theory implies the existence of one minimum, one maximum, and two saddles of Morse index 2. This is a consequence of a set of Betti numbers ($b_0 = b_4 = 1$, $b_1 = b_3 = 0, b_2 = 2$) for the $S_2 \times S_2$ space.

The complex projective space CP_n has Betti numbers

$$b_0 = b_2 = \cdots = b_{2n} = 1, \qquad b_1 = b_3 = \cdots = b_{2n-1} = 0.$$

Consequently, the simplest Morse-type function in the absence of any symmetry has one stationary point of every even Morse index.

We restrict ourselves here to the simplest examples of reduced phase spaces. Natural molecular examples lead to more complicated reduced phase spaces. Thus, the rotational structure of vibrational polyads formed by overtones of triply degenerate vibrational modes should be described by the effective Hamiltonian defined over the classical reduced space $\mathrm{CP}_2 \times S_2$ [13]. The same classical phase space corresponds to an effective Hamiltonian describing simultaneous excitation of vibrational polyads formed by triply and double degenerate vibrational modes in the absence of resonances between the two modes. Remark that CP_1 is isomorphic to

S_2. To take into account the rotational structure in this case we should extend this reduced space to $\mathrm{CP}_2 \times \mathrm{CP}_1 \times S_2$ [21]. Many other molecular examples are available but they are essentially constructed using S_2 or CP_n manifolds as basic units. So we turn to the analysis of the group action in the case of these simplest classical phase spaces.

3.2. GROUP ACTIONS, CRITICAL ORBITS, INVARIANT SUB-MANIFOLDS

The presence of symmetry is quite typical for molecular systems. It can originate from the symmetry of the physical spacetime, the presence of identical particles, or the specific form of interaction, the so-called hidden or dynamical symmetry.

As soon as the symmetry group is known, it is necessary to analyze the action of the symmetry group on the classical phase space. The stratification of the phase space due to symmetry imposes many additional restrictions on the qualitative behavior of the Hamiltonian system and on its evolution along with variation of physical parameters. The most direct application is the presence of critical orbits of the group action. Critical orbits are isolated in their strata. Due to their specific symmetry, critical orbits are stationary points for any smooth function defined on the classical reduced space. Another important feature of stratification is the presence of closed invariant sub-manifolds. To apply Morse theory in the presence of symmetry one should naturally take into account the existence of critical orbits and invariant manifolds ([1–3, 8–10]).

Let us consider as a standard example the action of the cubic symmetry group O_h on the two-dimensional sphere S_2 induced by the natural action of the same group on the three-dimensional space. This group is generated by reflections and its space of orbits is represented in terms of invariant polynomials as a curved filled triangle with three singular points (Figure 1). Three singular points of the orbit space correspond to three critical orbits formed, respectively, by 6, 8, and 12 equivalent points. Morse theory predicts that the simplest Morse-type function defined on the S_2 manifold in the presence of O_h symmetry has 26 stationary points (one 12-point orbit of saddle points and 8-point and 6-point orbits of maxima and minima).

In fact, the O_h symmetry of the effective rotational Hamiltonian can be observed for molecules possessing only tetrahedral geometrical symmetry T_d if this symmetry is extended by additional time reversal symmetry, $\mathcal{T}$. Time reversal symmetry does not preserve the symplectic structure and any symmetry transformations which include time reversal should be treated with care. At the same time, all stationary points of the Hamiltonian are, obviously, time reversal invariant. Time reversal itself leads immediately to a very important qualitative conclusion about the general effective rotational operator. All orbits of the time reversal action on the rotational phase sphere are formed of two points which are antipodal points on the sphere. This fact together with Morse theory arguments results in the following qualitative feature: the minimal number of stationary points of any effective

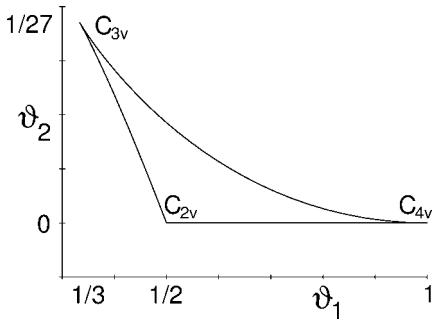

Figure 1. Orbifold for the natural action of the O_h group on the two-dimensional sphere $S_2 = x^2 + y^2 + z^2$ given in terms of invariant polynomials $\theta_1 = x^4 + y^4 + z^4$, $\theta_2 = x^2y^2z^2$. Singular points C_{4v}, C_{3v}, C_{2v} correspond respectively to 6-point, 8-point, and 12-point orbits on S_2. Notice that cusp points C_{4v}, C_{3v} persist under the change of invariant polynomials whereas the geometrical form itself can vary.

rotational Hamiltonian is six (two minima, two maxima, and two saddle points) ([22]).

It is interesting to note that in the case of O or T_h symmetry groups which are the subgroups of O_h of index 2, the complete system of invariant polynomials includes the same two invariant polynomials $\theta_1 = x^4 + y^4 + z^4$, $\theta_2 = x^2y^2z^2$ as in the case of the O_h group plus one additional auxiliary (linearly independent but algebraically dependent) invariant polynomial. For the T_h group this polynomial is $(x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$ and for the O group $xyz(x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$. Due to this fact the space of orbits for the O group can be constructed from two copies of the O_h space of orbits with the identification of corresponding points on the boundary. This means that the space of orbits of the O group action on S_2 is a topological sphere with three marked points, critical orbits. The space of orbits of the T_h group action can also be obtained from two copies of O_h space of orbits but these two copies should now be identified only for a part of boundary points, namely $C_{4v} - C_{3v} - C_{2v}$ (see Figure 1). The topological structure of the space of orbits in this case is a 2-disk with one singular point inside and two singular points on the boundary. The set of critical orbits for the O_h, O, and T_h group actions of S_2 is the same and it is easy to see that in the case of, for example, an O invariant Hamiltonian the absence of the auxiliary invariant in the series expansion of the Hamiltonian in terms of invariants results in the higher O_h symmetry. This is the case of an arbitrary O invariant Hamiltonian written up to eighth degree in x, y, z variables. This trivial fact is well known and widely used in physics. (The most familiar fact is that an O_h invariant function $F(x, y, z)$ written up to the third degree in x, y, z is automatically $O(3)$ invariant.) At the same time we want to stress this here by remark that less trivial generalization concerns the *question of the symmetry of Hamiltonian written in terms of only algebraically invariant polynomials whereas the complete set of invariants includes some additional auxiliary algebraically dependent invariant polynomials*.

3.3. EQUIVARIANT BIFURCATION THEORY

Modification of the qualitative internal structure of an individual band under the variation of some physical parameter(s) naturally calls for the bifurcation analysis of the family of effective Hamiltonians depending on one or several parameters. This is a vast subject. Molecular applications deal mainly with families of Hamiltonians depending on a low number of parameters (and often on one for simplicity). But at the same time, symmetry is important and should be taken into account. Increasing symmetry leads immediately to an extension of a list of possible bifurcations with the same number of control parameters. It is well known that in the absence of symmetry there is only one typical bifurcation of stationary points for a one-parameter family of functions, the so called cusp, the simultaneous creation or annihilation of two stationary points. The presence of symmetry leads to a larger number of generic bifurcations of stationary points ([8, 9]). For the case of effective rotational Hamiltonians it was shown by Pavlichenkov and Zhilinskii that the number of qualitatively different bifurcations of stationary points is five ([12]). The manifestation of all qualitatively different bifurcations was found in real molecular examples (for a review see [2, 14, 15]).

3.4. INTEGRITY BASIS

Mathematically technical but practically very important part of the qualitative analysis of concrete molecular Hamiltonians is the transformation of the initial Hamiltonian to the reduced one written in the form of series expansion in terms of invariant polynomials. This step from the formal point of view is the normalization procedure ([43–45]). To express unambiguously the normalized Hamiltonian it is quite useful to have integrity basis [1, 17, 27, 28] which typically consists of a number of algebraically independent (so called denominator) invariants, θ_i, $i = 1, \ldots, n$, where n is the dimension of orbit space for the classical phase space, and auxiliary (numerator) invariants φ_α. As soon as the integrity basis is known arbitrary invariant function can be written in the form of a series expansion

$$H = P(\theta_1, \theta_2, \ldots, \theta_n) + \sum_\alpha \varphi_a Q_\alpha(\theta_1, \theta_2, \ldots, \theta_n) \tag{2}$$

with P and Q_α arbitrary polynomials of n variables.

The construction of the integrity basis can be naturally done in many different ways, even if one looks for integrity basis with the minimal possible number of auxiliary invariants. The choice of concrete form of the integrity basis may seem to be of no importance because the topology of the orbit space and its stratification (i.e. the number and the type of critical orbits, invariant sub-manifolds, etc.) are independent on the particular choice of the integrity basis. At the same time, an interesting point is related with the ambiguity of the integrity basis choice due to different symmetry of the orbifold. It is known that as soon as the integrity basis for

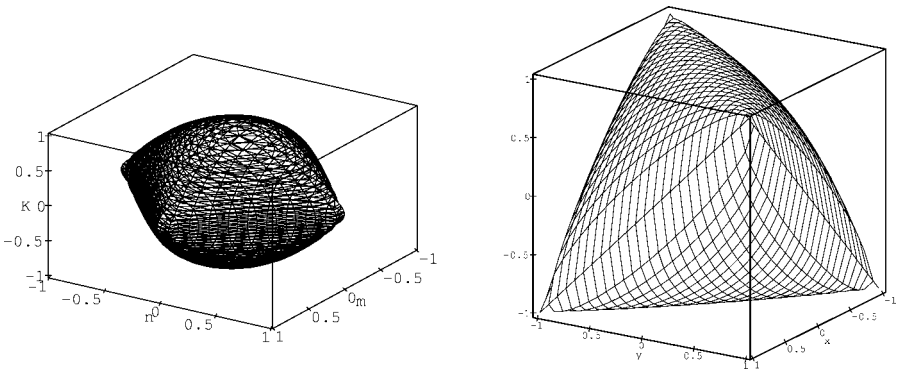

Figure 2. Orbifold for Rydberg state problem in the presence of parallel electric and magnetic fields with two alternative choices of integrity bases resulting in D_{4h} (left) and T_d (right) symmetry of the orbifold.

invariant polynomials is known, it can be used to represent the orbifold. Denominator invariants play the role of independent variables and numerator invariants label different carts forming the atlas on the orbit space. Sometimes the orbifold can be characterized by nontrivial symmetry acting in the space of invariant polynomials.

Let us consider as an example, the space of orbits of the effective Rydberg problem in the presence of parallel electric and magnetic fields. The symmetry group of this problem studied in details in [3, 18, 20] is $C_\infty \wedge \mathcal{T}_v$, i.e. axial symmetry extended by $\mathcal{T}_v$ operation which is a simultaneous action of time reversal and reflexion in the plane passing through symmetry axis. Depending on the choice of the integrity basis the orbifold has the point symmetry group T_d or D_{4h} (see Figure 2).

Apparently this symmetry reflects the hidden or parameter symmetry of the problem ([23–26]). *The detailed analysis of this symmetry and its implication in dynamical behavior remains an open problem.*

3.5. DENSITY OF STATES

Another important characteristic of the internal structure of the band is the number of quantum energy levels. As soon as the band itself is characterized by the integral of motion associated with the corresponding classical reduced phase space, the number of states should be considered as a function of this integral of motion. It is quite advantageous to represent the number of states in the form of a generating function ([30]). In order to remind the formalism let us consider one of the simplest cases: The number of states within polyads formed by K identical harmonic oscillators. The generating function for the number of states is ([30])

$$\begin{aligned} \frac{1}{(1-t)^K} &= C_0 + C_1 t + C_2 t^2 + \cdots + C_N t^N + \cdots \\ &= \sum_N \frac{(N+1)(N+2)\ldots(N+K-1)}{(K-1)!}\, t^N. \end{aligned} \tag{3}$$

The coefficient before t^N gives the number of states in the polyad with polyad quantum number N. It is important to note that coefficients C_N are in fact polynomials in N of degree $K-1$. In the quantum case, these coefficients are defined only for integer N values. This polynomial is in fact the Hilbert polynomial and its degree is completely determined by the number K of the degenerate oscillators. Coefficients of Hilbert polynomials can be trivially calculated in the simplest case under study.

Let us now consider more general generating function of the form

$$g_{d_1:d_2:\ldots:d_K}(t) = \frac{1}{(1-t^{d_1})(1-t^{d_2})\ldots(1-t^{d_K})}. \tag{4}$$

which corresponds to K harmonic oscillators with rational resonance condition between their frequencies. The number of states in polyads in this case can be represented as a quasi-polynomial ([30, 31]). Only in the trivial case of the $1:1\ldots:1$ resonance the oscillatory part of the number of state function equals zero and the quasi-polynomial turns out to be ordinary polynomial. Nevertheless even in the most general case the quasi-polynomial can be decomposed into a regular part and an oscillatory part in some precise unambiguous way and the regular part of this quasi-polynomial can be expressed as a polynomial function of d_i exponents using Todd polynomials ([1, 2, 32]). If we write a formal series

$$g_{d_1:d_2:\ldots:d_K}(t) = \sum_N C_N t^N, \tag{5}$$

the coefficient C_N of this series can be represented in the form

$$C_N = a_{K-1}N^{K-1} + a_{K-1}N^{K-1} + \cdots + a_0 + \text{oscillatory part}, \tag{6}$$

with a_j being the polynomials of d_i exposants

$$a_{K-1-i}(d_1, d_2, \ldots, d_K) \sim \frac{1}{(K-1-i)!}\mathrm{Todd}_i([d_1, d_2, \ldots, d_K]). \tag{7}$$

In fact the explicit form of Todd polynomials is given in terms of elementary symmetric functions of exponents $[d_1, d_2, \ldots, d_K]$. That is why the arguments are put inside square brackets. One formal definition of Todd polynomials is given by the relation [37]

$$\frac{\det A}{\det(I - \mathrm{e}^{-tA})} = (-1)^n t^{-n}\left\{\sum_i \mathrm{Todd}_i(P^1(A), \ldots, P^i(A))t^i\right\}, \tag{8}$$

where A is $n \times n$ matrix with eigenvalues $\lambda_1, \ldots, \lambda_n$ and $P^i(A)$ is the ith elementary symmetric function of the eigenvalues.

The formal way to find the regular part of the number-of-state function for an arbitrary generating function (with nontrivial numerator, for example) is to replace

the auxiliary parameter in the generating function by $\exp(-w)$ and expand the result in the Laurent series in w at $w = 0$. For the generating function (5) we have

$$\frac{1}{(1-\mathrm{e}^{-wd_1})\ldots(1-\mathrm{e}^{-wd_K})} = b_{K-1}w^{-K} + b_{K-2}w^{-K+1} + \cdots + b_0 w^{-1} + \cdots. \tag{9}$$

The s initial coefficients of this series are proportional to coefficients in (6).

$$b_j/(j)! = a_j. \tag{10}$$

This procedure can be generalized in order to find individual oscillatory contributions to the density of states. In this case the decomposition into Laurent series should be done near another pole of the generating function.

4. System of Bands and Rearrangements of Bands

Up to now we have considered the internal structure of individual energy bands. Now we turn to the question of the organization and reorganization of bands. The most natural physical model to describe the system of bands is based on the 'semi-quantum' approach. In this approach we associate the internal structure of bands with classical dynamics, whereas the existence of each band is due to quantum state in another 'external' variables. We have, therefore, internal classical variables and external quantum variables. The typical physical molecular example of such situation is the band of rotational energy levels for isolated vibrational state. With each value of the rotational angular momentum, J, the rotational multiplet is associated and its evolution with J correspond to the rotational band for isolated quantum vibrational state which is very well seen in many molecules. In the case of two or several, say K, quantum states the simplest situation corresponds to decomposition of the whole structure into K isolated bands or branches. If such separation exists for all studied values of the classical integral of motion the global structure is, in some sense, trivial and there is no interesting points to discuss about the global organization of bands. Nevertheless nontrivial situations exist and moreover, they are quite typical. Under the variation of the integral of motion or under the variation of some external control parameters, the organization of energy levels into bands can exhibit qualitative modifications. Such a phenomenon, which we refer as the redistribution of energy levels between branches, was discovered and conjectured to be universal for more than 10 years ago ([29]).

To understand this phenomenon, it is sufficient to study a very simple problem which is exactly soluble in quantum and classical mechanics. Let us consider a Hamiltonian describing the coupling of two angular momenta and interaction of one of this angular momenta with external magnetic field,

$$H = (1-t)S_z + t(\mathbf{J}\cdot\mathbf{S}). \tag{11}$$

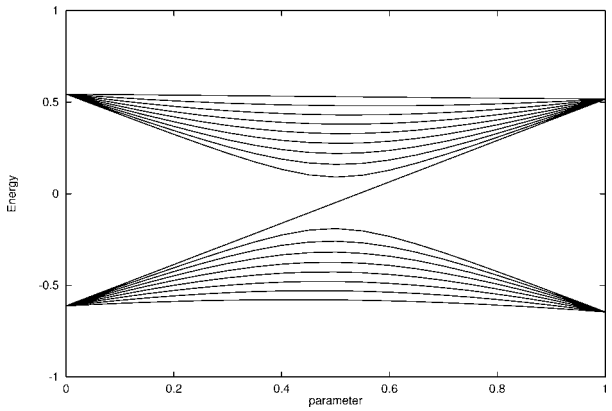

Figure 3. Energy level spectrum of the model Hamiltonian (11) with $S = 1/2$, $J = 4$.

Here $\mathbf{S} = (S_x, S_y, S_z)$ is the spin operator with $S = 1/2$, $\mathbf{J}$ is the angular momentum with sufficiently high J. The limit $t = 0$ corresponds to two bands with the same numbers of states, $2J + 1$; the $t = 1$ limit corresponds to two bands which have different number of states, $2J + 2$ and $2J$ (see Figure 3).

Although the conjecture relating the redistribution phenomenon with the modification of the topological invariant, namely the first Chern class, was formulated in the original publication ([29]), the formal construction explaining the appearance of topological Chern numbers for molecular energy bands was given only recently ([33, 34]).

The general idea is to describe the quantum K-state system together with the classical compact reduced phase space responsible for the internal structure of isolated bands as a complex vector bundle of rang K. The base of this vector bundle is the classical reduced phase space for 'slow' classical variables. Over each point of this base the complex fiber is the space of quantum wavefunctions associated with given classical manifold. In molecular applications we are interested mainly in classical manifolds CP_n ($n = 1, 2, 3, \ldots$). The quantum K-state model over the classical manifold CP_n thus corresponds to a vector bundle of rang K over CP_n. It turns out that Chern classes of vector bundles have very clear physical interpretation in terms of the number-of-state function of the bands [33]. This relation was demonstrated in details for vector bundles over $\mathrm{CP}_1 \sim S_2$ [33, 34], but the corresponding analysis for higher-dimensional base spaces and its relation to the general index formula for deformation quantization [41], especially in the presence of symmetry [42], is not yet fully explored.

4.1. TOPOLOGICAL QUANTUM NUMBERS FOR ENERGY BANDS

The formal topological classification of complex vector bundles over CP_N can be done by using rang and Chern classes of complex vector bundles ([36–40]). These Chern numbers play the role of topological quantum numbers for energy

bands ([35]). From the point of view of practical calculations it is quite useful to characterize the vector bundle by the Chern polynomial

$$1 + c_1 x + c_2 x^2 + c_3 x^3 + \cdots + c_s x^s, \tag{12}$$

where x is a formal variable and integer number c_i is ith Chern class which can be positive, negative, or zero. The index s of the highest nonzero Chern class c_s cannot be higher than the minimum of two numbers (r, n), where r is the rang of the vector bundle and n is the complex dimension of the base (classical reduced phase space). This means, in particular, that for vector bundles over $CP_1 \sim S_2$ only the first Chern class c_1 can be nontrivial. Vector bundles over CP_2 can have generically nonzero c_1 and c_2. At the same time, complex line bundles over CP_1 have only one nontrivial Chern number, c_1. Translation of these propositions into physical language means that, for example, rotational bands (over S_2) associated with one vibrational state can be characterized by only one topological quantum number c_1. At the same time, vibrational polyads formed by three degenerate modes (over CP_2) associated with an electronic state can be generally characterized by two topological quantum numbers c_1 and c_2.

One of the most interesting questions in physical applications which is directly related to the characteristic classes of vector bundles can be formulated as follows. Let us suppose that the quantum energy level system can be described as K identical bands associated with the reduced classical phase space CP_n. Is it possible that these K bands can reorganize in such a way that each new band has a nontrivial topological quantum number? The same question can be reformulated in even more physical terms: Is the redistribution of energy levels between energy bands possible and can it result in the formation of new nontrivial bands? ([46])

To answer this question some elementary properties of vector bundles and their Chern polynomials are necessary. For our purposes it is sufficient to know that the set of 'equivalent' vector bundles over a given phase space form a semi-group with 0 which can be extended to a (Grothendiek) group by adding some 'virtual' vector bundles. The operation of the direct sum of vector bundles is well defined and it corresponds to multiplication of corresponding Chern polynomials. Remark that after multiplication of Chern polynomials only the part containing possibly nonzero Chern classes for a given dimension of the base space should be kept.

EXAMPLES OF APPLICATION. (1) Is it possible for a trivial rang 2 vector bundle over CP_1 to be rearranged into two nontrivial line bundles? The following formal relation between Chern polynomials

$$1 = (1 + c_1 x)(1 - c_1 x) \tag{13}$$

gives the affirmative answer immediately. Equation (13) is correct because only linear part of the polynomial in the right-hand side part of (13) should be kept. Such decomposition is possible and the two nontrivial line bundles have first Chern number $\pm c_1$, where c_1 is an arbitrary integer. The physical meaning of this mathematical identity is the possibility of rearrangements of levels between the two

bands. We cannot verify by using a simple calculation whether this redistribution is generic or not and find the number of parameters (or symmetry) necessary to ensure the generic character of such a redistribution.

(2) What are the restrictions for rearrangements of energy levels between K quantum states defined over the classical phase space $CP_1 \sim S_2$? The formal answer follows from the Chern polynomial identity

$$1 = (1 + c_1 x)(1 + c_1' x)(1 + c_1'' x) \cdots \tag{14}$$

which is valid under only one restriction $c_1 + c_1' + c_1'' + \cdots = 0$.

(3) The redistribution of energy levels between two bands corresponding to two quantum states (with trivial structure) defined over the classical phase space CP_2 is impossible. This is a nontrivial restriction imposed by the topology. The mathematical origin of this statement is the multiplication of Chern polynomials for the two line bundles over CP_2.

$$(1 + c_1 x)(1 + c_1' x) = 1 + (c_1 + c_1')x + c_1 c_1' x^2. \tag{15}$$

In (15) the Chern polynomial in the right-hand side should be considered as a second degree polynomial because we study bundles over CP_2 (complex dimension 2). The resulting Chern polynomial becomes trivial (equal 1) only if $c_1 = 0$ and $c_1' = 0$. Thus the nontrivial decomposition is impossible.

(4) The redistribution of energy levels between three bands corresponding to three quantum states (with trivial structure) defined over CP_2 classical phase space is possible and it leads to one isolated band with nontrivial first Chern class and one nontrivial 'vector' band of rang 2 which is characterized by nontrivial first and second Chern classes. Again the proof follows from the formal identity

$$1 = (1 + c_1 x)(1 - c_1 x + c_1^2 x^2). \tag{16}$$

Remind that the term of the third degree in x in (16) should be neglected for the case of vector bundles over CP_2. The first Chern class c_1 for the line bundle can be arbitrary, but the first and the second Chern classes for the complementary rang two vector bundle are completely determined by the c_1 of the line bundle.

From the same equation (16), it is easy to see that nontrivial redistribution between three 'trivial' bands over CP_n, with $n \geqslant 3$, is impossible!

Many similar simple questions concerning possible rearrangements of the system of bands can be easily answered after reformulation of the same question in terms of nontrivial decompositions of trivial vector bundles. Despite the fact of using rather 'simple' mathematical tools, the physical answer remains nontrivial and unfamiliar to the molecular physics community. Surely, much more interesting applications can follow from more advanced mathematical analysis.

4.2. RELATION BETWEEN NUMBER OF STATES IN BANDS AND CHERN CLASSES

In the previous subsection we characterized the energy bands by topological quantum numbers (Chern classes) and remarked that there is a relation between these topological quantum numbers and the number of quantum states in the band. The basic formula for such a relation is the general index formula for the deformation quantization of vector bundles over compact manifolds. This or equivalent formula was given and is used by different authors in different contexts [47–49]. We refer just to [41] which is close in spirit to our applications. The number of quantum states for a vector bundle V defined over a compact manifold M (we restrict our analysis to the case of CP_n spaces) is given by the formula for the trace of the projector

$$\mathrm{Tr}\,\hat{1} = \int \mathrm{Ch}(V)\exp(Nx)\mathrm{Todd}(M). \tag{17}$$

In (17) $\mathrm{Tr}\,\hat{1}$ gives the number of states for the vector bundle V over manifold M. $\mathrm{Todd}(M)$ is the Todd polynomial for the manifold M, i.e. the Todd polynomial for the tangent fiber bundle over M. $\mathrm{Ch}(V)$ is the Chern character of the vector fiber bundle V, N is the quantum number corresponding to the integral of motion associated with the reduced classical phase space (the base of the vector bundle).

The practical application of (17) is difficult for molecular physicists because characteristic classes are not their common knowledge. Consequently, instead of discussing profound mathematics we just formulate simple recipe of practical calculations for interesting molecular applications. We suppose that M is a CP_n space and the vector bundle V is characterized by its rang r and its Chern classes, $c_1, c_2, \ldots$.

In fact Todd polynomials have appeared earlier in this publication (see Equations (7), (8)). Here we will just give Todd polynomials for CP_n spaces with $n = 1, 2, 3, 4$.

$$\mathrm{Todd}(\mathrm{CP}_1) = 1 + x, \tag{18}$$

$$\mathrm{Todd}(\mathrm{CP}_2) = 1 + \frac{3}{2}x + x^2, \tag{19}$$

$$\mathrm{Todd}(\mathrm{CP}_3) = 1 + 2x + \frac{11}{10}x^2 + x^3, \tag{20}$$

$$\mathrm{Todd}(\mathrm{CP}_4) = 1 + \frac{5}{2}x + \frac{35}{12}x^2 + \frac{35}{12}x^3 + x^4, \ldots \tag{21}$$

Remark that these formulae give particular Todd polynomials which follow from the generating function of the form $1/((1-t)^n)$ for the number of quantum states in vibrational polyads formed by n degenerate harmonic oscillators. The corresponding classical reduced phase space in this case is exactly CP_{n-1}.

The Chern character is the characteristic class which is additive with respect to the direct sum of vector bundles (Chern classes are multiplicative). As soon as the

rang and the Chern classes (or Chern polynomial) of the vector bundle are known, the procedure to find the Chern character is as follows.

(i) It is necessary to decompose the Chern polynomial into product of linear polynomials

$$1 + c_1 x + c_2 x^2 + \cdots = (1 + d_1 x)(1 + d_2 x) \cdots . \tag{22}$$

(ii) The Chern character then equals

$$r + \exp(d_1 x) + \exp(d_2 x) + \cdots . \tag{23}$$

Alternatively Chern character can be written as a polynomial using Chern classes

$$r + c_1 x + \tfrac{1}{2}(c_1^2 - 2c_2)x^2 + \tfrac{1}{6}(c_1^3 - 3c_1 c_2 + 3c_3)x^3 + \tag{24}$$

$$+ \tfrac{1}{24}(c_1^4 - 4c_1^2 c_2 + 2c_2^2 + 4c_1 c_3 - 4c_4)x^4 + \cdots . \tag{25}$$

Now, in order to calculate the formal integral (17) it is sufficient to decompose the expression under the integral into a formal series and to find the coefficient before the highest degree n, where n corresponds to the complex dimension of the manifold M.

For example, in the case of trivial line bundles over CP_n we have the following familiar expressions for the number of states in N polyads.

$$\mathrm{e}^{Nx}\ \mathrm{Todd}(\mathrm{CP}_1) = 1 + (N+1)x + \cdots, \tag{26}$$

$$\mathrm{e}^{Nx}\ \mathrm{Todd}(\mathrm{CP}_2) = 1 + \cdots + [(N+1)(N+2)/2]x^2 + \cdots, \tag{27}$$

$$\mathrm{e}^{Nx}\ \mathrm{Todd}(\mathrm{CP}_3) = 1 + \cdots + [(N+1)(N+2)(N+3)/6]x^3 + \cdots, \tag{28}$$

$$\mathrm{e}^{Nx}\ \mathrm{Todd}(\mathrm{CP}_4) = 1 + \cdots + [(N+1)(N+2)(N+3)(N+4)/24]x^4 + \cdots, \tag{29}$$

Generalization to the case of nontrivial vector bundles now becomes just a trivial task.

4.3. QUANTUM MONODROMY

Analysis of the redistribution phenomenon enables us to find another interesting relation with classical and consequently quantum monodromy ([50–55]). Namely in [54] it was shown that a family of effective Hamiltonians (11) has classical monodromy within a region of parameter values. In spite of the fact that the problem (11) is completely integrable, the action-angle variables are not globally defined ([51]). The presence of monodromy for this family reflects, according to the Duistermaat–Heckman theorem ([56–58]), the modification of Chern classes for the classical bundle of periodic trajectories. It seems that there exists a relation between the presence of monodromy and of higher obstructions to the existence of global action-angle variables and the modification of topological quantum numbers

for families of quantum problems. This is also an intriguing subject for further analysis.

5. Perspectives

This article is written on the occasion of the conference 'Symmetry and Perturbation Theory 2001'. It gives a rather fragmentary description of possible applications of symmetry and topology to qualitative description of molecular systems. The idea of the article is to stimulate the interest in molecular problems in the more mathematically oriented scientific community. Physical intuition suggests that different pieces of the puzzle can be put together and we will probably have many new interrelations between different branches of physics and mathematics. Let us go ahead together!

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References

1. Michel, L. and Zhilinskii, B.: Symmetry, invariants, topology. I. Basic tools, *Phys. Rep.* **341** (2001), 11–84.
2. Zhilinskii, B.: Symmetry, invariants, topology. II. Symmetry, invariants, topology in molecular models, *Phys. Rep.* **341** (2001), 85–171.
3. Michel, L. and Zhilinskii, B.: Symmetry, invariants, topology. III. Rydberg states of atoms and molecules. Basic group theoretical and topological analysis, *Phys. Rep.* **341** (2001), 173–264.
4. Zhang, W. M., Feng, D. H. and Gilmore, R.: Coherent states: theory and some applications, *Rev. Modern Phys. P* **62** (1990), 867–927.
5. Perelomov, A.: *Generalized Coherent States and their Applications*, Springer, New York, 1986.
6. Sadovskii, D. and Zhilinskii, B.: Group-theoretical and topological analysis of localized rotation-vibration states, *Phys. Rev. A* **47** (1993), 2653–2671.
7. Guillemin, V. and Sternberg, S.: *Variation on a Theme by Kepler*, American Math. Soc., Providence, RI, 1990.
8. Golubitsky, M. and Schaeffer, D.: *Singularity and Groups in Bifurcation Theory*, Vol. 1, Springer, New York, 1984;
   Golubitsky, M., Stewart, I. and Schaeffer, D.: *Singularity and Groups in Bifurcation Theory*, Vol. 2, Springer, New York, 1982.
9. Chossat, P. and Lauterbach, R.: *Methods in Equivariant Bifurcations and Dynamical Systems*, World Scientific, Singapore, 2000.
10. Sartori, G.: Geometric invariant theory: A model independent approach to spontaneous symmetry and/or supersymmetry breaking, *Riv. Nuovo Cimento* **14** (1991), 1–120.
11. Harter, W.: Computer graphical and semiclassical approaches to molecular rotations and vibrations, *Comput. Phys. Rep.* **8** (1988), 319–394.
12. Pavlichenkov, I. M. and Zhilinskii, B. I.: Critical phenomena in rotational spectra, *Ann. Phys. (N.Y.)* **184** (1988), 1–32.

13. Dhont, G., Sadovskii, D., Zhilinskii, B. and Boudon, V.: Analysis of the 'unusual' vibrational components of triply degenerate mode ν_6 of $Mo(CO)_6$ based on classical interpretation of the effective rotation-vibration Hamiltonian, *J. Molec. Spectrosc.* **201** (2000), 95–108.
14. Pavlichenkov, I. M.: Bifurcations in quantum rotational spectra, *Phys. Rep.* **226** (1993), 175–279.
15. Zhilinskii, B. I.: Topological and symmetry features of intramolecular dynamics through high resolution molecular spectroscopy, *Spectrochim Acta A* **52** (1996), 1471–1484.
16. Zhilinskii, B. I.: Qualitative analysis of vibrational polyads: *N* mode case, *Chem. Phys.* **137** (1989), 1–13.
17. Weyl, H.: *Classical Groups, their Invariants and Representations*, Princeton Univ. Press, New Jersey, 1939.
18. Sadovskii, D. A., Zhilinskii, B. I. and Michel, L.: Collapse of the Zeeman structure of the hydrogen atom in an external electric field, *Phys. Rev. A* **53** (1996), 4064–4067.
19. Sadovskii, D. A. and Zhilinskii, B. I.: Tuning the hydrogen atom in crossed field between the Zeeman and Stark limit, *Phys. Rev. A* **57** (1998), 2867–2884.
20. Cushman, R. and Sadovskii, D.: Monodromy in the hydrogen atom in crossed fields, *Physica D* **142** (2000), 166–196.
21. Van Hecke, Ch., Sadovskii, D., Zhilinskii, B. and Boudon, V.: Rotational-vibrational relative equilibria and the structure of quantum energy spectrum of the tetrahedral molecule P_4, Submitted to *Eur. Phys. J.*
22. Roberts, M. and Montaldi, J.: Relative equilibria of molecules, *J. Nonlinear Sci.* **9** (1999), 53–88.
23. Shirokov, A. M., Smirnova, N. A. and Smirnov, Yu. F.: *Phys. Lett. B* **434** (1998), 237.
24. Shirokov, A. M., Smirnova, N. A., Smirnov, Yu. F., Castaños, O. and Frank, A.: IBM: parameter symmetry, hidden symmetries and transformation of boson operators, *Rev. Mexicana Fís.* **45, S2** (1999), 7.
25. Kuznezov, D.: Incompleteness of representation theory: Hidden symmetries and quantum nonintegrability, *Phys. Rev. Lett.* **79** (1997), 537.
26. Smirnov, Yu. F., Sadovskii, D. and Zhilinskii, B.: in preparation.
27. Jaric, M., Michel, L. and Sharp, R.: Zeros of covariant vector fields for the point groups: Invariant formulation, *J. Phys. (Paris)* **45** (1984), 1–27.
28. Patera, J., Sharp, R. T. and Winternitz, P.: Polynomial irreducible tensors for point groups, *J. Math. Phys.* **19** (1978), 2362–2376.
29. Pavlov-Verevkin, V. B., Sadovskii, D. and Zhilinskii, B.: On the dynamical meaning of the diabolic points, *Europhys. Lett.* **6** (1987), 573–578.
30. Sadovskii, D. and Zhilinskii, B.: Counting levels within vibrational polyads: Generating function approach, *J. Chem. Phys.* **103** (1995), 10520–10536.
31. Stanley, R.: *Enumerative Combinatorics*, Vol. 1, Wadsworth Brooks, Montrey, CA, 1986.
32. Zhilinskii, B. I., El Idrissi, M. I. and Herman, M.: The vibrational energy pattern in acetylene (VI): Inter and intrapolyad structures, *J. Chem. Phys.* **113** (2000), 7885–7890.
33. Faure, F. and Zhilinskii, B.: Topological Chern indices in molecular spectra, *Phys. Rev. Lett.* **85** (2000), 960–963.
34. Faure, F. and Zhilinskii, B.: Topological properties of the Born–Oppenheimer approximation and implications for the exact spectrum, *Lett. Math. Phys.* **55**(3) (2001), 219–238.
35. Thouless, D. J.: *Topological Quantum Numbers in Nonrelativistic Physics*, World Scientific, Singapore, 1998.
36. Nakahara, M.: *Geometry, Topology and Physics*, IOP Publishing, Bristol, 1990.
37. Griffiths, P. and Harris, J.: *Principles of Algebraic Geometry*, Wiley-Interscience, New York, 1978.
38. Eguchi, T., Gilkey, P. and Hanson, A. J.: Gravitation, gauge theories and differential geometry, *Phys. Rep.* **66** (1980), 213–293.

39. Milnor, J. W. and Stasheff, J. D.: *Characteristic Classes*, Princeton Univ. Press, 1974.
40. Hirzebruch, F.: *Topological Methods in Algebraic Topology*, Springer, New York, 1966.
41. Fedosov, B.: The Atiyah–Bott–Patodi method in deformation quantization, *Comm. Math. Phys.* **209** (2000), 691–728.
42. Fedosov, B.: On G-trace and G-index in deformation quantization, *Lett. Math. Phys.* **52** (2000), 29–49.
43. Gaeta, G.: Bifurcations and symmetry breaking, *Phys. Rep.* **189** (1990), 1–87.
44. Cigogna, G. and Gaeta, G.: *Symmetry and Perturbation Theory in Nonlinear Dynamics*, Springer, New York, 1999.
45. Sadovskii, D. and Delos, J.: Bifurcation of the periodic orbits of Hamiltonian systems – an analysis using normal form theory, *Phys. Rev. E* **54** (1996), 2033–2070.
46. Lay Nam Chang and Yigao Liang: Conservation of topological quantum numbers in energy bands, *Modern Phys. Lett. A.* **3** (1988), 1839–1845.
47. Bellissard, J.: *Lectures*, Institut H. Poincaré, Paris, 1995.
48. Zelditch, S.: Private communication.
49. Hawkins, Eli: Geometric quantization of vector bundles, Preprint: math.QA/9808116.
50. Cushman, R. and Duistermaat, J. J.: The quantum mechanical spherical pendulum, *Bull. Amer. Math. Soc.* **19** (1988), 475.
51. Duistermaat, J. J.: On global action-angle variables, *Comm. Pure Appl. Math.* **33** (1980), 687.
52. Lerman, L. M. and Umanskii, Ya. L.: *Four Dimensional Integrable Hamiltonian Systems with Simple Singular Points (Topological Aspects)*, Transl. Math. Monogr. 176, Amer. Math. Soc., Providence, 1998.
53. San Vu Ngoc: Quantum monodromy in integrable systems, *Comm. Math. Phys.* **203** (1999), 465–479.
54. Sadovskii, D. and Zhilinskii, B.: Monodromy, diabolic points and angular momentum coupling, *Phys. Lett. A* **256** (1999), 235–244.
55. Cushman, R. and Sadovskii, D.: Monodromy in the hydrogen atom in crossed fields, *Physica D* **142** (2000), 166–196.
56. Duistermaat, J. J. and Heckman, G. J.: On the variation in the cohomology of the symplectic form of the reduced phase space, *Invent. Math.* **69** (1982), 259–269.
57. Guillemin, V.: *Moment Maps and Combinatorial Invariants of Hamiltonian T^n-spaces*, Birkhäuser, Basel, 1994, Ch. 2.
58. Audin, M.: *The Topology of Torus Actions on Symplectic Manifolds*, Birkhäuser, Basel, 1991, Ch. 5.