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Topological phase transitions in the vibration-rotation dynamics of an isolated molecule

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Abstract One of the characteristic features of rotation-vibration dynamics is the existence of a variety of energy bands which result from organization of energy levels into bands depending on control parameters. Symmetry and topology aspects of the organization of energy bands and generic modifications of this structure for molecular systems with symmetry are discussed in a way parallel to the description of topological quantum transitions extensively studied in condensed matter physics. A special class of axially symmetric molecular systems is analyzed. It is shown that only a finite number of different band structures are possible for rotation-vibrational problem with a finite number of vibrational states in the case of continuous axial symmetry, whereas for problems with finite group symmetry an arbitrary large number of different band structures are formally allowed.

Keywords Energy band · Chern number · Rotation-vibration

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1 Introduction

It is well-known that macroscopic systems can exist in different phases depending on such control parameters as temperature, pressure, external fields, ...

Dedicated to Gregory Ezra on occasion of his 60th birthday.

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Phase transitions between different states of matter are tightly related with symmetry. Landau theory of second-order phase transitions is, probably, the best known example of symmetry breaking associated with qualitative modification of properties of macroscopic thermodynamic systems. Recently, new interesting states of matter associated with qualitatively different properties were discovered like quantum Hall effect [21, 24], or topological insulators [19]. The specificity of these new phases is due to modification of some topological characteristics of matter accompanying the phase transition. The associated phase transitions were named topological phase transitions [20, 14, 6].

For finite particle quantum systems the problem of qualitative characterization of dynamical behavior can be considered as an analog to classification of different phases of matter and phase transitions between them [32]. Quantum bifurcations which are largely discussed in vibrational and rotational structure of rather small isolated molecules are close in spirit to second order thermodynamic phase transitions, especially from the point of view of the symmetry breaking aspect [33]. Different possible symmetry breaking phenomena are completely classified, for example, for rotational problems for isolated molecules depending on one control parameter [25] and this classification is parallel to the symmetry classification of second order thermodynamic phase transitions for crystals.

Quantum monodromy for a simple isolated molecular system [7, 31] was shown to be an important qualitative feature which is clearly manifested in the patterns formed by joint spectra of several mutually commuting (or even almost commuting) variables [8, 27, 28]. While its classical counterpart, the Hamiltonian monodromy, is strictly defined for integrable approximations, the Hamiltonian monodromy is shown to persist owing to its topological origin even in slightly non-integrable cases [4]. The proof of this fact is similar to the application of the KAM theory showing that regular tori for completely integrable systems still persist under small non-integrable deformation.

The present paper deals with such qualitative characteristics of rovibrational molecular problems as band structure and its modifications [26, 9, 10, 15]. Sect. 2 gives a brief review of the construction of semi-quantum models using the rotation-vibration problem and of the associated notion of energy bands using as example the rotation-vibration structure of a tetrahedral molecule CF_4 which is well known from experimental studies and brute force calculations. The two slightly different basic questions are posed:

i) What system of isolated bands can be formed under presence of some symmetry requirements?

ii) What kind of rearrangement of band structure is allowed under the variation of control parameters in the presence of symmetry?

In order to characterize isolated bands by a topological invariant, the Chern number of the associated fiber bundle, namely the eigenline bundle of the effective matrix Hamiltonians, is used [9, 10, 15]. Possible values of Chern numbers depend on the symmetry of the problem [34, 16].

Rearrangement of the band structure under the variation of control parameters of effective Hamiltonians is well discussed by constructing iso-Chern domains [17,18], separated by walls, and by studying the wall-crossing phenomenon [22] through local approximation of a Hamiltonian in question along with the orbit structure of the symmetry group action on dynamical variables [23]. The local approximation for “delta-Chern“ invariant is close in spirit to the simplest model used by Berry to demonstrate the existence of adiabatic quantum phase [2,11] but the interpretation of so obtained topological invariant is different and is based on the initial conjecture [26] on a relation between the phenomenon of rearrangement of energy bands in molecules and the modification of such a topological invariant as the Chern number.

The case of axial symmetry is studied in Sect. 3 and compared with previously studied cases of a finite symmetry group.

Possible physical and mathematical generalizations of the discussed approach are outlined in Sect. 4.

2 Full quantum and semi-quantum models. Basic notions

In order to explain “semi-quantum“ model we start with a phenomenological formal construction of an effective Hamiltonian using two subsets of dynamical variables: “rapid“ variables q and “slow“ variables Q. “Rapid“ variables are associated with inter-molecular dynamics characterized by relatively high energy excitations. “Slow“ variables describe a molecular subsystem with low energy excitations and with high density of the corresponding energy spectrum. Although it is a common practice to explain in similar terms the separation of electronic and nuclear variables in molecular problems, we mainly apply below this construction to rotational and vibrational variables. Taking into account the fact that vibrational excitations are typically much higher than the rotational excitations we can restrict ourselves to the model including only a finite (and in fact rather small) number of vibrational quantum states. At the same time in spite of the fact that the number of rotational states associated with each vibrational state is finite for any chosen value of the integral of motion, the square of the rotational angular momentum, J^2, the density of rotational states within multiplet is rather high and this allows us to use classical description of the rotational subsystem in place of a quantum one. As a result the semi-quantum model of a certain part of the rotation-vibration system of states consists in treating a classical rotational problem combined with a chosen finite set of quantum vibrational states. It corresponds to a classical limit over rotational variables for effective quantum rotation-vibration Hamiltonian for a finite set of vibrational states. We illustrate here the correspondence between a quantum effective Hamiltonian and a semi-quantum model on a concrete molecular example exhibiting band structure and its reorganization associated with redistribution of energy levels between different bands.

One such representative molecular example [3] is shown in figure 1. This figure shows only a part of the rotational structure of closely lying ν_3 and $2\nu_4$ bands of the tetrahedral CF_4 molecule. Three branches of ν_3 vibrational state (split by Coriolis interaction) at low J-values are situated at lower energies than six components of $2\nu_4$ state. The internal structure of each band is formed by rotational 6-fold, 8-fold, and 12-fold quasi-degenerate clusters and is not relevant to the present discussion of band rearrangements [13, 32]. In contrast, the number of energy levels in the band is a very important characteristics. The lower band shown in figure 1 at $J = 29$ (the left side of figure 1) consists of $2J + 3$ energy levels and corresponds to the effective rotational quantum number $R = J + 1$. The upper band represented in figure 1 at $J = 29$ consists of $2J + 5$ energy levels and corresponds to the effective rotational quantum number $R = J + 2$. At $J = 38$ (the right side of figure 1) the lower branch (among two branches represented in this figure) consists of $2J + 5$ energy levels and corresponds to the effective rotational quantum number $R = J+2$, whereas the higher in energy branch at $J = 38$ region consists of $2J + 3$ energy levels and corresponds to effective rotational quantum number $R = J+1$. The qualitative effect of the rearrangement of the band structure under the variation of one control parameter, J, is well known in molecular spectroscopy and can be qualified as a generic phenomenon. In order to demonstrate the similarity of this phenomenon with the topological phase transitions in condensed matter we need to pass from the effective quantum description to a semi-quantum model of this phenomenon.

Let us discuss the correspondence between full quantum and semi-quantum descriptions on the example of ν_3 and $2\nu_4$ bands of the CF_4 molecule. The rotational structure of the upper component of the ν_3 triply degenerate band and of the lower branch of the $2\nu_4$ system of bands of the CF_4 molecule clearly shows the redistribution of energy levels under the increase of J value from $J = 29$ till $J = 38$ (the region shown in figure 1). One sequence of 8-fold quasi degenerate rotational clusters goes from the upper branch to the lower one under the J increase. Simultaneously, along almost the same J values one sequence of 6-fold degenerate clusters goes from the lower branch to the upper one. As a result of this redistribution of energy levels the lower in energy branch at $J = 38$ consists of $2J + 5$ energy levels and can be attributed to $R = J + 2$, whereas the upper in energy branch has $2J + 3$ energy levels and can be labeled by $R = J + 1$.

A complete effective quantum Hamiltonian describing all three branches of ν_3 and six branches of $2\nu_4$ (both ν_3 and ν_4 are triply degenerate) system of rovibrational energy levels can be written as a linear combination of operators constructed in terms of vibrational and rotational irreducible tensor operators respecting the symmetry of the problem. Alternatively, it can be put in the form of a 9×9 matrix Hamiltonian associated with nine vibrational states (three components of ν_3 state and six components of $2\nu_4$ state), whose matrix elements are functions of rotational operators. For one chosen value of J, the rotational operators are represented as $(2J + 1) \times (2J + 1)$ matrices, so that the effective Hamiltonian takes the form of a square matrix of order $9(2J + 1)$. If we replace the quantum rotational operators by their classical analogs, we obtain a “semi-quantum“ model Hamiltonian which is a 9×9 matrix with its matrix elements being functions defined on the classical phase space for rotational variables. As soon as we can fix the J^2, the classical phase space for

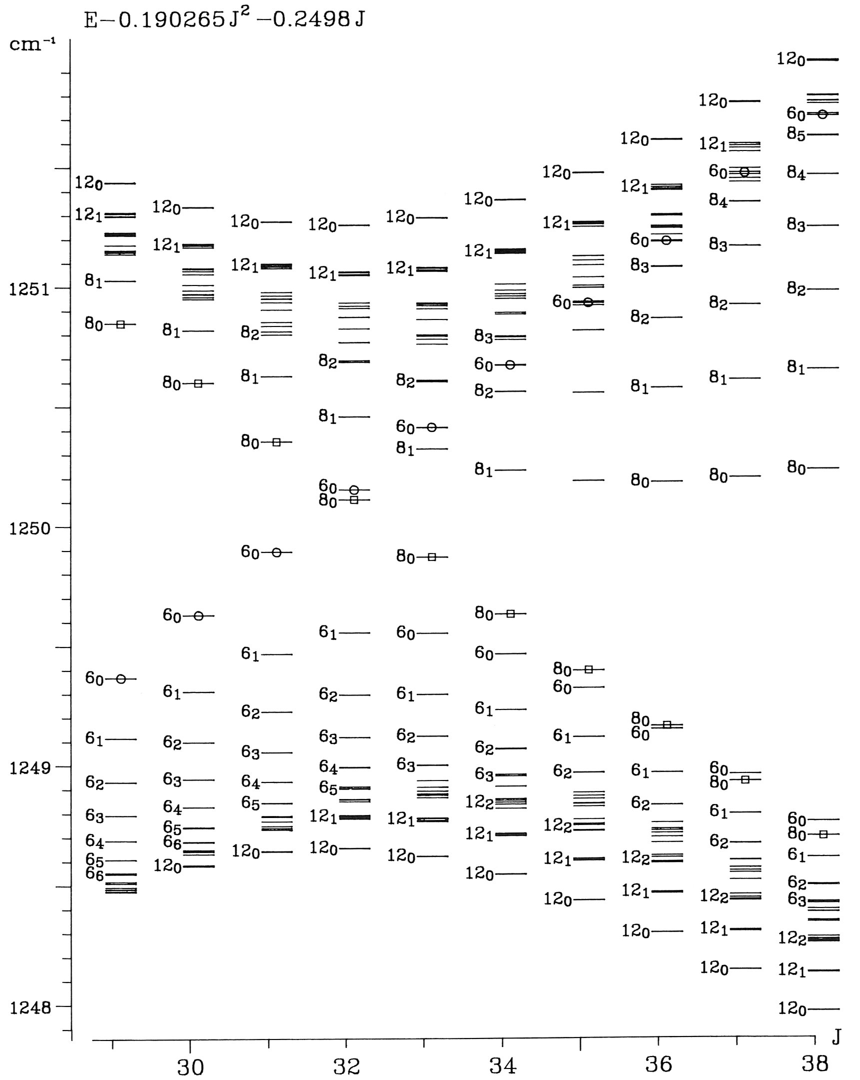

Fig. 1 Upper branch of ν_3 and lower branch of $2\nu_4$ bands of CF$_4$ molecule with T_d point symmetry group of the equilibrium configuration. 6_i, 8_j, 12_k are labels for six-fold, eight-fold, and twelve-fold rotational clusters characterized by the projection $\alpha = J - M$, $\alpha = i, j, k$ on C_4, C_3, and C_2 axes respectively.

rotational variables is nothing else but the two-dimensional sphere defined in J_x, J_y, J_z variables as $J_x^2 + J_y^2 + J_z^2 = J^2$.

We now have a matrix Hamiltonian defined over two-dimensional sphere and depending on extra parameters. There are phenomenological parameters of the effective Hamiltonian which can be, for example, fitted to reproduce experimental data and kept fixed for a chosen molecular system. Of special importance is a physically meaningful parameter such as J^2, the square root

J of which can be used as a parameter for the description of evolution of the rovibrational structure under rotational excitation. Such evolution is demonstrated in figure 1 where the system of energy levels is plotted against rotational quantum number J. This figure clearly shows the presence of energy bands and their rearrangement under the variation of a control parameter J. In order to formulate more accurately the concept of energy bands and their rearrangement, we need to introduce mathematically more precise language.

The system of eigenspaces of our matrix Hamiltonian forms a vector bundle of rank 9 with a base space being a classical phase space for rotational variables, i.e. a two-dimensional sphere S^2. This means that nine complex eigenspaces are associated with each point of the base space. In order for these eigenspaces to be defined unambiguously it is necessary that corresponding eigenvalues are non-degenerate. Let us suppose that eigenvalues are non-degenerate everywhere on the sphere. In such a case, the vector bundle can be considered as a direct sum of isolated individual eigenline bundles associated with respective eigenvalues. It is known that globally each complex eigenline bundle can be characterized by a topological invariant, the Chern number, which is an integer number, positive, negative or zero. The trivial line bundle has its Chern number equal to zero.

It is important to note that the absence of degeneracy points between eigenvalues of a matrix Hamiltonian defined over the two-dimensional sphere is a generic situation if the value of the rotational angular momentum J is fixed. This is because the codimension of degeneracy of two eigenvalues of an hermitian matrix is three [1,5], and because for a fixed J value the effective Hamiltonian depends only on two "parameters“, the coordinates of a point on the two-dimensional sphere (point of a classical phase space for rotational variables). Consequently, at fixed J values degeneracies are absent in general and then associated eigen-line bundles are defined, each of which is characterized by a topological invariant, its Chern number. To each eigenline bundle so constructed for a semi-quantum model, there corresponds one energy band, i.e. the energy surface $E_n(\theta, \phi)$ defined on the classical phase space, S^2 (here θ, ϕ are two spherical angles used as variables characterizing the position of a point of S^2 classical phase space). Note that so defined energy bands $E_n(\theta, \phi)$ and $E_m(\theta, \phi)$, $n \neq m$ can overlap in energy even in the absence of degeneracy points. The degeneracy means that there exists a point (θ_0, ϕ_0) on the sphere such that $E_n(\theta_0, \phi_0) = E_m(\theta_0, \phi_0)$, whereas overlapping means that there exist at least two distinct points (θ_1, ϕ_1) and (θ_2, ϕ_2) such that $E_n(\theta_1, \phi_1) = E_m(\theta_2, \phi_2)$. It is clear that specific quantum effects can appear when within the semi-quantum model the energy bands are isolated but overlapping. We are interested here in more serious effects manifesting themselves in the full quantum model in association with formation of degeneracy points of energy bands.

If we take the J as a control parameter (serving as a scaling factor for the semi-quantum Hamiltonian) and study one-parameter family of effective Hamiltonians depending on J, isolated degeneracies could appear for some values of J at some points on the sphere on account of the codimensionality of degeneracy. (Remind that the codimension of degeneracy point is three.) For such J-values eigen-line bundles are not defined over S^2, since the eigenspace associated with the degenerate eigenvalue does not naturally split into a direct sum of one-dimensional linear spaces at the degeneracy point of S^2. This means that the control parameter space (in our example this is the J line) is divided into connected regions by singular values of J, the values of J corresponding to formation of degeneracy points on S^2. Each connected region filled by regular values of control parameter (i.e. values for which there are no degeneracy points of eigenvalues) is named an "iso-Chern" domain because if we vary the control parameter value within this regular region, the topological invariant of the eigenline bundle cannot change. In general, values of control parameters corresponding to formation of degeneracy points on S^2 form "walls" between iso-Chern domains in the space of control parameters. In order to describe qualitative modification of eigen-line bundles and hence quantitative modification of Chern numbers, we have to study what happens when the control parameters vary along a path crossing a wall separating different iso-Chern domains in the space of control parameters. Apparently, the serious modifications occur only in a local three-dimensional neighborhood of the degeneracy point characterized by specific values of $(\theta_0, \phi_0, \lambda_0)$, two coordinates of degeneracy point on the classical phase space and one value of the control parameter measured along the path crossing the wall between iso-Chern domains. In addition, we need to remember that in the presence of a finite symmetry group acting on the classical phase space S^2, if there is a degeneracy point on S^2 every point of the orbit by the symmetry group is a degeneracy point as well. Thus it is necessary to take into account the stratification of the phase space by the action of symmetry group. The stratification of the rotational phase space by the symmetry group for spherical top molecules with tetrahedral or cubic symmetry is well known. Owing to invariance of rotational variables with respect to space inversion, the action of T_d point symmetry group on the rotational sphere is equivalent to the action of the octahedral point group O on the space sphere. There are three isolated orbits formed respectively by points with C_4, C_3, and C_2 local symmetry and generic orbits with trivial C_1 symmetry. The C_4 orbit consists of 6 equivalent points on the sphere, the C_3 orbit consists of 8 points and the C_2 orbit consists of 12 points. The number of points in a generic C_1 orbit is equal to the group order, 24. This means that the effect of formation of degeneracy points belonging to some orbit of the group action can be written as an effect of one local degeneracy point multiplied by the number of points forming the orbit of the symmetry group action.

The effect of crossing the wall between different iso-Chern domains in the control parameter space can be represented in the form of "delta-Chern" contribution from each isolated degeneracy point. It was shown, that the crossing of the wall along a path gives rise to a Chern number modification by ±1 from each generic degeneracy point [17]. In full quantum picture this phenomenon manifests itself through the redistribution of one quantum level between two bands forming degeneracy point in the semi-quantum model [9]. Taking into

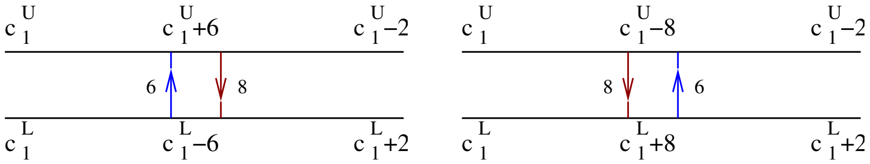

Fig. 2 Possible scenario for modification of topological invariants of isolated bands within semi-quantum model for rotation-vibration bands of CF_4 molecule shown in figure 1.

account the symmetry group G of the problem and the local symmetry (or stabilizer), $G_0 \subset G$, of the degeneracy point, we can express the global "delta-Chern" contribution Δc_1 as

$$\Delta c_1 = \frac{|G|}{|G_0|}\delta. \tag{1}$$

Here $|G|$ and $|G_0|$ are orders of groups G and G_0; δ is the local delta-Chern contribution from one isolated degeneracy point with stabilizer G_0. The absolute value of δ depends on the order of the degeneracy point. In generic situation the degeneracy point between two energy surfaces is nothing else but a conical intersection point and it is associated with $\delta = \pm 1$. To be precise in the sign of this local delta-Chern contribution is a much more subtle problem [17,18]. At the same time from the pattern of energy levels it is often easy to interpret a very characteristic behavior of energy levels as a function of "control parameter", J, in terms of topological invariant, the Chern number. Let us discuss the pattern formed by rotation-vibration energy levels of the CF_4 molecule represented in figure 1 in these terms. The sequence of six-fold rotational clusters going from the lower energy band to the upper one should be associated (within the semi-quantum model) with formation of degeneracy points with C_4 local symmetry at $J \sim 32$. At approximately the same J value another degeneracy point with C_3 local symmetry (in fact eight equivalent points forming orbit with C_3 local symmetry group) should be formed. Appearance of this point in the semi-quantum model is associated with the redistribution of the eight-fold cluster between two bands within a fully quantum description. Degeneracy point appears in the semi-quantum model for an isolated J-value. Appearance of degeneracy points with C_4 and with C_3 local symmetries is independent and naturally the corresponding J-values are not obliged to be integers. Two schematic scenarios can be suggested depending on relative order of J-values associated with formation of C_4 and C_3 degeneracy points. Figure 2 represents these two scenario. Two energy bands clearly seen in quantum energy level pattern at $J = 29$ are labeled according to the idea of the semi-quantum model by respective Chern numbers c_1^U for the upper band and by c_1^L for the lower band. Modification of the topology of individual bands in the semi-quantum model is reflected by the modification of the number of quantum levels within each band as compared to standard $2J+1$ values for pure rotational multiplet.

The modification of the topological Chern invariant by one within the semi-quantum model is associated with the modification of the number of quantum energy levels by one in an isolated energy band for a full quantum picture [9]. This means that we can convert the topological invariant c_1 into more standard spectroscopic characteristics, effective rotational quantum number R by relating R, J, and c_1 through

$$R = J + c_1/2. \qquad (2)$$

It is quite natural that topologically trivial bands associated in the semi-quantum model with $c_1 = 0$ Chern number correspond in a full quantum picture to isolated energy bands consisting of $2J + 1$ rotational energy levels. Nevertheless, in case of degenerate vibrational states it is not possible to split the whole rotational structure into several isolated bands consisting each of $2J + 1$ energy levels. This effect can be easily seen by studying the decomposition of the whole set of rovibrational states into individual rotational multiplets.

The whole set of rotation-vibrational levels for vibrational state belonging to degenerate representation $\mathit{\Gamma}_n$ of dimension n of the symmetry group G can be classified by irreducible representations of the symmetry group G by reducing the (J) representation of the rotational $SO(3)$ group to rotational subgroup G and by multiplying the so obtained reducible representation by $\mathit{\Gamma}_n$ and decomposing the resultant representation into irreps of G,

$$\mathit{\Gamma}_n \times (J) = \mathit{\Gamma}_n \times \sum_i m_i \mathit{\Gamma}_i = \sum_j d_j \mathit{\Gamma}_j = \sum_k^n \gamma_k \times \left(J + c_1^{(k)}/2\right), \qquad (3)$$

where γ_k is one of one-dimensional representations of G. [1] In order to check if the decomposition of the whole set of so obtained representations into several isolated rotational multiplets is possible for a finite group G, it is necessary to verify if this set can be split into the sum $\sum_k (J+\mathit{\Delta}_k)\times\gamma_k$, where each $(J+\mathit{\Delta}_k)$ representation of the $SO(3)$ group is considered as a reducible representation of the symmetry group G. Expression (3) should be checked for finite groups G for all (J). But in fact, it is sufficient to check it out only for a finite number of J-values because of a cyclic structure of the decomposition of irreducible representations (J) of $SO(3)$ group into irreps of its finite subgroup. The minimal number $J_{\min}$ of representations (J) to be checked can be estimated from relation $J_{\min} = |G|/2$, where $|G|$ is the order of group G, or more precisely, the order of the image of the group G in the studied representation.

Expression (3) gives therefore an interesting possibility to impose restrictions on possible values of Chern numbers of individual bands in the presence of invariance of the rotation-vibration problem under a finite symmetry group. To formulate these restrictions more accurately let us consider first the

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[1] The number of one-dimensional representations of a group is equal to the order of Abelianization, i.e. the order of the Abelian group $G/[G,G]$, the quotient of G by the commutator $[G,G]$.

rotation-vibration problem for the tetrahedral molecule in a doubly degenerate E-vibrational state. Expression (3) reads in this case

$$E \times (J) = (J + \Delta)_g + (J - \Delta)_u; \quad \Delta = \pm 2 \bmod 6. \tag{4}$$

Here $(J{+}\Delta)_\alpha$, $\alpha = g, u$ means that the vibrational symmetry for isolated band is of type A_1 or A_2, abbreviated for simplicity as g or u, because there are only two different one-dimensional irreducible representations. Taking into account (2) we can rewrite condition (3) in terms of equivalent restriction on topological invariants, Chern numbers, for isolated line bundles into which the rotational structure of a doubly degenerate vibrational E state can be split. Namely we have $c_1^E = \pm 4 \bmod 12$. Note that the realization of the decomposition with a given Δ or c_1 for a fully quantum problem is possible only if $J \geq \Delta$. The suggestion to avoid this inconvenience in quantum classical correspondence is formulated in the next section by introducing the "ghost" band. The semi-quantum model has no such restriction and we can say that formally an infinite number of possibilities exists for a decomposition of rotational structure for E vibrational state. Naturally the sum of Δ or c_1 over two isolated bands obtained after splitting of the rotational structure of E state equals zero. Thus only one number is sufficient to characterize topological invariants for two bands.

The case of triply degenerate vibrational state is more complicated. Now to describe all possible decompositions of the rotational structure of a triply degenerate vibrational state we need two parameters because the sum of Δ or c_1 over all three components is zero. It is suitable to write equation (3) in this case as [34,23,18]

$$\begin{gathered} F \times (J) = (J + \Delta_{\text{max}}) + (J + \Delta_{\text{mid}}) + (J + \Delta_{\text{min}}); \\ \Delta_{\text{max}} + \Delta_{\text{mid}} + \Delta_{\text{min}} = 0. \end{gathered} \tag{5}$$

Eq. (5) is written in a simplified form because it does not take into account the difference between two three-dimensional representations F_1 and F_2 and one-dimensional representations A_i. But the possible values of Δ_i, shown in figure 3 are identical for F_1 and F_2.

It is also interesting to see the regularity in the possible values of Δ. In fact the whole pattern of possible Δ values can be reconstructed from an "elementary cell" represented in figure 3 by hatching.

We can now summarize our discussion of the CF_4 molecule from the point of view of correspondence between the rotational structure of several vibrational states in terms of effective fully quantum Hamiltonian and that in terms of semi-quantum model. The notion of an energy band which is empirically used for the quantum problem finds its justification within the semi-quantum construction which allows us to associate with each isolated energy band a topological invariant and to split the space of control parameters into iso-Chern domains and walls between them. Going from the quantum Hamiltonian to a semi-quantum model and studying the wall-crossing enables one to characterize for the quantum problem the transformation from one qualitative

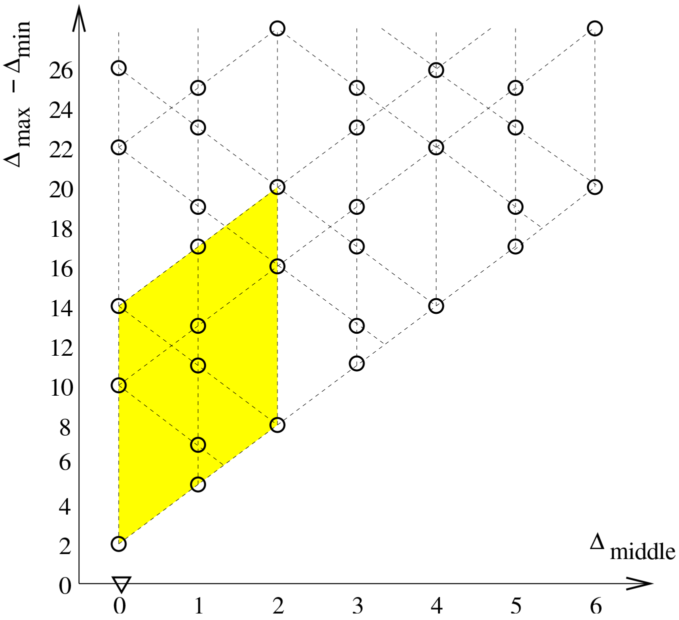

Fig. 3 Possible decompositions of rotational structure for triply degenerate vibrational F state into three isolated bands.

type of internal dynamics to another one and to relate this transformation to a precise topological invariant "delta-Chern". Possible values of delta-Chern are strongly related with the symmetry group of the problem, in particular with the stratification of the classical phase space for rotational motion by the symmetry group action. Different possible decompositions of the rotation-vibration energy level system into an elementary band system are described in terms of possible decompositions of trivial vector bundles into a sum of eigenline bundles with specific Chern numbers whose choice is restricted by symmetry.

Qualitative modifications of the band structure in isolated molecules are therefore similar to topological phase transitions intensively studied in solid state physics. The analysis made in this section uses essentially the fact that the symmetry group of the problem is finite. An important consequence of this assumption is a formally infinite number of possible nonequivalent reorganizations of band structure and infinite choices of possible different band structures compatible with a given initial finite set of vibrational states for sufficiently high J-values.

3 Band structure in the presence of axial symmetry

We now return to the analysis of the semi-quantum model describing rotation vibration structure in the presence of axial symmetry. To simplify the analysis we will consider the $SO(2)$ rotational group as an invariance group of the problem. An effective rotation-vibration Hamiltonian under study describes rotational structure of K vibrational states whose symmetry with respect to the $SO(2)$ group is given by a reducible representation written in the form $m_1 \oplus m_2 \oplus \ldots \oplus m_K$. Here we are reminded of the fact that the $SO(2)$ group is Abelian and all its irreducible representations are one-dimensional. For a chosen value of the rotational angular momentum, J, there are $2J+1$ rotational functions which span the irreducible representation (J) of the $SO(3)$ group. The decomposition of the representation (J) of $SO(3)$ group into irreps of $SO(2)$ subgroup, which is supposed to be the symmetry group of the problem is given by the well known relation

$$(J) = \sum_{m=-J}^{J} m. \tag{6}$$

This means that the complete set of rotation-vibration states of the effective Hamiltonian under study spans the reducible representation of the $SO(2)$ group

$$\left(\sum_{i=1}^{K} m_i \right) \otimes (J) = \sum_{i=1}^{K} \sum_{m=-J+m_i}^{J+m_i} m. \tag{7}$$

This reducible representation is fixed by the formulation of the effective problem and relevant for the full quantum effective problem and for the semi-quantum model. The questions which we want to answer now are:

i) What system of bands is possible for this problem?

ii) What kind of elementary rearrangements of bands are allowed under variation of a control parameter? (We can take as a control parameter the absolute value of J.)

iii) How to describe the rearrangement of band structure by the topological invariant, the Chern number?

We start by looking at simplest interesting case of effective Hamiltonian, namely the Hamiltonian for two vibrational states.

To specify the problem we need to define symmetry types of vibrational states and construct the complete set of rotation-vibration functions for a given value of the integral of motion, J. For two vibrational states of m_1 and m_2 symmetry and for a given J value for rotation, the $2(2J+1)$ rotation-vibration basis functions schematically shown in figure 4, left sub-figure, can be grouped into two sets each consisting of $2J+1$ states or into two subsets consisting of different number of basis functions. In order to interpret each subset as a rotational multiplet with some effective rotational number R, it is necessary that each multiplet is formed by a consecutive m values and the same decomposition should be valid for any sufficiently high J values. Taking $J \geq |m_2 - m_1|/2$ we obtain the representation of the basis set shown in figure 4 with $m_1 \leq m_2$ and $J + m_1 \geq -J + m_2$. In Figure 4, each of the bullets represents a basis function. The total number of the basis functions is kept before and after

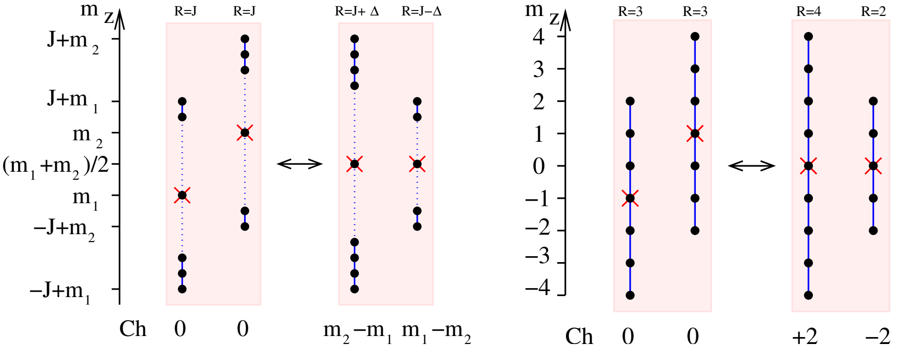

Fig. 4 Two possible band systems which are allowed for rotational structure of two vibrational states in the presence of $SO(2)$ symmetry for a fixed J-value. R is effective rotational quantum number for an isolated band. Left: General case of two vibrational states transforming according m_1 and m_2 representations of $SO(2)$. Right: Concrete realization for $m_1 = -1, m_2 = +1$ and $J = 3$. m_z indicates the symmetry of rotation-vibration state. "Ch" means Chern number for an isolated band. $\Delta = (m_2 - m_1)/2$. Cross shows the center of each individual band. Note that the whole set of upper ends of bands remains invariant under band rearrangement as well as the collection of lower ends of bands.

the rearrangement, but we have to note that the basis functions themselves are not literally identical before and after the rearrangement.

To relate the decomposition of the basis of rotation-vibration functions with a bundle structure associated with the semi-quantum model, we note that the decomposition into two groups with the same number of functions, one of which has $SO(2)$ labels varying from $-J+m_1$ to $J+m_1$ and the other from $-J+m_2$ to $J+m_2$ corresponds to the construction of two trivial vector bundles over the sphere with zero Chern number for each. If the decomposition is changed, the only one alternative decomposition into two bands is possible. One band covers the space consisting of basis functions with $SO(2)$ labels varying from $-J+m_1$ till $J+m_2$ whereas another band covers the space formed by functions with $SO(2)$ labels varying from $-J+m_2$ till $J+m_1$. Obviously such a decomposition is possible if $J \geq |m_2 - m_1|/2$. This is quite natural for a semi-quantum model, since the J-values have been necessarily assumed to be high when going to a classical limit over rotational variables for forming the semi-quantum model. The Chern numbers for these two bands become equal to $\pm(m_2 - m_1)$. It is important to note that these two bands can be considered as effective rotational multiplets associated with vibrational states transforming according to an irreducible representation $m = (m_1 + m_2)/2$ of the symmetry group $SO(2)$.

Nevertheless, formally the description of the reorganization of energy bands can be given even in the case of $J < |m_2 - m_1|/2$. To illustrate such a possibility let us look at an example of two rotational multiplets with vibrational symmetry $m_1 = -5$ and $m_2 = +5$. Normally, for $J \geq 5$ we have two possibilities to form two bands.

i) We can have two bands with the same number of states, $2J + 1$, with vi-

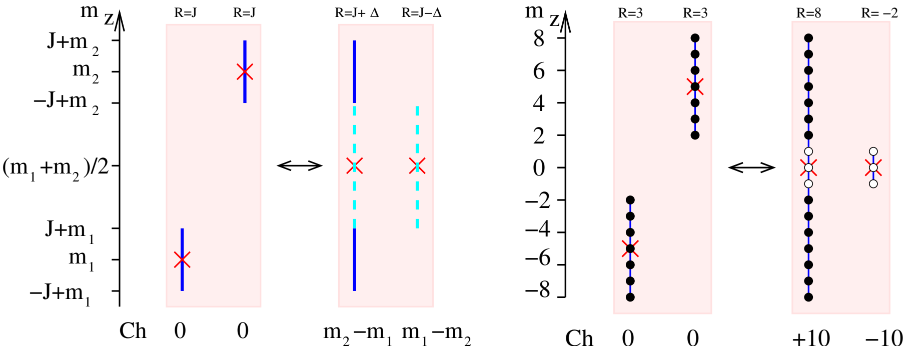

Fig. 5 The interpretation of two possible band systems which are allowed for rotational structure of two vibrational states in the presence of $SO(2)$ symmetry for a fixed J-value in case of $J < |m_2 - m_1|/2$. Left: General case of two vibrational states transforming according m_1 and m_2 representations of $SO(2)$. “Ghost band“ and the annihilated part of the only observed band are shown by dash line. Right: Concrete realization for $m_1 = -5, m_2 = +5$ and $J = 3$. States which belong to ghost band and to annihilated part of the observed band are shown by empty dots. m_z indicates the symmetry of rotation-vibration state. “Ch“ means Chern number for an isolated band. $\Delta = (m_2 - m_1)/2$. Cross shows the center of each individual band.

brational symmetries $m_1 = -5$, $m_2 = +5$, and with the trivial Chern number zero.
ii) We can form two bands composed by different number of quantum states and corresponding to different effective rotational quantum number, $R = J - 5$ and $R = J + 5$, and the vibrational symmetry $m = 0$. In the classical limit these two bands have Chern numbers $\pm(m_1 - m_2) = \pm 10$.

For $J < |m_1 - m_2|/2$, i.e. in the considered case for $J < 5$, two isolated bands with the same number of quantum states in each band exist but between these two bands there exist an interval of m values which are not associated with quantum states. Figure 5 illustrates the situation for the general case of $J < |m_1 - m_2|/2$ and for the concrete case of $J = 3$ and $m_1 = -5$, $m_2 = +5$. To keep formally the possibility to reorganize the bands we introduce “ghost“ states which fill the interval between two bands and interpret the resulting system as formed by two virtual bands: one with energy states with $-J + m_1 \le m \le J + m_2$ and another with “ghost“ states with $J + m_1 + 1 \le m \le -J + m_2 - 1$. Figure 5, right illustrates the general situation for $J = 3$ and $m_i = \pm 5$. The two bands after rearrangement correspond to $R = J \pm (m_2 - m_1)/2$, i.e. for $R = 8$ and $R = -2$. The band with $R = -2$ is interpreted as a “ghost band“, which does not appear as a system of really observable states but as a formal band which annihilates the same number of quantum states from the other band and the overall system of energy levels consists of really observable states. The band with $R = 8$ has only 14 observable states instead of the formal number $2R + 1 = 17$, because three states, namely those associated with $m = 0, \pm 1$ are annihilated by the “ghost band“.

The suggested interpretation allows us to use the classical limit for the description of the rearrangement of bands for any J value. Physically, this means that for low J values it is still possible to have two topologically different situations. One corresponds to splitting of observable levels into two bands with trivial Chern number 0 and with the effective rotational quantum number $R = J$ for both bands. The both bands are observable in this case. Another situation corresponds to formation of only one observable band with nontrivial Chern number c and with the effective rotational number $R_\mathrm{o} = J + c/2$. The second band becomes "ghost", i.e. unobservable. The "ghost" band is characterized by a negative value of $R_\mathrm{g} = J - c/2 \leq -1$ and, consequently, by the negative number of quantum states, $2R_\mathrm{g} + 1 \leq -1$. This negative number of states for the "ghost" band leads to the fact that the number of observable quantum states for the observable band is different form $2R_\mathrm{o} + 1 = 2J + c + 1$ and equals $4J + 2$. The number $4J + 2$ is the total number of observed energy levels for a given J value within the model of two bands. The difference between the number of observed states and the formal number of states expressed in terms of J and Chern number suggests to name this band a "fractional" band.

Note that the "ghosts" are used to compensate unphysical degrees of freedom [12] and lead, in particular, to the appearance of negative spins [30,29]. In our interpretation of the band structure at low J values, $J < |m_1 - m_2|/2$, we replace actually the classical problem with two degrees of freedom (one degree of freedom is associated with the projection of angular momentum and another with two components of vibrational states) by an effective observable problem with one degree of freedom (projection of effective rotational momentum R). The "ghost" band corresponding to a negative R_g value causes the appearance of the difference between the number of "physically observable states", i.e. $4J + 2$, and formally associated to the only observable band $2R_\mathrm{o} + 1$. The ratio between the really observable states in the "fractional" band with R_o quantum number and the virtual number of states in the band, $2R_\mathrm{o} + 1$, i.e. $\frac{4J+2}{2R_\mathrm{o}+1}$ increases when J varies from 0 till $J = |m_1 - m_2|/2$. For $J = |m_1 - m_2|/2$ the "ghost" band is materialized. Its quantum number R_g becomes equal to 0 and remains positive for higher J values. Simultaneously with materialization of the "ghost" band, the fractional band becomes a normal band with the number of observable states equal to $2J + c + 1$. In the presence of the "ghost" band the observable "fractional" band can be characterized by a fractional quantum factor $\frac{4J+2}{2R_\mathrm{o}+1}$ which can be expressed explicitly in terms of J, m_1, m_2. Namely, we have for the fractional factor ν_{J,m_1,m_2} the following expression

$$\nu_{J,m_1,m_2} = \frac{4J + 2}{2J + |m_1 - m_2| + 1}, \quad J < |m_1 - m_2|/2, \tag{8}$$

which is valid only in the presence of a "ghost" band. For $J = |m_1 - m_2|/2$, the ghost band is materialized and becoming normal band with $R = 0$, i.e. with one observable quantum state. To extend expression (8) for $J \geq |m_1 - m_2|/2$ we need to subtract from the numerator the number of states belonging to another band, namely $2J - |m_1 - m_2| + 1$. This gives for all $J \geq |m_1 - m_2|/2$ the fractional factor 1.

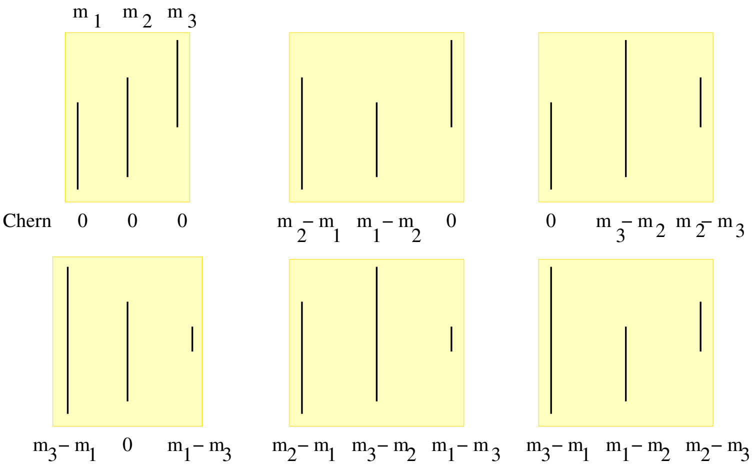

Fig. 6 Six possible band structures for rotation-vibrational energy levels for three vibrational states transforming according three different irreducible representations m_1, m_2, m_3 of the $SO(2)$ symmetry group.

4 Generalizations

Generalization of our analysis to the case of an arbitrary number of vibrational states in the presence of a continuous $SO(2)$ symmetry is straightforward. For N vibrational bands belonging to different m_i vibrational representations the total of $N!$ different possible band structures are possible because we can form a band by combining any lower end at $-J - m_i$ with an arbitrary upper end at $J + m_j$. Six alternative band structures for the rotation-vibration energy level system formed by three vibrational states are represented in figure 6.

Again we should note that the indicated in figure 6 six band structures correspond to the case of sufficiently high J values. At low J it is possible that there exist one or two “ghost“ bands and only two or even one band remain observable. The best way to see possible band structures for low J-values is to make a continuation in J: Starting with a sufficiently high J value, we lower the J value, keeping invariant the topological structure, i.e., Chern numbers, to look for effective rotational quantum numbers expressed in terms of J and Chern numbers.

To characterize the band structure for rotation-vibration problem for N vibrational states belonging to $m_1, m_2, \ldots, m_N$ irreducible representations of the $SO(2)$ symmetry group we need to specify for each band within the semi-quantum approach the Chern number and the position of the center of band. As an initial band system we can take bands with zero Chern numbers and with band centers $m_1, m_2, \ldots, m_N$. Since the number of bands before and after rearrangement is supposed to be conserved within the semi-quantum models under study, different band structures correspond to different permutations of the ends of bands so that we can classify band structures in exactly the same way as permutations of N objects, i.e. by the cycle structure of permu-

Table 1 Band structures for a model with two quantum states with $SO(2)$ symmetry m_1, m_2. First line of the table shows the trivial band structure. Second line gives the only possible alternative case. Chern numbers and center positions for each of two bands are given for sufficiently high N values.

Cycle	Chern number		Band center	
1^2	0	0	m_1	m_2
2	$m_2 - m_1$	$m_1 - m_2$	$\frac{m_1+m_2}{2}$	$\frac{m_1+m_2}{2}$

Table 2 Irreducible band structures associated with cyclic structure 3 of permutation group S_3 for a model with three quantum states with $SO(2)$ symmetry m_1, m_2, m_3. First line of the table shows the trivial band structure. Two irreducible cases follow below. Chern numbers and center positions for each of three bands are given for two possible irreducible band structures for sufficiently high N values.

Cycle	Chern number			Band center		
1^3	0	0	0	m_1	m_2	m_3
3	$m_2 - m_1$	$m_3 - m_2$	$m_1 - m_3$	$\frac{m_1+m_2}{2}$	$\frac{m_2+m_3}{2}$	$\frac{m_3+m_1}{2}$
	$m_3 - m_1$	$m_2 - m_3$	$m_1 - m_2$	$\frac{m_1+m_3}{2}$	$\frac{m_2+m_3}{2}$	$\frac{m_1+m_2}{2}$

Table 3 Irreducible band structures associated with cyclic structure 4 of permutation group S_4 for a model with four quantum states with $SO(2)$ symmetry m_1, m_2, m_3, m_4. First line of the table shows the trivial band structure. Six irreducible cases follow below. Chern numbers and center positions for each of four bands are given for all six possible irreducible band structures for sufficiently high N values.

Cycle	Chern number				Band center			
1^4	0	0	0	0	m_1	m_2	m_3	m_4
4	$m_2 - m_1$	$m_3 - m_2$	$m_4 - m_3$	$m_1 - m_4$	$\frac{m_1+m_2}{2}$	$\frac{m_2+m_3}{2}$	$\frac{m_3+m_4}{2}$	$\frac{m_1+m_4}{2}$
	$m_4 - m_1$	$m_3 - m_4$	$m_2 - m_3$	$m_1 - m_2$	$\frac{m_1+m_4}{2}$	$\frac{m_3+m_4}{2}$	$\frac{m_2+m_3}{2}$	$\frac{m_1+m_2}{2}$
	$m_2 - m_1$	$m_4 - m_2$	$m_3 - m_4$	$m_1 - m_3$	$\frac{m_2+m_1}{2}$	$\frac{m_4+m_2}{2}$	$\frac{m_3+m_4}{2}$	$\frac{m_1+m_3}{2}$
	$m_3 - m_1$	$m_4 - m_3$	$m_2 - m_4$	$m_1 - m_2$	$\frac{m_3+m_1}{2}$	$\frac{m_4+m_3}{2}$	$\frac{m_2+m_4}{2}$	$\frac{m_1+m_2}{2}$
	$m_3 - m_1$	$m_2 - m_3$	$m_4 - m_2$	$m_1 - m_4$	$\frac{m_3+m_1}{2}$	$\frac{m_2+m_3}{2}$	$\frac{m_4+m_2}{2}$	$\frac{m_1+m_4}{2}$
	$m_4 - m_1$	$m_2 - m_4$	$m_3 - m_2$	$m_1 - m_3$	$\frac{m_4+m_1}{2}$	$\frac{m_2+m_4}{2}$	$\frac{m_3+m_2}{2}$	$\frac{m_1+m_3}{2}$

tations. For two bands there are only two classes, 1^2 and 2. Table 1 describes two possible band structures for two bands. In case of N bands we can name “irreducible band structures“ all systems of bands associated with cyclic permutations of maximal length, N. There are $(N-1)!$ such band systems. All other band structures are associated with rearrangements between subsets of initially trivial bands. Irreducible band structures for models with three and four bands are given in tables 2, 3.

Each band structure can be associated with a classifying operator in such a way that the same eigenvalue of the classifying operators corresponds to all quantum states belonging to the same band and different eigenvalues correspond to different bands. The simplest example of such a classifying operator naturally appears in a particular case when all “vibrational states“ form a reducible representation of the $SO(2)$ group which can be considered as an irreducible representation (S) of $SU(2)$ or $SO(3)$ group. The coupled basis in this case is the eigen-basis of $\mathbf{SJ} = (\mathbf{R}^2 - \mathbf{J}^2 - \mathbf{S}^2)/2$ operator. The transformation between an uncoupled and a coupled basis of two angular momenta $\mathbf{S}$

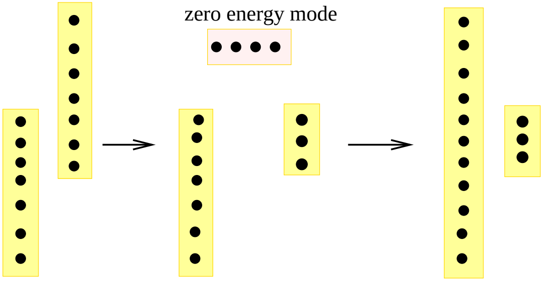

Fig. 7 Rearrangement of bands through formation of zero mode states in the case of sufficiently high J values. For this figure $J = 3$ and $m_1 = -2, m_2 = 2$. Quantum states are shown by black fill dots.

and **J** can be considered as a well known example of a transformation between two different band structures. A classifying operator for one (uncoupled) band structure is the S_z operator. Each of its eigenvalues is $2J + 1$ degenerate and corresponds to a band with trivial Chern number 0. The classifying operator for coupled basis is **SJ**. If $J \geq S$ there are $2S+1$ bands characterized by quantum number $R = J + S, J + S - 1, \ldots, J - S$. From the point of view of the semi-quantum model these bands are characterized by topological invariants, Chern numbers, $2S, 2(S - 1), \ldots, 2(-S)$.

A generalization of the present angular momentum coupling is possible to the case of a weighted action of the symmetry group $SO(2)$ on vibrational and rotational variables. A weighted action is defined in such a manner that $SO(2)$ invariant subspaces are given by

$$W^{(\ell)}_{J,S} = \mathrm{span}\{|k\rangle \otimes |r\rangle; k + 2r = \ell, |k| \leq J, |r| \leq S\}. \tag{9}$$

In particular, vibrational states with $m_1 = -1$, $m_2 = 1$ are comparable with the *effective* spin $S = 1/2$. In a similar way, four vibrational states with symmetry ±1, ±3 are comparable with the *effective* spin $S = 3/2$. However, in this case, the transformation to the coupled basis with respect to a certain classifying operator describes only one among $4! = 24$ possible bases. All these 24 band structures are listed in table 4.

The band system corresponding to angular momentum coupling between J and *effective* spin $S = 3/2$ in presence of weighted symmetry is associated with the cycle structure 2^2 of the group of permutation S_4 (see line 10 in table 4).

Up to now we have discussed different possible band structures but did not touch the question of “elementary“, i.e. generic transformations between different band structures.

The rearrangement of band structure is possible within semi-quantum model through formation of degeneracy points of different eigenvalues of a matrix Hamiltonian. Generically the formation of degeneracy points is possible only between two eigenvalues. Consequently, an “elementary rearrangement“ occurs between two neighboring in energy bands.

Table 4 Band structures for a model with four quantum states with $SO(2)$ symmetry $\pm 1, \pm 3$. Chern numbers and center positions for each of four bands are given for all 24 possible band structures.

N	Cycles	Chern number				Band center			
1	1^4	0	0	0	0	-3	-1	1	3
2	$2, 1^3$	2	-2	0	0	-2	-2	1	3
3		4	0	-4	0	-1	-1	-1	3
4		6	0	0	-6	0	-1	1	0
5		0	2	-2	0	-3	0	0	3
6		0	4	0	-4	-3	1	1	1
7		0	0	2	-2	-3	-1	2	2
8	2^2	2	-2	2	-2	-1	-1	1	1
9		4	4	-4	-4	-1	1	-1	1
10		6	2	-2	-6	0	0	0	0
11	$3, 1$	2	2	-4	0	-2	0	-1	3
12		4	-2	-2	0	-1	-2	0	3
13		4	0	2	-6	-1	-1	2	0
14		6	0	-4	-2	0	-1	-1	2
15		2	4	0	-6	-2	1	1	0
16		6	-2	0	-4	0	-2	1	1
17		0	2	2	-4	-3	0	2	1
18		0	4	-2	-2	-3	1	0	2
19	4	2	2	2	-6	-2	0	2	0
20		2	4	-2	-4	-2	1	2	-1
21		4	-2	$+4$	-6	-1	0	1	0
22		4	2	-4	-2	-1	2	1	-2
23		6	-2	-2	-2	0	2	0	-2
24		6	-4	2	-4	0	1	0	-1

In order to give a concrete simplest form of the local Hamiltonian associated with the formation of a degeneracy point and with a point on the path crossing (in the control parameter space) the wall between iso-Chern domains let us take an example of two vibrational states belonging to two irreducible representations of the $SO(2)$ group $\pm k$ and suppose that the rotational momentum N is sufficiently high. This allows us to treat in parallel the semi-quantum and the full quantum models.

The whole linear space of quantum states within the full quantum problem has dimension $2(2N+1)$ and can be described in terms of decoupled basis $|M_N, \pm k\rangle$, $|M_N| \leq N$ or in terms of coupled basis $|M_J = M_N \pm k, M_N, \pm k\rangle$.

The decoupled basis is suitable to use if we want to classify states according to eigenvalues of the "vibrational" operator $V_z = \begin{pmatrix} k & 0 \\ 0 & -k \end{pmatrix}$ as a classifying operator. The operator V_z plays the role of effective "spin operators" together with $V_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ and $V_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$.

The operator V_z has two eigenvalues $\pm k$. It splits $2(2N+1)$ quantum states into two bands with the same number of states in the band according to its eigenvalue. The operators $V_\pm$ are formally defined as operators transforming vibrational functions $V_+|-k\rangle = |k\rangle$, $V_-|k\rangle = |-k\rangle$. Using $N_z, N_\pm$ rotational operators an $SO(2)$ invariant operator constructed from rotational and vibrational operators in the simplest form can be written as $\mathbf{NV} = N_z V_z + V_+ N_-^{2k} + V_- N_+^{2k}$. This operator can be used as classifying operator within a coupled rotation-vibrational basis. One of the resulting bands consists of $2(N+k)+1$ eigenstates, whereas another band has $2(N-k)+1$ eigenstates.

To describe the transformation from one band system to another one, as it is schematically shown in figure 7, we suggest the following explicit polynomial form of the operator describing the wall-crossing

$$H_{\text{wall cross}} = a \prod_{\alpha=0}^{2k-1} \left(N_z + V_z - (N+k-\alpha)\right) + b \,\left(V_- N_+^{2k} + V_+ N_-^{2k}\right). \quad (10)$$

This operator is $SO(2)$ invariant and consequently commutes with J_z. The operator (10) has $2k$ zero eigenvalues associated with the eigenfunctions of the J_z operator with eigenvalues $N+k, N+k-1, \dots, N-k+1$.

Eigenstates with zero eigenvalue of the local Hamiltonian (10) are named zero-mode states. They are responsible for topological phase transitions.

Crossing a wall in the control parameter space gives rise to a deformation of the model Hamiltonians in such a manner that the zero energy modes disappear in the full quantum model and that the degeneracy of eigenvalues disappears in the semi-quantum model. In general it is possible to imagine several different situations. In the case of one zero eigenvalue, (the case with $k = 1/2$), under the variation of control parameters corresponding to the crossing of the boundary, this zero eigenvalue simply crosses the zero energy either from the positive side to the negative side or vice versa. This is a generic behavior.

In the case of two zero eigenvalues the scenario of their behavior under the variation of control parameters can be similar. It is possible that two eigenvalues come from the same side (positive or negative), become degenerate at zero, and go to another side crossing the zero. This scenario repeats the generic scenario with one zero eigenvalue except that the zero eigenvalue becomes degenerate and the redistribution consists of two eigenvalues. Such a scenario was discussed on a concrete example of a molecular system in [3] for the CF_4 molecule, where the redistribution of two 6-fold clusters was observed between two bands. The fact of six-fold quasi-degeneracy is naturally not important in our present context. It is a consequence of finite cubic symmetry. The important point here is the fact of a simultaneous transfer of two clusters. This means that for each degeneracy point and, in other words for each wall-crossing model Hamiltonian two zero eigenvalues are formed. In contrast, transfer of only one cluster (or of only one of two levels for each local Hamiltonian) between these bands is forbidden by symmetry. Formation of several zero mode states is illustrated schematically in figure 7.

Another possible scenario with two zero eigenvalues corresponds to two eigenvalues coming to zero from different sides (one from the positive and another from the negative). After crossing the boundary the two zero eigenvalues leave again to two different sides. The cumulative effect of crossing the boundary is: no redistribution of energy levels between bands. This situation can be compared with the spin Hall effect, where Hall currents related to electrons with spin projections $+1/2$ and $-1/2$ are non-zero but opposite and the net effect is zero. Apparently such a situation cannot appear in a problem with $m_1 - m_2 \neq 0$. We need to combine the case with $m_1 - m_2 = 0$ with additional symmetry responsible for the formation of zero energy mode. Note that the requirement $m_1 - m_2 = 0$ (in case of zero Chern numbers for each band) for such scenario appears for the case of the axial symmetry group $SO(2)$. In case of a finite symmetry group the numbers of states in two bands can be different but the formation of two zero energy states coming along the deformation from two different bands remains possible.

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