Topologically coupled energy bands in molecules

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Abstract

We propose a concrete application of the Atiyah–Singer index formula in molecular physics, giving the exact number of levels in energy bands, in terms of vector bundle topology. The formation of topologically coupled bands is demonstrated. This phenomenon is expected to be present in many quantum systems.
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1. Introduction

Molecular spectra of small molecules possess thousands of energy levels which are known with high precision and characterize the dynamical behavior of nuclei and electrons in very fine detail. Thus a qualitative approach may be useful in front of the huge complexity of the spectrum [1–3]. A major simplification arises in molecules because the dynamics contains different typical time scales, in other terms, fast and slow dynamical motions, which are coupled together. There are roughly three different typical time scales, a short time ($\tau_e \simeq 10^{-16} \to 10^{-15}$ s) related to fast motion of the light electrons, a longer time scale

($\tau_v \simeq 10^{-14} \to 10^{-13}$ s) related to the slower vibrational motion of the heavier nuclei, and an even longer time scale ($\tau_{\rm rot} \simeq 10^{-13} \to 10^{-12}$ s) related to the rotational motion of the molecule.

This separation of time scales manifests itself in the full spectrum by energy levels which are regrouped together in so called quantum energy bands. The fine structure of the bands reflects the slow motion, whereas the coarser repartition of different energy bands is related to the faster motion.

In order to have a nice understanding of these band structures, it is very useful and natural for such fast and slow coupled systems to use the Born–Oppenheimer (adiabatic) approach. In this description, the slow motion is described by classical dynamical variables $X_{\rm slow}$ belonging to a classical phase space $\mathcal{P}_{\rm slow}$, and for a given value of $X_{\rm slow}$ considered as fixed, the instantaneous fast quantum motion is described by

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a Hamiltonian $\widehat{H}_{\text{fast}}(X_{\text{slow}})$ acting in a Hilbert space $\mathcal{H}_{\text{fast}}$. The description of the dynamics by $\widehat{H}_{\text{fast}}(X_{\text{slow}})$ will be called the "semi-quantum description" in this Letter. The full quantum dynamics can be recovered from the semi-quantum description, by quantization of the slow variables X_{slow}. By this quantization procedure, the operator valued function $\widehat{H}_{\text{fast}}(X_{\text{slow}})$ gives a Hamiltonian operator $\widehat{H}_{\text{tot}}$ acting in full Hilbert space $\mathcal{H}_{\text{slow}} \otimes \mathcal{H}_{\text{fast}}$. Eigenvalues of $\widehat{H}_{\text{tot}}$ are the experimentally observed energy levels.

In the semi-quantum description, the eigenvalues $E_1(X_{\text{slow}}), E_2(X_{\text{slow}}), \ldots$ of $\widehat{H}_{\text{fast}}(X_{\text{slow}})$, depend on the dynamical variables X_{slow}. Each eigenvalue function $E_i(X_{\text{slow}})$ is called a semi-quantum energy band. Its image is a continuous interval of energy, as opposed to the quantum energy band defined above, containing discrete energy levels. For each eigenvalue $E_i(X_{\text{slow}})$, the associated eigenspace of $\widehat{H}_{\text{fast}}(X_{\text{slow}})$, interpreted as an instantaneous stationary mode of the fast dynamics, depend also on the dynamical variables X_{slow}. In geometrical terms, for each semi-quantum band, this collection of eigenspaces (parametrized by $X_{\text{slow}} \in \mathcal{P}_{\text{slow}}$) defines a vector bundle over the base space $\mathcal{P}_{\text{slow}}$ [4], [5, p. 13]. Each eigenspace is called the fiber over the point X_{slow}. The topology of the vector bundle reveals the possible twists of the fibers over the space $\mathcal{P}_{\text{slow}}$, as in the well-known example of the Möbius strip. The topological characterization of the vector bundle therefore contains quantitative information concerning the band, robust under perturbations. It is known that the topology of a complex vector bundle is partially characterized by a Chern class, which can be identified in practice by a collection of integer numbers (Chern numbers)[1].

The purpose of the present Letter is to show that for general fast and slow coupled quantum systems, the Atiyah–Singer formula gives a relation between the topological characterization of the vector bundle defined within the semi-quantum description on one side, and the exact number of levels contained in the quantum band on the other side. We will see that the Atiyah–Singer formula gives not only the total number of levels, but more precisely the local density of levels

in each band. The topological characterization of the bands within the semi-quantum description is also useful to understand and predict the evolution of band structures as some external parameters are varied. In particular, we describe a new qualitative phenomenon related with the formation of topologically coupled bands (nondecomposable vector bundles).

We emphasize that we assume adiabatic separation between the fast and slow dynamics but the coupling between them is not assumed to be weak. In fact, topological bifurcation phenomena need strong enough coupling to appear.

The mathematical approach we need to characterize these qualitative modifications, is a semi-classical analysis within the Born–Oppenheimer approximation and topological analysis of vector bundles. Precise mathematical theories are developed in [7–9]. In particular, in C. Emmrich and A. Weinstein Letter [9] (which is an important prerequisite for the present Letter), it is shown how a vector bundle defined within the semi-quantum description can be associated to a group of quantum levels, through the construction of a projector acting in $\mathcal{H}_{\text{slow}} \otimes \mathcal{H}_{\text{fast}}$. The rank of this projector is precisely the number of levels contained in the quantum band and given by the Atiyah–Singer index formula.

As explained above, several typical molecular examples can be suggested to illustrate the presence of such a band structure and the evolution of it with the variation of external parameters.

(i) Vibrational structure of different electronic states. The existence of a fine vibrational structure associated with different electronic states is the standard consequence of the Born–Oppenheimer (adiabatic) separation of electronic and nuclear variables in molecules based on the smallness of the ratio $(m_e/M_n)^{1/4} \sim 1/10$ (here m_e and M_n are the electron mass and the typical mass of nuclei) [10].

(ii) Rotational structure of different vibrational states. The rotational excitations are typically smaller than the vibrational ones. The quantum spectrum has a fine rotational band structure associated with a more crude vibrational structure. The absolute value J of the angular momentum is a strict integral of motion for an isolated molecule, and can be used as a natural parameter to analyze the evolution of rotational bands [2,3].

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[1] The Chern class completely characterizes the topology of vectors bundles over $\mathbb{C}P^2$ considered in this Letter. However this is not true in general [6].

(iii) A more sophisticated example considered in this Letter and described in more details below, arises for systems which possess vibration modes with (quasi)-degenerate frequencies. Such a situation typically takes place in problems with symmetry. The description of the degenerate vibrations in the harmonic oscillator approximation gives an energy spectrum formed by degenerate energy levels, the so called polyads. Each polyad is characterized by the total number of vibrational quanta N, it contains. In systems where these vibrational modes are coupled with electronic states, one obtains an electronic-vibrational (vibronic) band structure. A typical question is the evolution of this vibronic band structure with N [11,12] and its persistence (or reorganization) as a function of external physical parameters.

In all these previous examples, when an external parameter is varied, along with modifications of the internal structure of each isolated band, one observes more serious modifications of the global band structures [13–17]. Sometimes two semi-quantum energy bands degenerate. In the corresponding quantum spectrum, a certain number of levels pass from one quantum band to the other, resulting in a redistribution of levels between bands. These qualitative phenomena reflect band structure properties which are robust under modification of parameters, except for abrupt structure changes, and can be suitably expressed by the topological description suggested above: they correspond to topological bifurcations of the vector bundles.

Such a description has been done for rotational bands in [18,19], where the slow rotational motion takes place on a two dimensional sphere phase space, $\mathcal{P}_{\text{slow}} = S^2$. It has been shown there that the semi-quantum description associates to each individual rotational band a line bundle over the sphere S^2. The topology of this bundle is characterized by an integer Chern index C. The exact number of levels in the quantum energy band is given by $\mathcal{N} = (2J + 1) - C$ (this is a particular case of the index formula). Generic isolated degeneracy between two consecutive semi-quantum bands are responsible for a change of topology $\Delta C = \mp 1$ of the line bundles, as well as an exchange of one energy level $\Delta \mathcal{N} = \pm 1$ between the two quantum bands.

For rotational bands, the topological phenomena are quite simple due to the fact that the slow rotational motion has one degree of freedom. We present now a more interesting example both from the physical and mathematical point of view, where the slow motion comes from molecular vibrations and has two degrees of freedom ($\mathcal{P}_{\text{slow}}$ is a four dimensional compact phase space). As explained in [18,19], modifications of the band structures are due to degeneracies, and to the property that for a general family of Hermitian matrices, degeneracies occur with three external parameters; this is the Wigner–Von Neumann theorem, see [20, §79]. The simplicity of the topological phenomena in the rotational bands case is due to the fact that $X_{\text{slow}} \in P_{\text{slow}} = S^2$ gives only two external parameters (less than three). So if dim $P_{\text{slow}} = 4$, we expect qualitatively new results. On an other hand, nontrivial topological bundle need a compact base space. For those reasons $P_{\text{slow}} = \mathbb{C}P^2$ is a natural candidate.

2. Description of the slow dynamics with $\mathbb{C}P^2$ classical phase space

The fast and slow coupled system investigated in the sequel of this paper corresponds respectively to slow vibrations of the nuclei coupled to fast electronic excitations. We first describe independently the slow motion and couple it to the fast motion only after. The slow motion we consider comes from three vibrations with the same frequency (called 1:1:1 resonance, or triply degenerate vibrational modes) described by

$$H_{\text{vib}} = \sum_{k=1,2,3} \frac{1}{2}\left(p_k^2 + q_k^2\right) = \sum_{k=1,2,3} |Z_k|^2, \qquad (1)$$

where a complex notation $Z_k = (q_k + ip_k)/\sqrt{2}$ is used. The time evolution of a point $Z = (Z_1, Z_2, Z_3)$ in phase space $\mathbb{C}^3$ is given by a phase factor: $Z(t) = \exp(-it)Z(0)$. The family of (closed) trajectories of a given energy, say $E = 1$, forms a four dimensional phase space $[4 = 6 - 1(\text{energy}) - 1(\text{time})]$ which is a reduced phase space from the classical mechanics point of view (the reduction is with respect to the action of $\mathcal{H}_{\text{vib}}$). This space is known in mathematics as the complex projective space and noted $\mathbb{C}P^2 = P(\mathbb{C}^3)$: a point in $\mathbb{C}P^2$ corresponds to a given closed trajectory of energy E and will be noted by $[Z]$ in

the sequel. The corresponding quantum Hamiltonian $\widehat{H}_{\mathrm{vib}} = \sum_{k=1,2,3} a_k^+ a_k + 3/2$ is obtained by replacing $Z_k, \overline{Z_k}$ by operators a_k, a_k^+ respectively. A given energy level is thus an integer N plus $3/2$, and this level has degeneracy

$$\mathcal{N}_0 = (N+1)(N+2)/2.$$

The associated eigenspace $\mathcal{H}_{\mathrm{slow}} = \mathcal{H}_{\mathrm{polyad}} = \mathbb{C}^{\mathcal{N}_0}$ is called the polyad N, and corresponds to the classical phase space $\mathcal{P}_{\mathrm{slow}} = \mathbb{C}P^2$ [21].

At this point, the Hamiltonian H_{vib} restricted to $\mathcal{P}_{\mathrm{slow}}$ is just a constant and consequently any point of $\mathcal{P}_{\mathrm{slow}}$ (representing some closed trajectory) does not vary with time. Respectively the spectrum of $\widehat{H}_{\mathrm{vib}}$ restricted to $\mathcal{H}_{\mathrm{slow}}$ is degenerated. The slow motion comes once we introduce a perturbation in the Hamiltonian, or couple it with other degrees of freedom. Indeed, such a perturbation will give a slow precession of the orbits $Z(t)$, in other terms a slow motion of the representative point in $\mathbb{C}P^2$.

3. Coupling with the fast motion

We suppose now that the "slow" vibrational motion described above is coupled with fast electronic degrees of freedom, more precisely with three "electronic" states belonging to the quantum Hilbert space $\mathcal{H}_{\mathrm{fast}} = \mathcal{H}_{\mathrm{elec}} = \mathbb{C}^3$. We will discuss the physical meaning of this model in a subsequent section. For now, this model is constructed from a criterion of mathematical simplicity. In particular we will see that three electronic states is the smallest number of states giving interesting effects.

We will introduce the simplest form of the coupling, in a way similar to the standard spin-orbit coupling $\widehat{\mathbf{S}} \cdot \mathbf{L}$ described in [18,19] (in these notations, the spin is quantum, whereas the angular momentum $\mathbf{L}$ is classical). For this, we remark that one can write $\widehat{\mathbf{S}} \cdot \mathbf{L}/|\mathbf{L}| = |\mathbf{L}\rangle\langle\mathbf{L}| - 1/2$, where $|\mathbf{L}\rangle\langle\mathbf{L}|$ is the projector for the quantum spin state onto the direction of the classical $\mathbf{L}$ vector.[2]

In the spirit of semi-quantum approach, the slow vibrational motion is treated classically, and the coupling with fast electronic states is described by a classical Hamilton function defined on phase space $P_{\mathrm{slow}} = \mathbb{C}P^2$ with values in the space of 3×3 Hermitian matrices acting in $\mathcal{H}_{\mathrm{fast}}$:

$$\left(H_1([Z])\right)_{i,j=1,2,3} = \overline{Z_i} Z_j \Bigg/ \left(\sum_{k=1,2,3} |Z_k|^2\right)$$
$$= \left(|Z\rangle\langle Z|\right)_{i,j}. \tag{2}$$

In the last expression $|Z\rangle \in \mathcal{H}_{\mathrm{elec}}$ is a normalized vector. This expression shows that $H_1([Z])$ can be interpreted geometrically as a projector in $\mathcal{H}_{\mathrm{elec}}$ space onto the one dimensional space, a line, defined by the value of $[Z]$. From this, the eigenvalues of $H_1([Z])$ are $E_{\mathrm{Line}} = 1$, and $E_{\mathrm{Orth}} = 0$ with multiplicity two. "Orth" is for the two dimensional space orthogonal to the line.

The eigenspace of the matrix H_1 associated to the eigenvalue $E_{\mathrm{Line}} = 1$ is one dimensional. It defines therefore a rank 1 vector bundle over $\mathbb{C}P^2$ (The rank r of a vector bundle is the dimension of the fibers, here the eigenspaces). This vector bundle, denoted V_{Line} has a nontrivial topology as we will see below. The eigenspace associated with the eigenvalue $E_{\mathrm{Orth}} = 0$ is two-dimensional, and define a rank 2 vector bundle over $\mathbb{C}P^2$, denoted V_{Orth}, which is also nontrivial.

In order to see qualitative modifications of the band structure, we introduce an external parameter λ and construct a one-parameter family of Hamiltonians H_λ, $\lambda \in [0,1]$, which relates the Hamiltonian H_1 introduced above, with a Hamiltonian H_0 which does not depend on $[Z]$ (no vibronic coupling) and possess three nondegenerate electronic states described by a constant diagonal matrix:

$$H_\lambda([Z]) = (1-\lambda)H_0 + \lambda H_1([Z]),$$
$$\text{with } H_0 = \mathrm{Diag}(-1, 0, 1). \tag{3}$$

For each eigenvalue of H_0, the associated one-dimensional eigenspace define a rank 1 vector bundle over $\mathbb{C}P^2$. These three vector bundles noted T_1, T_2, T_3,

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[2] An equivalent way to justify the choice of the coupling Hamiltonian H_1 in Eq. (2), is because of its invariance with respect to the $SU(3)$ symmetry group (instead of the SO(3) group for the spin orbit coupling). For that purpose, we extend the $SU(3)$ symmetry of the three-dimensional harmonic oscillator $\mathcal{H}_{\mathrm{vib}}$ to

the three electronic states, supposing that the space $\mathcal{H}_{\mathrm{elec}} = \mathbb{C}^3$ is the three-dimensional fundamental representation of $SU(3)$. The Hamiltonian H_1 is then chosen to be invariant under the diagonal action of $SU(3)$ on $\mathbb{C}P^2 \times \mathbb{C}^3$.

Fig. 1. Spectrum of $\widehat{H}_1$ in terms of $SU(3)$ representations.

are trivial in the sense that the fibers (the eigenspaces) do not depend on $[Z]$.

4. Topological description of the vector bundles

In this section, we still consider the semi-quantum description defined by the matrix function $H_\lambda([Z])$ and the vector bundles defined from it. We give here a full description of the topology of these vector bundles.

The matrix $H_\lambda([Z])$ has three eigenvalues

$$E_1(\lambda, [Z]) \leqslant E_2(\lambda, [Z]) \leqslant E_3(\lambda, [Z])$$

forming three semi-quantum energy bands when $[Z] \in \mathbb{C}P^2$ varies. Fig. 2(a) shows the image of these three eigenvalues functions on the energy axis as a function of parameter λ (they can be computed analytically). Degeneracies between consecutive bands occur for certain values of $(\lambda, [Z])$. On Fig. 2(a), the projection of these degeneracy manifolds are represented by solid lines. Between bands 2 and 3, there is a degeneracy surface in the range $1/2 < \lambda < 2/3$, given in coordinates by[3]

$$Z_1 = 0, \qquad |Z_3/Z_2|^2 = 2(1 - 2\lambda)/(3\lambda - 2).$$

For a fixed value of λ, the associated eigenspaces of the eigenvalues E_1, E_2, E_3 also depend on $[Z]$ and therefore define vector bundles over $\mathbb{C}P^2$.

The topology of a general vector bundle F over $\mathbb{C}P^2$ is characterized by its rank r (the dimension of the fibers) and a polynomial $C(F) = 1 + Ax + Bx^2$, called the total Chern class, with integer coefficients $A, B \in \mathbb{Z}$, see [4, p. 299]. A rank $r = 1$ bundle
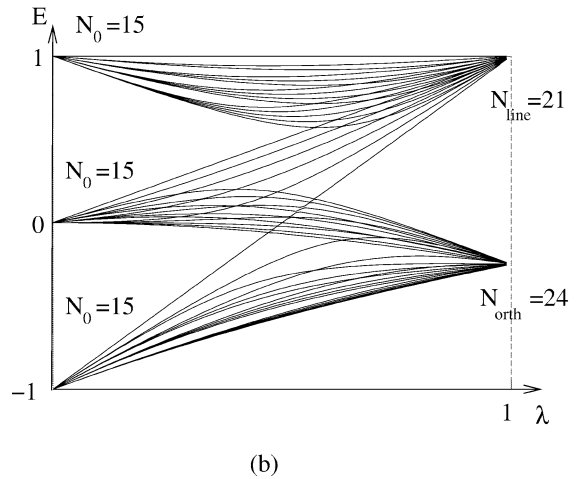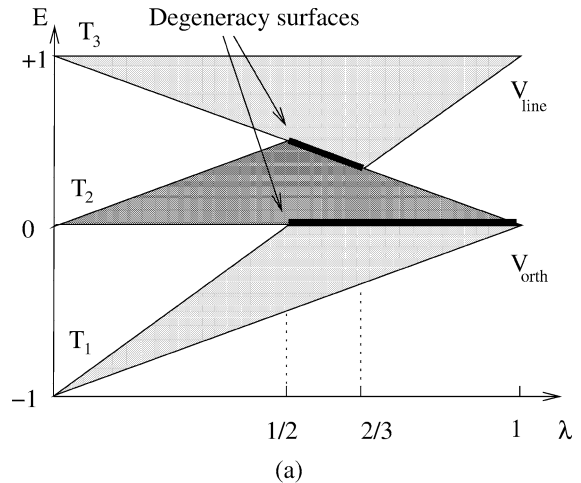

(a)

(b)

Fig. 2. (a) The semi-quantum band spectrum in the Born–Oppenheimer approximation, interpreted as vector bundles. (b) The exact spectrum of $\widehat{H}_\lambda$, for $N = 4$, with a transfer of $\Delta N = N + 2 = 6$ levels towards the upper group. The Atiyah–Singer formula (4) gives the number of levels of a given quantum band, say N_{Line}, in terms of the topology of the vector bundle V_{Line}.

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[3] For a general family of Hermitian matrices, degeneracies occur with three external parameters. Here, with the five external parameters $(\lambda, [Z])$, degeneracies are expected to hold on two-dimensional surfaces. The degeneracy surface between bands 2 and 3 is a homologically nontrivial sphere S^2 in $\mathbb{R} \times \mathbb{C}P^2$ homologous to $\{cste\} \times \mathbb{C}P^1$.

has necessarily $B = 0$.[4] A trivial bundle has Chern numbers $A = B = 0$.

The Chern class of the sum $F \oplus F'$ of two vector bundles is the product of polynomials

$$C(F \oplus F') = C(F) \wedge C(F')$$
$$= 1 + (A + A')x + (AA' + B + B')x^2,$$

keeping only terms of degree not greater than 2.

For $\lambda < 1/2$, on Fig. 2(a), there are three distinct bands, and so three associated vector bundles of rank $r = 1$, noted T_1, T_2, T_3. We already explained that these bundles are trivial in the sense that for $\lambda = 0$ the eigenspaces do not depend on $[Z]$, and by continuity the topology is also trivial for any $\lambda < 1/2$. The Chern classes are $C(T_i) = 1$, with $A = B = 0$.

For $1/2 < \lambda < 2/3$, there are degeneracy surfaces, and the three previous bundles T_1, T_2, T_3 "interact" together and form a vector bundle $T = T_1 \oplus T_2 \oplus T_3$ of rank 3. This is exactly the vector space $\mathcal{H}_{elec} = \mathbb{C}^3$ which does not depend on $[Z]$, so T is also trivial, this confirms that $C(T) = C(T_1) \wedge C(T_2) \wedge C(T_3) = 1$.

For $2/3 < \lambda < 1$, the previous bundle T decomposes into two bundles $T = V_{Line} \oplus V_{Orth}$. The upper energy band corresponds to a rank 1 vector bundle V_{Line}. By continuity, its topology can be computed at $\lambda = 1$, and corresponds to the well-known nontrivial tautological bundle over $\mathbb{C}P^2$ with $C(V_{Line}) = 1 + x$, see [4, p. 306]. The lower band corresponds to the orthogonal bundle V_{Orth}. This is a nontrivial bundle of rank $r = 2$, with $C(V_{Orth}) = 1 - x + x^2$, because $1 = C(T) = C(V_{Line}) \wedge C(V_{Orth})$. The vector bundle V_{Orth} cannot be decomposed into two rank 1 bundles just because its Chern class cannot be factorized, $1 - x + x^2 \neq (1 + Ax) \wedge (1 + A'x)$ with integers A, A'. Therefore we obtain that V_{Orth} is composed of *two bands which are topologically coupled*: a continuous perturbation cannot create a gap in it. To be decoupled, they would need a topological interaction with an external third band. This interesting phenomenon seems to be new in molecular physics.

It should also be noted that the coupling of the slow classical subsystem with at least three electronic quantum states is a necessary condition to see the formation of topologically nontrivial bands from initially isolated trivial bands. In the above model, two isolated trivial bands cannot be transformed into nontrivial bands for the following topological reason: the Chern class of a trivial rank 2 bundle over $\mathbb{C}P^2$ is $C(T) = 1$, and the decomposition into two rank one bundles $T = F_1 \oplus F_2$ gives the factorization

$$C(\mathbb{C}^2) = 1 = (1 + A_1x)(1 + A_2x)$$
$$= 1 + (A_1 + A_2)x + A_1A_2x^2$$

which implies that $A_1 = A_2 = 0$, and that F_1 and F_2 are trivial bundles. This constraint does not exist in the case of vector bundles over the sphere S_2, where the Chern class is just a degree one polynomial (the only constraint is $A_1 = -A_2$).

Remark that with no coupling ($\lambda = 0$), the vector bundles have a trivial topology, and that a strong enough coupling between the slow and fast motion is necessary to have nontrivial topology (here $\lambda > 2/3$). In other words, the topological phenomena investigated in this Letter are nonperturbative effect with respect to the coupling strength.

5. The full quantum spectrum

We consider now the full quantum problem where the slow vibrational motion is also quantized. The total Hilbert space, we are interested in is then $\mathcal{H}_{tot} = \mathcal{H}_{slow} \otimes \mathcal{H}_{fast} = \mathcal{H}_{polyad} \otimes \mathcal{H}_{elec}$ and has dimension $3\mathcal{N}_0$. The quantum Hamiltonian operator $\widehat{H}_\lambda$ is obtained from the matrix valued function $H_\lambda([Z])$ in Eq. (3) by replacing $Z_k, \overline{Z}_k$ by operators a_k, a_k^+ respectively. As a consequence of quantization of the vibrations, the continuous distribution of energies in the semi-quantum description is now replaced by a fine structure. See Fig. 2(b). As expected there is a great similarity between the semi-quantum band spectrum and the exact quantum spectrum. This similarity is proved in [9] where it is shown how a vector bundle defined within the semi-quantum description can be associated to a group of quantum levels, in the semi-classical limit $N \to \infty$, through the construction of a projector. The rank of this projector, given by the

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[4] To be more precise, the Chern class $C(F) \in H^\bullet(\mathbb{C}P^2, \mathbb{Z})$ is an element of the integer cohomology ring. Because the Betti numbers of $\mathbb{C}P^2$ are $(1, 0, 1, 0, 1)$, $C(F)$ can be written as a polynomial $C(F) = 1 + Ax + Bx^2$, where the variable x is generator of $H^2(\mathbb{C}P^2, \mathbb{Z}) \equiv \mathbb{Z}$, and $x^2 = x \wedge x$ is the generator of $H^4(\mathbb{C}P^2, \mathbb{Z}) \equiv \mathbb{Z}$. In dynamical terms, x is the symplectic two-form on phase space $\mathbb{C}P^2$, and $x^2 = x \wedge x$ is the Liouville volume form.

Atiyah–Singer index formula below, gives the number of levels in the band. Before analyzing the general formula, let us now just consider the two extreme cases.

For $\lambda = 0$, every eigenvalue $E = -1, 0, 1$ of the Hamiltonian $\widehat{H}_0$ has a multiplicity $\mathcal{N}_0 = (N+1)(N+2)/2$. For $\lambda = 1$, we can understand the multiplicity in the spectrum from group theory arguments. From its invariance under the $SU(3)$ group action, the eigenspaces of $\widehat{H}_1$ are irreducible representations of this group with respective dimensions $\mathcal{N}_{\text{Line}}, \mathcal{N}_{\text{Orth}}$. The eigenspaces of $\widehat{H}_1$ are obtained by Young tableau techniques, see Fig. 1. We expect that $\widehat{H}_1$ has two different eigenvalues close to $E_{\text{Line}} = 1$, and $E_{\text{Orth}} = 0$ (in the semi-classical limit $N \to \infty$). The Weyl's formula gives the dimensions

$$\mathcal{N}_{\text{Line}} = (N+2)(N+3)/2,$$

$$\mathcal{N}_{\text{Orth}} = N(N+2).$$

As λ varies from 0 to 1, we get a redistribution of the energy levels from three groups of levels towards two groups.

6. Number of energy levels in a band and the index theorem

The relation between the topology of a vector bundle F defined in the Born–Oppenheimer approximation, and the number of levels in a band of the exact energy spectrum is given by the remarkable index formula of Atiyah–Singer ([4, p.330], [7,8]), which, in the case of the molecular model studied in this Letter, reads as follows:

$$\mathcal{N}(F) = \left[\text{Ch}(F) \wedge \text{Ch}(\text{Polyad}_N) \wedge \text{Todd}\left(T\mathbb{C}P^2\right)\right]_{/x^2},$$
(4)

where $\text{Ch}(F) = r + Ax + \frac{1}{2}(A^2 - 2B)x^2$ is the Chern character of the vector bundle F, determined from its topology. $\text{Ch}(\text{Polyad}_N) = \exp(Nx)$ characterizes the quantization of the polyad phase space, and $\text{Todd}(T\mathbb{C}P^2) = 1 + \frac{3}{2}x + x^2$ is related to the topology of the tangent bundle of the phase space $\mathbb{C}P^2$. To make calculation using the right hand side of the formula (4), one has to multiply the three polynomials, and keep the coefficient of the term x^2. This

gives

$$\mathcal{N}(F) = \frac{r}{2}N^2 + \left(\frac{3r}{2} + A\right)N$$
$$+ \left(r + \frac{3A}{2} + \frac{A^2}{2} - B\right).$$
(5)

We now give a short and mathematically more accurate description which is not necessary for the physical comprehension but can be useful for a more mathematically oriented reader. $\text{Ch}(\text{Polyad}) = \exp(Nx)$ is the Chern Character of the holomorphic line bundle $H^{\otimes N} \to \mathbb{C}P^2$ which enters in the geometric quantization description of the Hilbert space $\mathcal{H}_{\text{polyad}}$, where $H \to \mathbb{C}P^2$ is the canonical (positive) line bundle over $\mathbb{C}P^2$, see [22, Chap. 8], [23]. The Hilbert space $\mathcal{H}_{\text{polyad}}$ is seen as the space of holomorphic sections of $H^{\otimes N}$. In general the Atiyah–Singer index formula gives an index which is the difference in dimensions between an operator and its adjoint. A special case of this index formula is the Riemann–Roch–Hirzebruch formula [24, p. 153]. It applies to holomorphic bundles. This theorem together with the Kodaira vanishing theorem [23], shows that this index is the dimension of the Hilbert space of holomorphic sections, which is precisely the quantum Hilbert space considered here $\dim \mathcal{H}_{\text{polyad}} = [\text{Ch}(H^{\otimes N}) \wedge \text{Todd}(T\mathbb{C}P^2)]_{/x^2}$. However the index formula we need involves the nonholomorphic bundle F. Fortunately the Riemann–Roch–Hirzebruch formula is still applicable in our case, because in the $N \to \infty$ limit, the non holomorphic bundle $F \otimes H^{\otimes N}$ can be deformed to a holomorphic one (F is considered as a perturbation), see [7]. This gives

$$\mathcal{N}(F) = \left[\text{Ch}\left(F \otimes H^{\otimes N}\right) \wedge \text{Todd}\left(T\mathbb{C}P^2\right)\right]_{/x^2},$$

and finally use

$$\text{Ch}\left(F \otimes H^{\otimes N}\right) = \text{Ch}(F) \wedge \text{Ch}\left(H^{\otimes N}\right)$$

to get (4).

For $\lambda = 0$, with trivial vector bundles, $A = B = 0$, $r = 1$, the index formula gives $\mathcal{N}_0$. It is also easy to check that this formula gives the values of $\mathcal{N}_{\text{Line}}$ and $\mathcal{N}_{\text{Orth}}$ computed before. The Young tableau techniques was possible at $\lambda = 1$ thanks to a special symmetry. Here the index formula with its topological nature is much more general and is valid for any values of λ. In the interval $1/2 < \lambda < 2/3$, the topology modification

of the vector bundles is related to the level exchange: there is a transfer of $\Delta N = \mathcal{N}_{\text{Line}} - \mathcal{N}_0 = N + 2$ levels to the upper group, through the degeneracy surface.[5]

We now give two comments on the above index formula from the semi-classical point of view. If one defines $h_{\text{eff}} = 1/N$ as the effective Planck constant of the problem, and $\text{Vol} = 1/2$ as the volume of the classical slow phase space, one can rewrite the result (5) giving the total number of states for a rank 1 bundle, as

$$\mathcal{N}(F) = \text{Vol}/h_{\text{eff}}^2 + \left(\frac{3r}{2} + A\right)/h_{\text{eff}}$$
$$+ \left(r + \frac{3A}{2} + \frac{A^2}{2}\right).$$

In the semi-classical limit $h_{\text{eff}} \to 0$, the first term is interpreted as the semi-classical Weyl term which counts the number of Planck cells in the classical phase space. The topology of the vector bundles gives corrections to the sub-leading terms in $1/h_{\text{eff}}$. The second comment is that the index formula is more precise than just giving the total number of states in a band. It also gives the local density of states in phase space. Indeed, from their construction as subspaces of $\mathcal{H}_{\text{fast}}$, the fibers of the vector bundles have a well defined Berry's connection (or Levi-Civita connection, see [5, p. 20]), with a curvature two form, say Ω^{Berry}. Intuitively, this curvature reflects the local twist among the fast dynamical spaces $\mathcal{H}_{\text{fast}}(X_{\text{slow}})$, over the local dynamical point $X_{\text{slow}} \in \mathcal{P}_{\text{slow}}$. Be aware that the connection is not a topological object (rather a geometrical one), in the sense that it will change under a continuous modification of the Hamiltonian. Using that connection, one can express the Chern class of a vector bundle F as $C(F) = \det(1 + \frac{1}{2\pi i}\widehat{\Omega}^{\text{Berry}})$. $C(F)$ is a differential form on $\mathbb{C}P^2$. One has similar expressions for Chern characters and Todd class. The index formula can then be written as

$$\mathcal{N}(F) = \int_{\mathbb{C}P^2} \mu,$$

where

$$\mu = \left[\text{Ch}(F) \wedge \text{Ch}(\text{Polyad}_N) \wedge \text{Todd}\big(T\mathbb{C}P^2\big)\right]_{/\text{Vol}}$$

is a density on the classical phase space $\mathbb{C}P^2$. The density μ can be expressed from the Berry's curvature Ω^{Berry}, and is interpreted as the local density of states on phase space. If we restrict to rank 1 bundles, one can deduce the energy density of states in the quantum band, as the image of μ by the energy function $[Z] \in \mathbb{C}P^2 \to E([Z])$, given by the associated eigenvalue of $H([Z])$. The density μ can also be written as series in $1/h_{\text{eff}}$, with the usual Weyl leading term, and topological corrections in sub-leading terms.

7. Physical meaning of the model

In this section, we discuss the physical relevance of the simple model (3) considered above, on two different examples.

We first justify why we consider only one vibrational polyad N coupled with only three electronic states. In general, for a slow and fast coupled quantum system, fast degrees of freedom have much higher energy excitations than the slow one's. Due to this higher scale of energy, it is sufficient to take into account only finite (and rather low in fact) number of quantum states of this fast subsystem. In the absence of quasi-degeneracies in the fast subsystem one state should be sufficient, but in the case of the presence of degeneracies or quasi-degeneracies we should naturally treat together all the quasi-degenerate quantum levels.

Such a situation takes place, for example, for the dynamic Jahn–Teller effect of type F–f [20,25], which describes the coupling of the triply degenerate vibrational modes (f), with a multiplet of triply degenerate electronic states (F). Although in the standard treatment of Jahn–Teller effect the coupling between vibrational states from different polyads is explicitly taken into account [25–27], in the limit of weak Jahn–Teller coupling, the restriction to the effective model for an isolated polyad N is quite natural [28,29]. We have dealt with this effective model in this Letter.

Another similar and natural example is the vibrational structure of combination bands $\nu_3 + N\nu_4$ in tetrahedral AB_4 type molecules. Due to tetrahe-

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[5] The value $\Delta N = (N + 1) + 1$ can be interpreted as $(N + 1)$ quantized states of the degeneracy sphere plus an extra level due to the topology of the degeneracy bundle.

dral symmetry both vibrational modes ν_3 and ν_4 are triply degenerate, i.e., each is described by (1:1:1) resonance Hamiltonians. The ν_3 frequency which is mainly due to A–B stretching vibrations is typically higher than the ν_4 frequency, associated with bending. In the absence of resonance between ν_3 and ν_4 we can treat separately the combination band $\nu_3 + N\nu_4$, i.e., the restriction of the spectrum to the polyad N of the ν_4 modes, in interaction with the polyad "$N = 1$" of the ν_3 modes, containing three quantum states.

In these both physical examples, the Jahn–Teller coupling and the purely vibrational coupling, the physical problem can be formalized in the same way, and leads to a mathematical model very similar with the model treated in this paper: we have to consider the coupling of the vibrational polyads formed by triply (quasi)degenerate modes, with three quantum states. The vibrational polyads have low-frequency motion for large N (it is the "slow" subsystem) and three quantum states have a high-frequency motion (it is the "fast" subsystem). The total dynamical space is the Hilbert space $\mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{slow}} \otimes \mathcal{H}_{\text{fast}} = \mathcal{H}_{\text{polyad}N} \otimes \mathbb{C}^3$.

We now discuss the physical meaning of the coupling Hamiltonian in Eq. (3), and in particular the meaning of the external parameter λ which was important in the discussion of the topological bifurcations and of the redistribution of quantum levels.

The simplest Hamiltonian we could assume, has no coupling and no interaction, a degeneracy of electronic states and a degeneracy of vibrational states within polyads. This is a constant Hamiltonian. For the Jahn–Teller example, some possible physically interesting corrections to this simplest model are:

(i) Vibrational couplings and anharmonicities which result in splitting the degeneracies in vibrational polyads, but make no distinction between different electronic states.

(ii) Pure electronic splitting, which does not influence the internal vibrational polyad structure and can be present either due to initial splitting of accidentally quasi-degenerate electronic states (in the absence of symmetry), or produced by symmetry breaking effects like the appearance of low-symmetry external electric or magnetic fields. This case is modeled by the Hamiltonian H_0.

(iii) Vibronic coupling between electronic and vibrational states. This case is modeled by the Hamiltonian H_1, and describes the Jahn–Teller $F-f$ coupling.

We will suppose that the purely vibrational coupling (i) is not important, because it modifies only the internal structure of energy bands. The two really different limit cases are (ii) and (iii) above. In case (ii), purely electronic splitting is large compared to vibronic coupling, and at the opposite, in case (iii) the vibronic coupling is the most essential. Naturally, this last case is possible only with strictly degenerate (for example due to symmetry) electronic states. From the Jahn–Teller case (iii), modeled by $\widehat{H}_1$, the $\widehat{H}_0$ limit (ii) can be reached by adding a sufficiently strong external magnetic field. The effect of the magnetic field is formally represented by the parameter λ in Eq. (3).

For mathematical convenience the $\widehat{H}_1$ displays a $SU(3)$ symmetry, which is not expected physically. But what is important is that the Jahn–Teller $F-f$ Hamiltonian and $\widehat{H}_1$ possess the same band decomposition. In other words their semi-quantum description must possess vector bundle spectral decomposition with identical topology; one can then say that these two Hamiltonians belong to the same topological class. In that class, $\widehat{H}_1$ is the simplest representative because it displays a $SU(3)$ symmetry (equivariance). On the contrary $\widehat{H}_0$ and $\widehat{H}_1$ belong to different topological classes. From a qualitative point of view, the physically interesting phenomenon is the transition between these different topological classes.

For the purely vibrational coupling example, the $\widehat{H}_0$ Hamiltonian corresponds to the vibrational structure formed by overtones of triply degenerate harmonic oscillator with frequency ν_4, coupled with three close but non-degenerate vibrational states with higher frequencies ν_3. The $\widehat{H}_1$ term introduces the interaction between low and high frequency states. It becomes the leading term as soon as the splitting between high frequency states goes to zero or equivalently as soon as the coupling between low and high frequency motion becomes more important than the high frequency splitting. This means, for example, that the formal parameter λ in Eq. (3) can be associated with the polyad quantum number N which is naturally responsible for the strength of the interaction between slow and fast subsystems.

8. Conclusions

In comparison with the ro-vibrational model described on a S^2 phase space of dimension 2 [18], the model presented in this paper is much more rich due to the dimension 4 of the phase space $\mathbb{C}P^2$. The new phenomenon consists in a formation of the degeneracy surface together with the transition of a whole group of levels, instead of formation of isolated degeneracy points with transition of one level through each of them, for the case of S^2 phase space. The band topology is described by two integers (first and second Chern classes) which play the role of the topological quantum numbers for energy bands. Topologically coupled energy bands (i.e., nondecomposable vector bundles), can appear for problems with the four-dimensional $\mathbb{C}P^2$ phase space. On the contrary, for the S^2 phase space, one needs only a single Chern index to characterize the coupling with the fast quantum subsystem, and every elementary semi-quantum band has rank 1.

The model presented in this paper can be adapted to different situations in molecular physics where the slow motion phase space can be $S^2, \mathbb{C}P^2, \mathbb{C}P^3, \ldots$ and products of them, depending of the relevant degrees of freedom, which can be rotational, vibrational, or electronic. As a concrete molecular object which fits well the assumptions made by the present model, we can mention the ro-vibronic structure of Jahn–Teller molecule $V(CO)_6$ [29]. This concrete example needs a slight extension to the model with a $\mathbb{C}P^2 \times S^2$ slow phase space coupled with three quantum states, and is especially interesting for further analysis.

Our approach can also be used in other areas of physics where the Born–Oppenheimer approximation is relevant and where the slow subsystem can be considered as classical and coupled to several quantum states.

From the mathematical point of view we have shown a concrete manifestation of Atiyah–Singer's index formula in molecular physics. This gives new field of applications to the index formula. Up to now it was mainly related to quantum chromodynamics with the topology of instantons and gluon fields ([4, p. 355]). The topology of bands are also known to have an importance in solid state physics for the integer quantum Hall effect [30,31]. Molecular systems supply a lot of new examples where the qualitative and quantitative predictions of Atiyah–Singer's index formula can be unambiguously tested and verified with high accuracy by experimental measurements and numerical calculations.

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