Topological Chern Indices in Molecular Spectra

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Topological Chern indices are related to the number of rotational states in each molecular vibrational band. Modification of the indices is associated to the appearance of "band degeneracies," and exchange of rotational states between two consecutive bands. The topological dynamical origin of these indices is demonstrated through a semiclassical approach, and their values are computed in two examples. The relation with the integer quantum Hall effect is briefly discussed.

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Topological numbers play an important role in many areas of physics [1], but their appearance in molecular physics and especially in rovibrational problems has not been systematically appreciated so far. Simple molecular systems typically allow adiabatic separation of vibrational and rotational motion. For nondegenerate isolated electronic state (this is the case of ground state for most molecules) the rovibrational energy level system consists of vibrational bands, each associated with one or several degenerate vibrational states. If the rovibrational coupling is not too strong, further splitting of the rovibrational structure into subbands can be clearly seen. The well-known example is the splitting of the triply degenerate vibrational structure for a spherically symmetrical molecule into three subbands due to the first-order Coriolis interaction [2,3]. Within each subband formed by $2j + 1 - C$ levels, with, respectively, $C = +2, 0, -2$, all energy levels are usually characterized by the quantum number j of the total angular momentum, and by another quantum number $R = j + C/2$ which characterizes the coupling of j with the vibrational angular momentum.

In this Letter, we show that the integer C can be defined in a much more general situation as an additional quantum number having a precise topological meaning, namely a Chern index, whose construction will be explained below. This index is defined in the classical limit of the rotational motion. It can be associated with any vibrational band presented in the energy level pattern of molecular systems. Formula (3) relates this topological index to the number of rotational states within the band. A modification of the index is associated with the formation of a contact (a degeneracy) between two consecutive vibrational bands, and is shown to generically imply an exchange of one rotational state between the two bands.

Such a relation was first conjectured in 1988 [4] after the study of the simple model (1), and a number of effective Hamiltonians reconstructed from experimental data [see Refs. [5–7] for the molecular examples: SiH_4, CD_4, SnH_4, CF_4, $Mo(CO)_6$]. The universal character of the redistribution phenomena and its relevance to integer Hall effect was discussed on several occasions in the molecular spectroscopy context [8] and in a more formal mathematical setting [9,10].

To explain the physical phenomenon and to prepare the formulation of a rigorous statement let us consider a toy problem which involves two quantum angular momenta $\mathbf{J}$ and $\mathbf{S}$, with fixed modulus $\mathbf{J}^2 = j(j + 1)$ and $\mathbf{S}^2 = s(s + 1)$ with j, s integer or half-integer: $\mathbf{J}$ acts in the space $\mathcal{H}_j$ of dimension $(2j + 1)$ which is the irreducible representation space of the SU(2) group. Similarly, $\mathbf{S}$ acts in the space $\mathcal{H}_s$ of dimension $(2s + 1)$. The total space is $\mathcal{H}_{\text{tot}} = \mathcal{H}_j \otimes \mathcal{H}_s$ with dimension $(2j + 1)(2s + 1)$.

The most general quantum Hamiltonian $\hat{H}(\mathbf{S}, \mathbf{J}/j)$ we will consider is a Hermitian operator acting in $\mathcal{H}_{\text{tot}}$ and its action in space $\mathcal{H}_j$ is supposed to be expressed in terms of the operators $\mathbf{J}/j$. The factor $1/j$ is introduced here to ensure the existence of the classical limit for $j \to \infty$. An extremely simple form of $\hat{H}$ is

$$\hat{H} = (1 - t)S_z + \frac{t}{j}(\mathbf{J} \cdot \mathbf{S}), \tag{1}$$

with $j > s$, $t \in \mathbb{R}$, which was used initially in Ref. [4] to study the redistribution phenomenon and further in Ref. [11] to establish its relation with the classical monodromy. We use this Hamiltonian (1) to illustrate the strict statement (3), but we will see that its validity extends to a general $\hat{H}(\mathbf{S}, \mathbf{J}/j)$.

In the two extremes limits $t = 0$ (no "spin-orbit" coupling), and $t = 1$ ("spin-orbit" coupling), the energy level spectrum of (1) shows different patterns of energy levels into bands indexed by g. For $t = 0$ all energies $E_g = g$, $g \in \{-s, \ldots, +s\}$ appear with the same multiplicities $N_g = (2j + 1)$. For $t = 1$ the spectrum is split into degenerate multiplets characterized by different eigenvalues of the coupled angular momentum $\mathbf{N}^2 = (\mathbf{J} + \mathbf{S})^2$. As in the case of standard spin-orbit coupling with $j > s$ there are $2s + 1$ different levels $E_g = [n(n + 1) - j(j + 1) - s(s + 1)]/(2j)$, $g = n - j \in \{-s, \ldots, +s\}$, with different multiplicities $N_g = (2j + 1) + 2g$. The two different limiting cases for the structures of the $(2s + 1)$ bands suggest to introduce

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a new quantum number C_g associated with the value of N_g within each band.

To define C_g for a general Hamiltonian $\hat{H}(\mathbf{S}, \mathbf{J}/j)$ we assume that $j \gg s$, so that it is physically reasonable to consider $\mathbf{J}_{\rm cl} = \mathbf{J}$ as classical, whereas $\mathbf{S}$ remains quantum. The classical dynamics for $\mathbf{J}_{\rm cl}$ can be defined through the SU(2) coherent states $|\mathbf{J}_{\rm cl}\rangle$ [12]. The classical phase space for $\mathbf{J}_{\rm cl}$ is the sphere S_j^2. From $d\mathbf{J}_{\rm cl}/dt = \partial_{\mathbf{J}_{\rm cl}} H_{\rm cl} \times \mathbf{J}_{\rm cl}$ and because of the factor $1/j$ in Eq. (1), $\mathbf{J}_{\rm cl}$ corresponds to a slow dynamical variable compared to $\mathbf{S}$, and the Born-Oppenheimer approximation suggests for each $\mathbf{J}_{\rm cl}$, consideration of the Hermitian operator $\hat{H}_s(\mathbf{J}_{\rm cl}) = \langle \mathbf{J}_{\rm cl}|\hat{H}|\mathbf{J}_{\rm cl}\rangle$ acting on $\mathcal{H}_s$, with spectrum $\hat{H}_s(\mathbf{J}_{\rm cl})\,|\psi_{g,\mathbf{J}_{\rm cl}}\rangle = E_{g,\mathbf{J}_{\rm cl}}|\psi_{g,\mathbf{J}_{\rm cl}}\rangle$, $g \in \{-s, \ldots, +s\}$. We suppose that for each $\mathbf{J}_{\rm cl}$, the $(2s+1)$ eigenvalues are isolated: $E_{-s,\mathbf{J}_{\rm cl}} < E_{-s+1,\mathbf{J}_{\rm cl}} < \cdots < E_{+s,\mathbf{J}_{\rm cl}}$. This is the generic situation, because degeneracies are of codimension 3, and $\mathbf{J}_{\rm cl} \in S_j^2$ is only two dimensional.

For each level g, let us note $[|\psi_{g,\mathbf{J}_{\rm cl}}\rangle]$ the eigenvector defined up to a multiplication by a phase $e^{i\alpha}$. The application $\mathbf{J}_{\rm cl} \rightarrow [|\psi_{g,\mathbf{J}_{\rm cl}}\rangle]$ defines then a $U(1)$ fiber bundle over the sphere S_j^2, which is the set of all the possible phases α for every value of $\mathbf{J}_{\rm cl}$. The topology of this bundle is characterized by a Chern number $C_g \in \mathbb{Z}$ [13]. C_g reveals the possible global twist of the fiber of phases α over the sphere S_j^2, in the same way the well-known Möbius strip is the real line fiber bundle over the circle S^1 with a global twist -1 (rotation of π), see Fig. 1.

Note that

$$\sum_{g=-s}^{+s} C_g = 0\,, \tag{2}$$

just because of the additivity of Chern indices, and because the eigenvectors $(|\psi_{g,\mathbf{J}_{\rm cl}}\rangle)$ span the space $\mathcal{H}_s$ which does not depend on $\mathbf{J}_{\rm cl}$.

The Born Oppenheimer approach tells that the total spectrum $\hat{H}|\phi_i\rangle = E_i|\phi_i\rangle$, $i \in \{1, \ldots, (2s+1)(2j+1)\}$ in $\mathcal{H}_{\rm tot}$, can be represented as formed in $2s+1$ groups of levels (bands) with eigenfunctions of each group spanning vector spaces: $L_g \subset \mathcal{H}_{\rm tot}$, $g \in \{-s, \ldots, +s\}$. We specify now the number N_g of levels in each group:

For a general Hamiltonian $\hat{H}(\mathbf{S}, \mathbf{J}/j)$, and for j large enough then $dim L_g = dim \mathcal{H}_j - C_g$, so

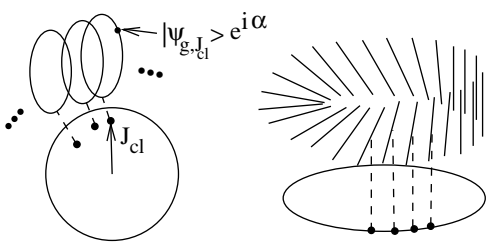

FIG. 1. The Chern index C_g expresses the twist made by the circles for the phases α of the eigenvectors $e^{i\alpha}|\psi_{g,\mathbf{J}_{\rm cl}}\rangle$ over the sphere of spin $\mathbf{J}_{\rm cl}$, in a similar way the Möbius strip has a twist made by the lines over a circle.

$$N_g = (2j+1) - C_g\,; \tag{3}$$

i.e., the number N_g of states $|\phi_i\rangle$ in each band L_g of $\mathcal{H}_{\rm tot}$ is given by the quantum number j and an additional quantum number C_g, namely the topological Chern index. This result has been formulated in a more mathematical context by Bellissard [9] and by Zelditch [10] but was not published due to its "apparent mathematical simplicity."

We will prove formula (3) below.

A few remarks are in order here. Since $(2j+1)$ is the number of quanta in the classical phase space S_j^2 for spin $\mathbf{J}_{\rm cl}$, Eq. (3) looks like a Weyl formula with a correction. The index C_g has been defined and can be computed in "a semiquantal" approach where $\mathbf{J}_{\rm cl}$ is considered as a classical variable and $\mathbf{S}$ quantum. Nevertheless, Eq. (3) provides information on the full quantum problem: the spectrum of $\hat{H}$. Finally, the topological nature of C_g reveals a qualitative and robust property of the spectrum of $\hat{H}$, stable under perturbations, provided no degeneracy appears between consecutive bands. One can say that C_g expresses a topological coupling between the dynamical variables $\mathbf{J}$ and $\mathbf{S}$.

We suggest two approachs for the computation of the Chern indices of different bands. The first one we use below is algebraic. The second one uses Berry's connection, and is based on the curvature formula [13]. This last formula could be useful for numerical computations. The algebraic calculation is based on the geometric interpretation of the Chern index C_g as the total intersection number between the one-dimensional curve $[|\psi_{g,\mathbf{J}_{\rm cl}}\rangle]_{\mathbf{J}_{\rm cl}}$ in the projective space $\mathbb{P}(\mathcal{H}_s)$, with the hyperplane $(|\psi_0\rangle)^\perp = \{|\varphi\rangle$ such that $\langle\varphi|\psi_0\rangle = 0\}$. Here $|\psi_0\rangle \in \mathcal{H}_s$ is arbitrary. Each intersection has number $\sigma = +1$ (-1) if the curve orientation is compatible (incompatible) with the orientation of the hyperplane. C_g is the sum of these intersection numbers [14].

The application of this algebraic method of calculation to the two limiting cases of Hamiltonian (1) is immediate. For $t = 0$ the Hamiltonian $\hat{H}_s(\mathbf{J}_{\rm cl}) = S_z$ does not depend on $\mathbf{J}_{\rm cl}$, the application $\mathbf{J}_{\rm cl} \rightarrow [|\psi_{g,\mathbf{J}_{\rm cl}}\rangle]$ is constant, the topology of the bundle is trivial with zero Chern index: $C_g = 0$, in accordance with Eq. (3). For $t = 1$ we have

$$\hat{H}_s(\mathbf{J}_{\rm cl}) = \langle \mathbf{J}_{\rm cl}|\hat{H}|\mathbf{J}_{\rm cl}\rangle = \frac{1}{j}\,(\mathbf{J}_{\rm cl} \cdot \mathbf{S})\,,$$

with $\mathbf{J}_{\rm cl}$ a vector on the sphere S_j^2, and $\mathbf{S}$ a vectorial operator in $\mathcal{H}_s$. The eigenvector $|\psi_{g,\mathbf{J}_{\rm cl}}\rangle$ is easily obtained from the eigenvector $|m_s = g\rangle \propto S_+^{(s+g)}|0\rangle$ of S_z by a rotation which transforms the z axis to the $\mathbf{J}_{\rm cl}$ axis on the sphere. It is convenient to choose a coherent state $|\mathbf{S}_{0,\rm cl}\rangle$ as the reference state $|\psi_0\rangle$, where $\mathbf{S}_{0,\rm cl}$ is an arbitrary classical spin $\mathbf{S}$. An intersection of the curve $[|\psi_{g,\mathbf{J}_{\rm cl}}\rangle]_{\mathbf{J}_{\rm cl}}$ with the hyperplane $(|\psi_0\rangle)^\perp$ is then given by the equation $\langle \mathbf{S}_{0,\rm cl}|\psi_{g,\mathbf{J}_{\rm cl}}\rangle = 0$ which has a very simple interpretation: the point $\mathbf{S}_{0,\rm cl}$ is a zero of the Husimi representation $\mathrm{Hus}(\mathbf{S}_{\rm cl}) = |\langle \mathbf{S}_{\rm cl}|\psi_{g,\mathbf{J}_{\rm cl}}\rangle|^2$ of the state $|\psi_{g,\mathbf{J}_{\rm cl}}\rangle$ on the sphere

S_s^2 (the classical phase space of $\mathbf{S}$), shown in Fig. 2. The Husimi representation has $(s - g)$ zeros inside the (oriented) trajectory, and $(s + g)$ zeros outside [15]. When the axis $\mathbf{J}_{\rm cl}$ moves with direct orientation on the whole sphere, the $(s - g)$ zeros pass with positive orientation over the fixed point $\mathbf{S}_{0,\rm cl}$, giving $\sigma_1 = s - g$, whereas the $s + g$ zeros pass with negative orientation over $\mathbf{S}_{0,\rm cl}$, giving $\sigma_2 = -(s + g)$. So $C_g = \sigma_1 + \sigma_2 = -2g$ in accordance with Eq. (3).

In this last example, the variation of Chern indices $\Delta C_g = -2g$ occurs at $t = 1/2$, with a degeneracy between the bands at $\mathbf{J}_{\rm cl} = (0, 0, -j)$, giving $\hat{H}_s(\mathbf{J}_{\rm cl}) = 0$. In the case of two bands ($s = 1/2$, $g = \pm 1/2$) then $\Delta C_{g=\pm} = \mp 1$, and the two bands have a conical contact at the degeneracy. In the vicinity of the degeneracy, and for $j \to \infty$, we observe that $[J_-, J_+] = -2J_z \simeq 2j$, so $a = J_-/\sqrt{2j}$, $a^+ = J_+/\sqrt{2j}$ fulfilled the harmonic oscillator commutation relations. In the basis $|\pm\rangle = |m_s = \pm 1/2\rangle$ of $\mathcal{H}_s$, the expression of $\hat{H}$ can be simplified and gives

$$\hat{H} = \frac{1}{2\sqrt{2j}} \begin{pmatrix} -\tilde{t} & a \\ a^+ & \tilde{t} \end{pmatrix}, \tag{4}$$

with $\tilde{t} = (2t - 1)\sqrt{2j}$. We also scale the energy with $\tilde{E} = E2\sqrt{2j}$, and note $|n\rangle \propto a^{+n}|0\rangle$. The stationary equation $\hat{H}|\phi\rangle = E|\phi\rangle$ can easily be solved, giving for $n = 1, 2, \ldots,$ $|\phi_n^{\pm}\rangle = |n\rangle|-\rangle + \sqrt{n}/(\tilde{E}_n^{\pm} + \tilde{t})\,|n - 1\rangle|+\rangle$ with $\tilde{E}_n^{\pm} = \pm\sqrt{n + \tilde{t}^2}$, and one single state $|\phi_0\rangle = |0\rangle|-\rangle$ with $\tilde{E}_0 = \tilde{t}$. Figure 3 shows this spectrum with the simplified expressions of $|\phi_n^{\pm}\rangle$ obtained for large $|\tilde{t}|$. These simplified expressions involving the states $|n\rangle$ of the harmonic oscillator express the quantized modes for small oscillations near the extrema of the two bands [16]. We clearly observe the exchange of one state in the spectrum, giving $\Delta N_{g=\pm} = \pm 1$. As a consequence, $\Delta N_g + \Delta C_g = 0$. This gives for each band a conserved quantity, namely $(N_g + C_g)$. The variation $\Delta C_+ = -1$ can also be considered as "the topological charge" associated to the degeneracy of the 2×2 matrix (4) where $a_{\rm cl} = x_{\rm cl} - ip_{\rm cl}$ is a classical variable.

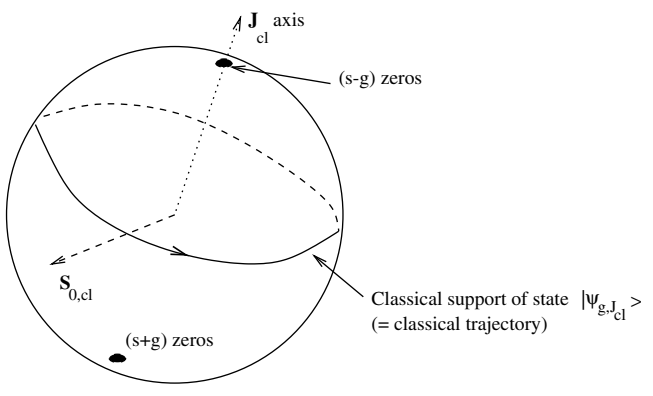

FIG. 2. The Husimi distribution for the state $|\psi_{g,\mathbf{J}_{\rm cl}}\rangle$ on the sphere S_s^2 for spin $\mathbf{S}$. $\mathbf{S}_{0,\rm cl}$ is a reference point.

For a general Hamiltonian $\hat{H}(\mathbf{S}, \mathbf{J}/j)$ the simple model Eq. (4) provides the general mechanism for the exchange of one state in the vicinity of every degeneracy between two consecutive bands. In the trivial case $\hat{H}_0 = S_z$, we have computed the value of the conserved quantity: $N_g + C_g = 2j + 1$. We deduce that it is still correct when $\hat{H}_0$ is deformed to $\hat{H}(\mathbf{S}, \mathbf{J}/j)$, proving (3).

The second example addresses the Chern indices of the two-state model corresponding to $s = 1/2$, i.e., to $\dim\mathcal{H}_s = 2$. In a given fixed basis, say $|m_s = \pm 1/2\rangle$, the matrix of $\hat{H}_s(\mathbf{J}_{\rm cl})$ has the form:

$$\hat{H}_s \equiv \begin{pmatrix} h_{11}(\mathbf{J}_{\rm cl}) & h_{12}(\mathbf{J}_{\rm cl}) \\ \overline{h_{12}}(\mathbf{J}_{\rm cl}) & h_{22}(\mathbf{J}_{\rm cl}) \end{pmatrix}. \tag{5}$$

This matrix will give two vibrational subbands with Chern indices C_- and C_+. In Ref. [17], it is shown that the Chern indices have the following property: Let $\mathbf{J}^*$ be the zeros of $h_{12}(\mathbf{J}_{\rm cl})$, and $\sigma(\mathbf{J}^*)$, their degree defined as follows: take a small direct circle around $\mathbf{J}^*$; its image by $h_{12}(\mathbf{J}_{\rm cl})$ is a closed curve around 0 with $\sigma(\mathbf{J}^*)$ turns. Define the set $S^+ = \{\mathbf{J}_{\rm cl} \in S_j^2$ such that $[h_{22}(\mathbf{J}_{\rm cl}) - h_{11}(\mathbf{J}_{\rm cl})] > 0\}$. Then

$$C_+ = \sum_{J^* \in S^+} \sigma(\mathbf{J}^*) = -C_- \,. \tag{6}$$

A direct consequence of this property is that a change of Chern index can occur only when simultaneously $h_{12}(\mathbf{J}^*) = h_{22}(\mathbf{J}^*) - h_{11}(\mathbf{J}^*) = 0$. This corresponds to a degeneracy in the spectrum of $\hat{H}_s$, and a conical contact of the two bands.

Formula (6) can be applied to a Hamiltonian describing the rotational structure of the doubly degenerated vibrational state of a tetrahedral (or octahedral) spherical top molecule [18]. The most general Hamiltonian, taken up to the third degree in $\mathbf{J}$, has the form (5) with

$$h_{12}(\mathbf{J}) = (J_x^2 - J_y^2)/j^2 + iXJ_xJ_yJ_z/j^3,$$
$$h_{22}(\mathbf{J}) - h_{11}(\mathbf{J}) = [3J_z^2 - j(j + 1)]/j^2,$$

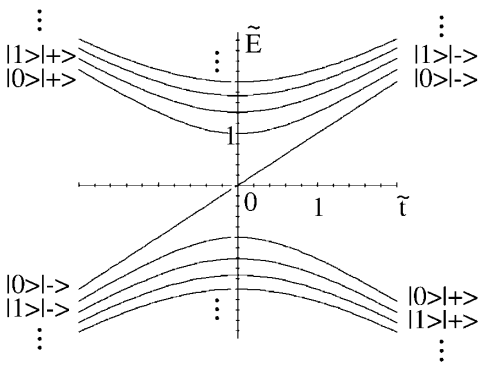

FIG. 3. Spectrum of rotational states for the Hamiltonian (4). $\tilde{t} = 0$ corresponds a conical contact (degeneracy) between the two bands, with a topological charge $\Delta C_+ = -1$, and an exchange of one rotational state, $\Delta N_+ = +1$.

with parameter $X \in \mathbb{R}$. In this case the set S^+ includes all points around the north and south pole for which $J_z > \frac{1}{\sqrt{3}}\sqrt{j(j+1)}$ or $J_z < \frac{-1}{\sqrt{3}}\sqrt{j(j+1)}$. As $h_{12}(\mathbf{J}) = 0$ for simultaneously $J_x = \pm J_y$, and $J_x J_y J_z = 0$ there are two points $J^* \in S^+$: the north pole $J_z = j$ and the south pole $J_z = -j$. We consider $\mathbf{J}$ going through a closed path surrounding each J^* to calculate $\sigma(\mathbf{J}^*)$. This gives for north and for the south poles $\sigma_{\text{north}} = \sigma_{\text{south}} = 2\,\text{sgn}(X)$, so that $C_+ = 4\,\text{sgn}(X)$ and $C_- = -C_+$.

This calculation explains why the rotational structure of doubly degenerate vibrational state is generally split into two subbands with, respectively, $2j + 5$ and $2j - 3$ levels [6,19]. In our current approach the appearance of two bands with Chern indices ± 4 for the Hamiltonian (5) is due to the formation of eight degeneracies [equivalent by symmetry] between the two vibrational bands at $X = 0$ parameter value. More generally the characterization of the rovibrational structure of molecules and its possible modification under the variation of some physical parameters like total angular momentum can be done systematically by using Chern indices as topological quantum numbers. In Ref. [7] a similar effect was discussed without explicit introduction of Chern indices.

The molecular application studied in this Letter was mainly inspired by the role played by topological Chern indices in the integer quantum Hall effect [20]. In this context, Chern indices describe the topology of Floquet bands $(\mathbf{k}) \rightarrow [|\psi_g(\mathbf{k})\rangle]$ where $\mathbf{k}$ is the Bloch wave vector, and give a quantum Hall conductance $\sigma_g = (e^2/h)C_g$ under the hypothesis of adiabatic motion of $\mathbf{k}$ when a weak electrical field is applied. Contrary to Eq. (2), their sum for a given Landau level is $\sum_g C_g = +1$, because of the nontrivial topology of the quantum space [20]. Many properties of the Chern indices are similar: a change $\Delta C_g = \pm 1$ is related to a conical degeneracy between consecutive bands. The application of semiclassical calculations of C_g done for the Hall conductance in Ref. [21], will be the subject of future work.

In summary, we have discussed the role of Chern quantum numbers to molecular spectroscopy. The interpretation of good integer quantum numbers associated with rotational structure of different vibrational bands in terms of topological Chern numbers has naturally a wide applicability. These indices can be introduced any time when the adiabatic separation of variables enables one to split the global structure into bands associated with the "fast motion" and their internal structure described by a "slow motion" on a compact phase space. We have considered here only the problem when the dimension of the classical phase space formed by the slow variable $\mathbf{J}_{\text{cl}}$ is 2. Only the first Chern class appears in this case. Extension to higher dimension requires more delicate physical interpretation and more sophisticated mathematical tools in relation with the index theorem of Atiyah-Singer. In molecular spectroscopy many problems with intramolecular dynamics are known in great detail. They can be used to test the applicability of this new concept.

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