

Qualitative theory of energy patterns for finite particle quantum systems: Symmetry and topology aspects.

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Mathematical Methods for Ab Initio Quantum Chemistry, Nice

Plan

1. Molecular preliminaries. Qualitative reasoning.
2. General scheme of qualitative analysis.
3. Examples

Rotational clusters and quantum bifurcations

Resonant vibrations, non-linear modes

H atom in fields, quantum monodromy

Rearrangement of bands, Chern classes, wall-crossing

Typical rovibrational spectrum of a small molecule



Equilibrium configuration - tetrahedron - T_d point group.

Internal degrees of freedom:

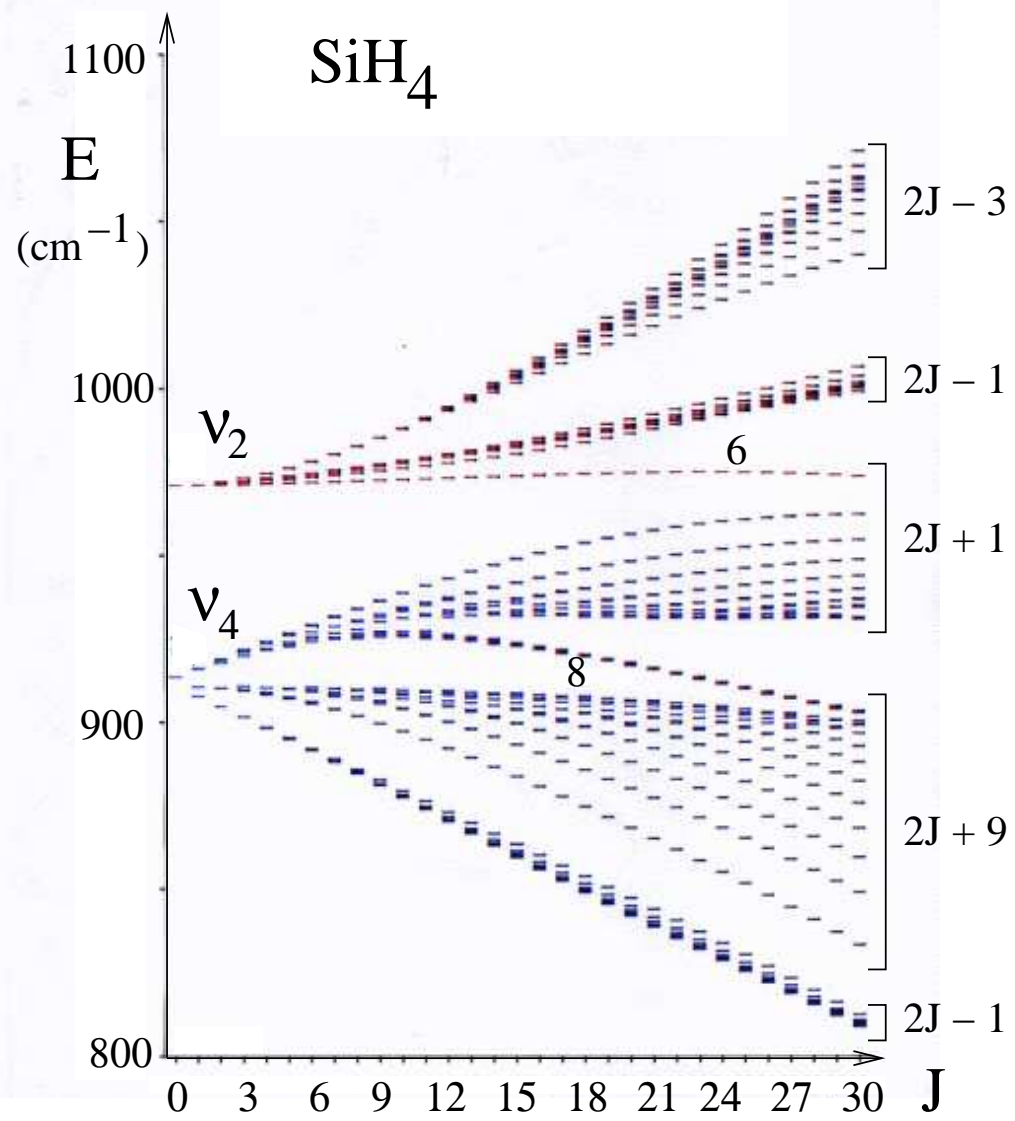
Rotation (non-rigid spherical top) + nine vibrations

ν_1 - nondegenerate, A_1 irrep,

ν_2 - doubly degenerate, E irrep,

ν_3 - triply degenerate, F_2 irrep,

ν_4 - triply degenerate, F_2 irrep.



Energy level representation in

Energy (E) - Angular momentum (J)

coordinates corrected with the scalar function $E(J)$ to see better the band structure and the evolution of internal structure of bands as a function of a strict integral of motion J .

Qualitative features to explain:

- i) Rotational clusters (6-fold, 8-fold, 12-fold quasidegenerate)
- ii) Modification of cluster structure (appearance of 12-fold cluster as J increases).
- iii) Number of energy levels in a band:
 $2J + 1 + \Delta$, ??? Δ ???
- iv) Rules for redistribution of energy levels between branches.

General idea of qualitative approach

- To study a family of objects/models depending on a number of *control parameters* (external or internal).
- To find characteristics which are defined for almost all values of control parameters and are *piece-wise constant*.

This allows to split the space of control parameters into disjoint regions by a codimension one boundary (*wall*). Qualitative modifications under control parameter variation are associated with *wall-crossing*.

We use the notion “*wall-crossing*” just to show that for the studied molecular examples the qualitative description can be regarded as one concrete realization of general “*wall-crossing*” formalism^a.

^a see M. Kontsevich, Y. Soibelman, Wall-crossing structures in Donaldson-Thomas invariants, integrable systems and Mirror Symmetry. LNM, in press; arXiv:1303.3253

D.Gaiotto, G.W. Moore, A. Neitzke, Wall-crossing, Hitchin systems, and the WKB approximation, Adv.

Math. 234, 239-403 (2013)

General scheme of qualitative analysis.

Classical limit of effective quantum Hamiltonians.

Symmetry group action analysis.

Simplest Morse type functions.

Qualitative patterns and their modifications (bifurcations, monodromy, redistribution, ...)

Topological quantum numbers.

Classical limit

Examples of *classical limit manifolds* for effective quantum Hamiltonians.

Hamiltonian	Phase space
Rotational	S_2
Vib. polyads	CP_{n-1}
Rot-vib. polyads	$S_2 \times CP_{n-1}$
Rydberg	$S_2 \times S_2$

n being the number of degenerate (or quasi-degenerate) vibrational modes.

Qualitative tools

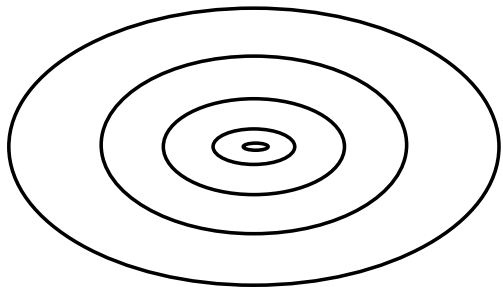
One degree of freedom dynamical (reduced) systems.

Classical phase portraits.

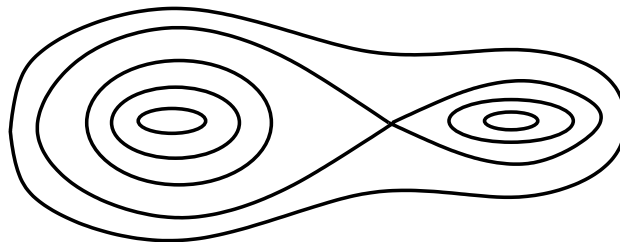
Reeb diagrams.

Lattices of quantum states.

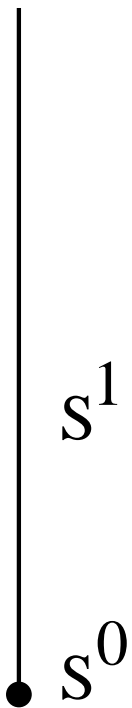
Simplest examples of symmetry and topology manifestations.



e



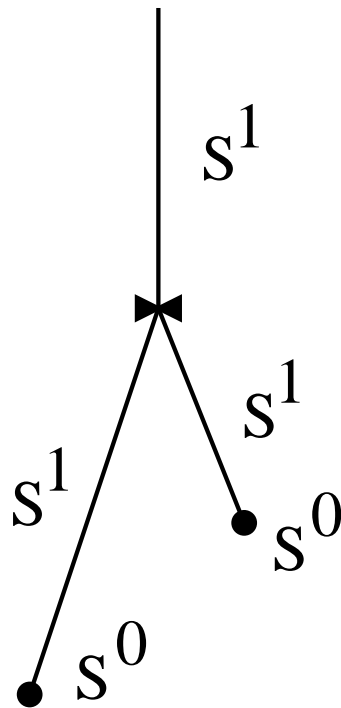
f



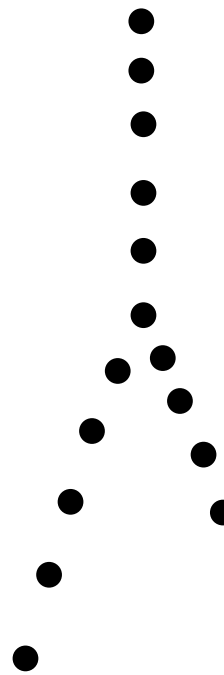
a



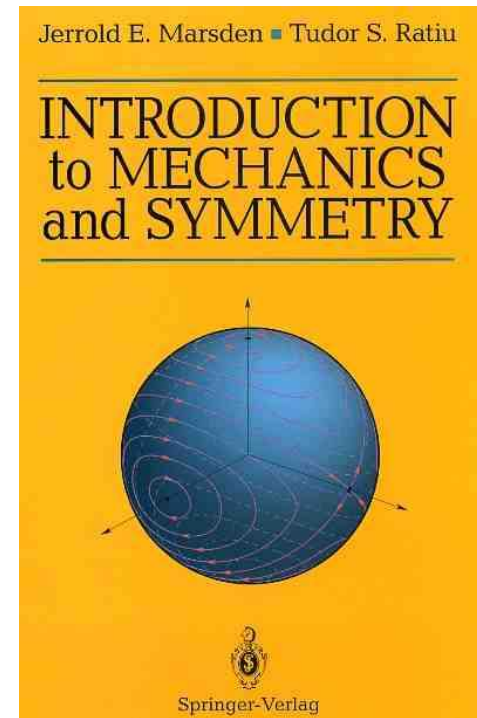
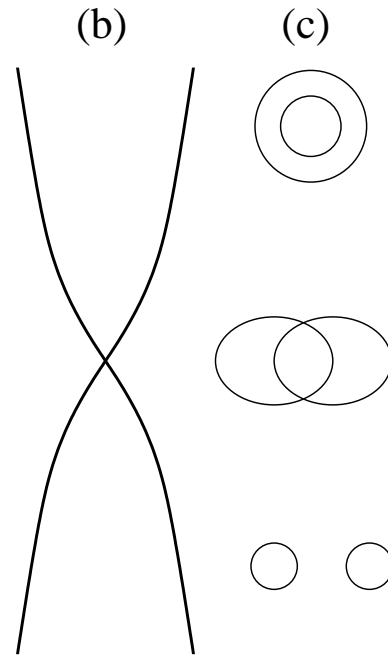
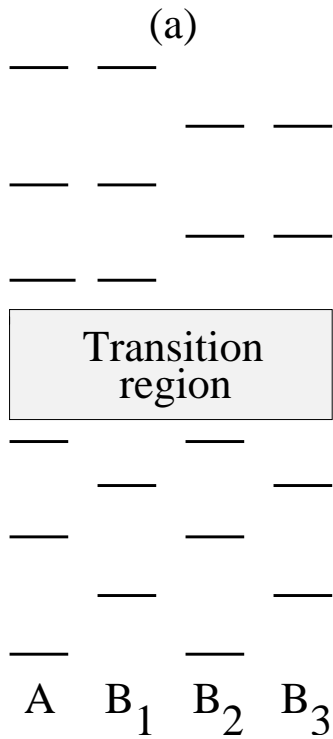
b



c



d



(a) Schematic representation of the energy level structure for asymmetric top molecule.

(b) Foliation of the classical phase space (S^2 sphere)

(c) Geometric representation of the constant energy sections.

Examples of **symmetry group action** on classical limit manifolds.

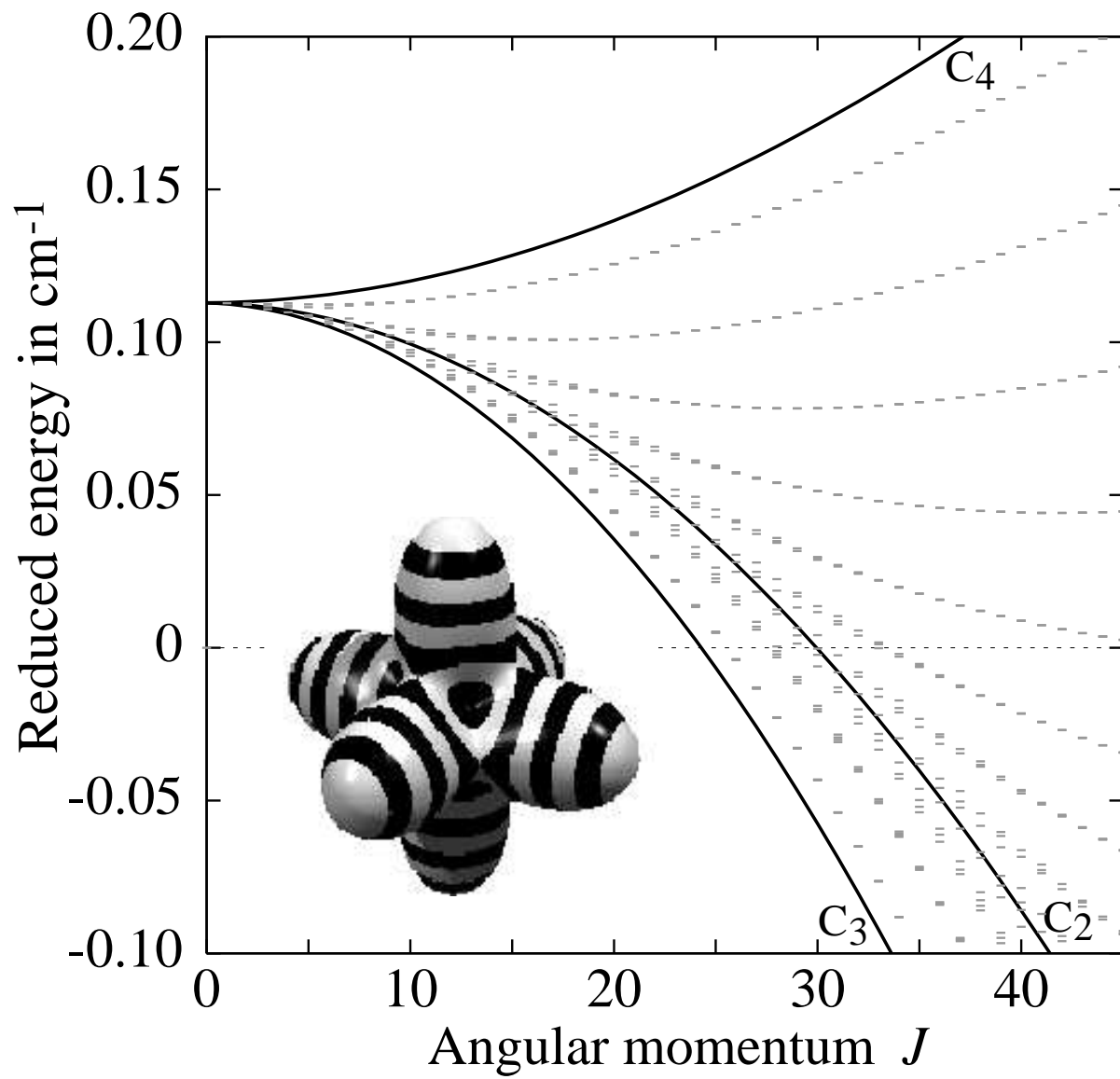
Images rather than group themselves are important.

For AB_4 molecule the symmetry group is

$$T_d \times \mathcal{T} \sim O_h$$

T_d point group extended by time reversal \mathcal{T} .

O_h group action on CP_1 phase space for vibrational E polyads is equivalent to natural D_{3h} action on a S_2 sphere.



Simplest Morse type functions:

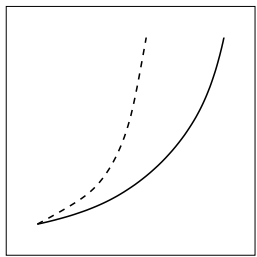
Rotational energy surface for asymmetrical, symmetrical and spherical top molecules at low excitation.

(There are two simplest Morse type functions for the rotational energy surface of AB_4 (or AB_6 , ...) molecule.

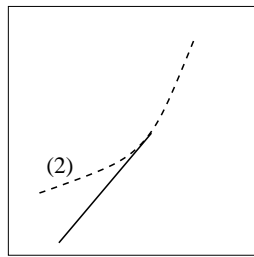
As J increases the rotational energy surfaces become typically more complicated (of non-simplest Morse type). Additional stationary points appear through bifurcations.

1 degree of freedom; 1 control parameter

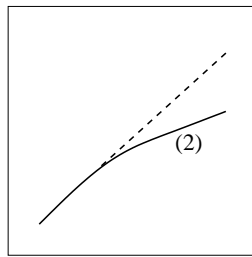
Table 1: Bifurcations in the presence of symmetry. Solid lines denote stable stationary points. Dash lines - unstable stationary points. Numbers in parenthesis indicate the multiplicity of stationary points.



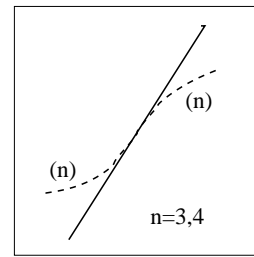
C_1^\pm



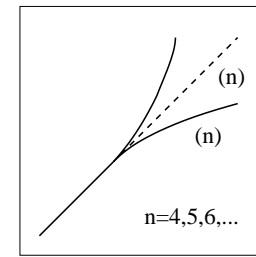
$C_2^{N\pm}$



$C_2^{L\pm}$



$C_n^N, n = 3, 4$



$C_n^{L\pm}, n \geq 4$

I.M. Pavlichenkov, B.Zhilinskii. Critical phenomena in rotational spectra.

Ann. Phys. **184**, 1-32 (1988)

Table 2: Molecular examples of quantum bifurcations in the rotational structure of individual vibrational components under the variation of the absolute value of angular momentum, J . J_c is the critical value corresponding to bifurcation.

Molecule	Component	J_c	Bifurcation type
SiH ₄	$\nu_2(+)$	12	C_2^{N+}
SnH ₄	$\nu_2(-)$	10	$C_2^{N+}, C_3^N, C_4^N, C_2^{N-}$
CF ₄	$\nu_2(+)$	50	C_4^{L+}
H ₂ Se	$ 0\rangle$	20	C_2^{L+}
(CH ₃) ₂ SO	ν_{23}	27	C_2^{L+}

Semi-quantum approach:

One part of variables (rotational) is treated as classical whereas another (vibrational) as quantum.

Symbol of the Hamiltonian is a matrix defined over classical limit manifold.

Example: (rotational Hamiltonian for three vibrational states).

$$H = \begin{pmatrix} H_{11}^J(\theta, \varphi) & H_{12}^J(\theta, \varphi) & H_{13}^J(\theta, \varphi) \\ H_{21}^J(\theta, \varphi) & H_{22}^J(\theta, \varphi) & H_{23}^J(\theta, \varphi) \\ H_{31}^J(\theta, \varphi) & H_{32}^J(\theta, \varphi) & H_{33}^J(\theta, \varphi) \end{pmatrix}$$

θ, φ are the angles characterizing the orientation of the angular momentum \mathbf{J} .

Eigenvalues of matrix Hamiltonian play the role of rotational energy surfaces for different vibrational quantum states.

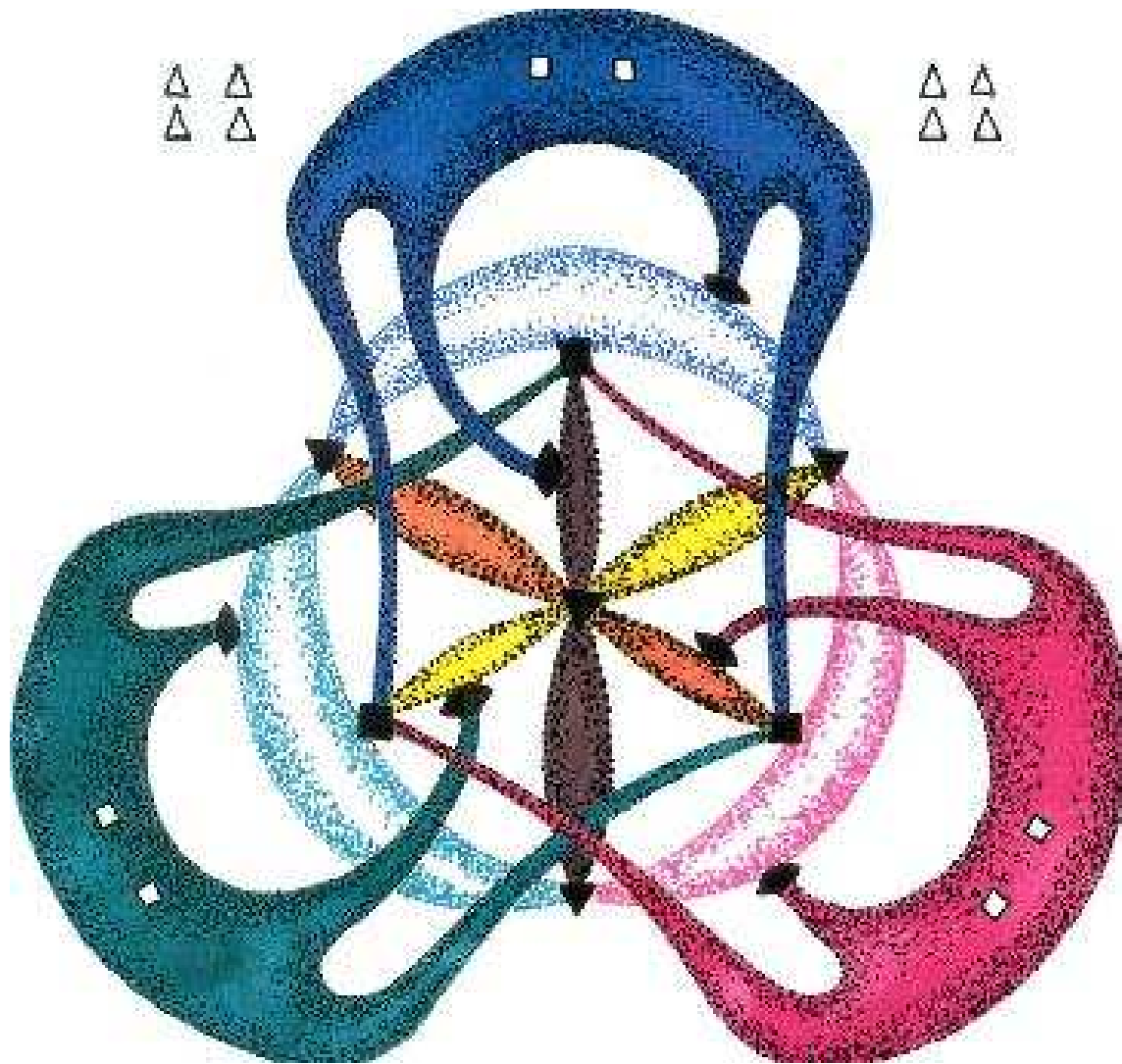
Eigenvectors form a vector bundle over classical phase space being the base space of the bundle.

Presence or absence of *degeneracy* is extremely important.

Alternative complete classical description of the same model can be done by a Hamiltonian function defined over classical limit manifold

$$S_2 \times CP_2$$

for the complete rotation-vibration problem.



T_d (or O , or O_h) group action on CP_2 .

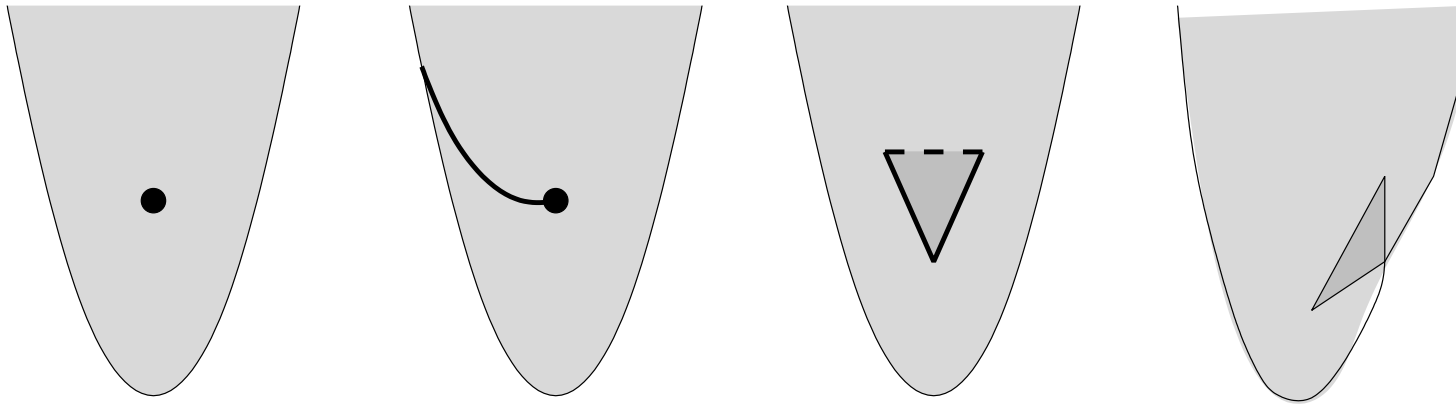
Vibrational quasi-modes.

27 nonlinear normal modes for triply degenerate vibrational polyads correspond to 27 relative equilibria on the reduced phase space of the triply degenerate oscillator (reduced phase space is topologically CP_2).

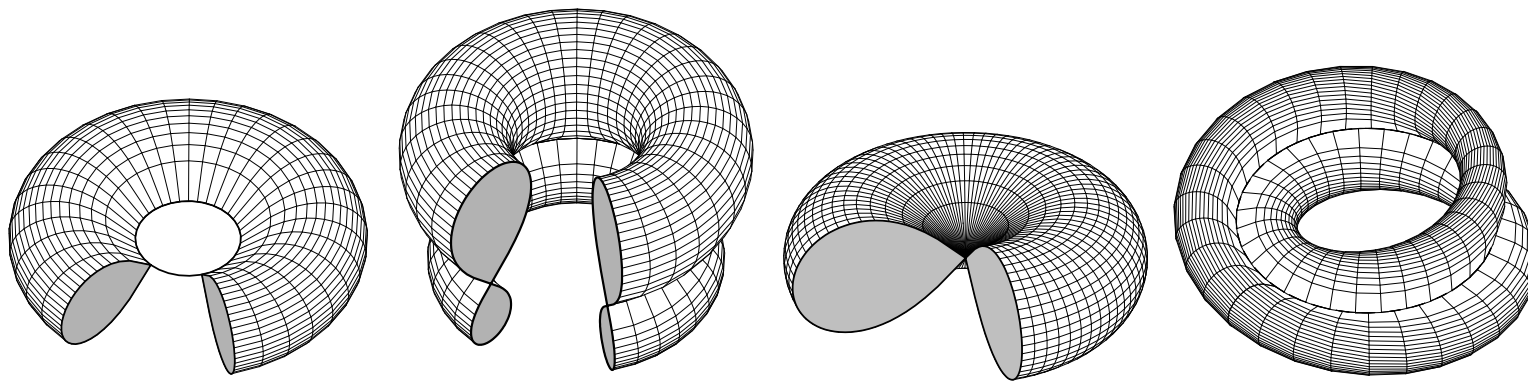
For vibrational $n\nu_2^{(E)}$ polyads (reduced space is topologically $CP_1 \sim S^2$ with D_{3h} action) there are 8 nonlinear normal modes.

CH_4 molecule has 63 nonlinear normal modes (one for ν_1 , 8 for ν_2 , 27 for ν_3 , 27 for ν_4).

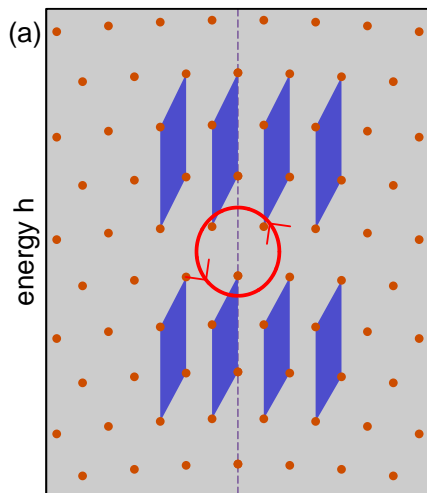
Integrable models. Classical and Quantum monodromy.



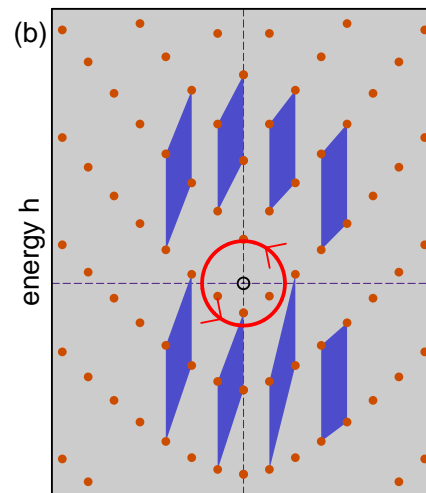
Typical images of the energy momentum map for completely integrable Hamiltonian systems with two degree of freedom in the case of integer monodromy, fractional monodromy, nonlocal monodromy, and bidromy. Values in light shaded area lift to single 2-tori; values in dark shaded area lift to two 2-tori.



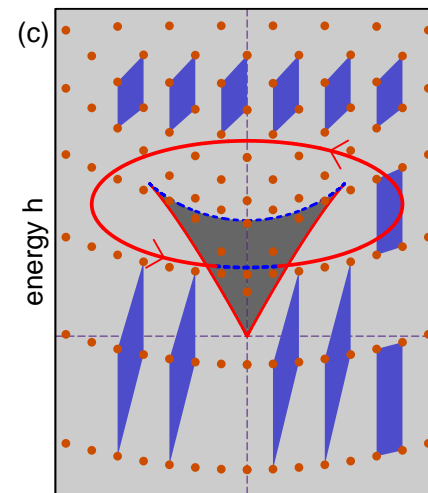
Two dimensional singular fibers in the case of integrable Hamiltonian systems with two degrees of freedom (left to right): singular torus, bitorus, pinched and curled tori.



value of the first action

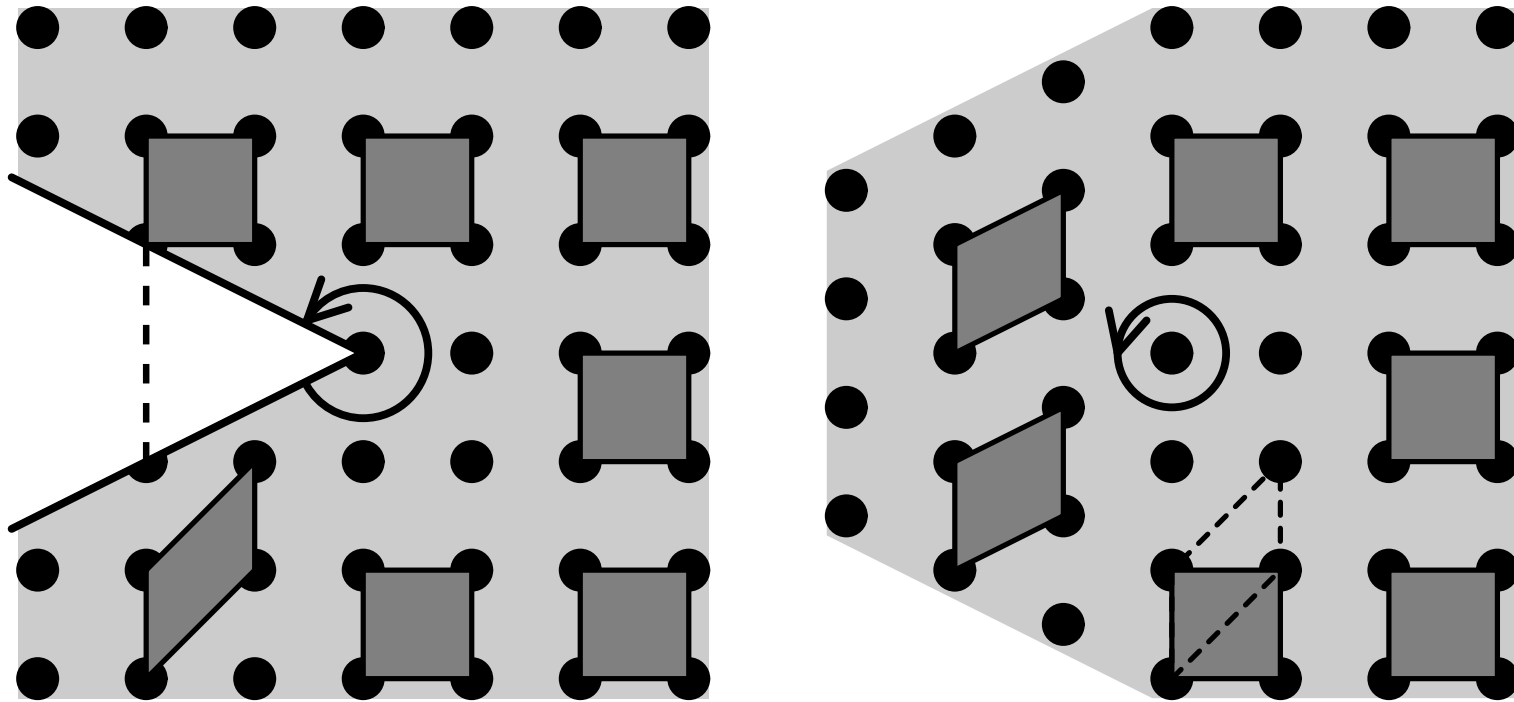


value of the first action

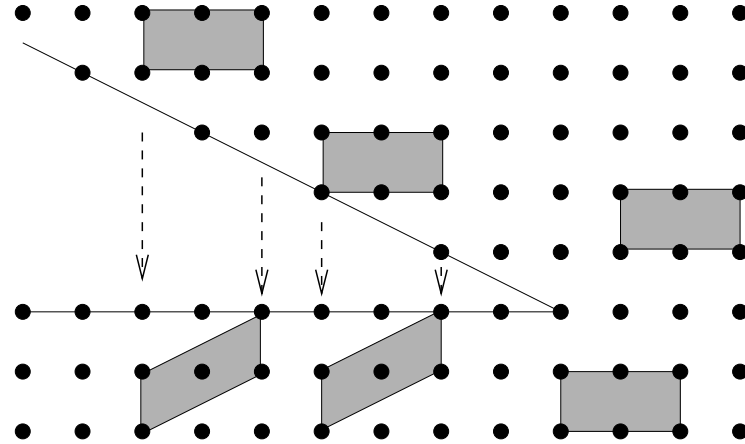
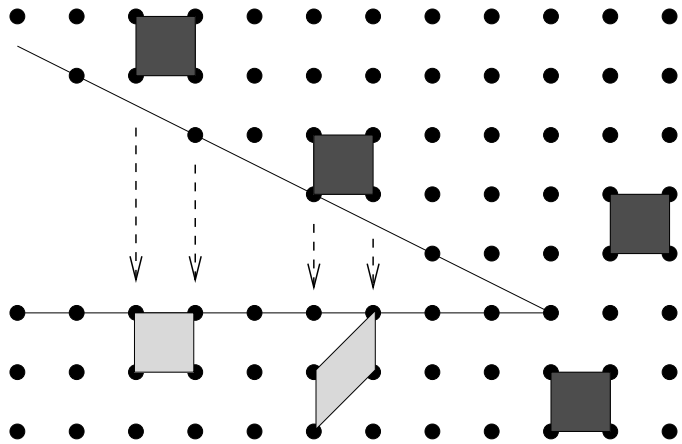


value of the first action

Quantum joint spectra for typical regions of the image of energy - momentum map for integrable problems.



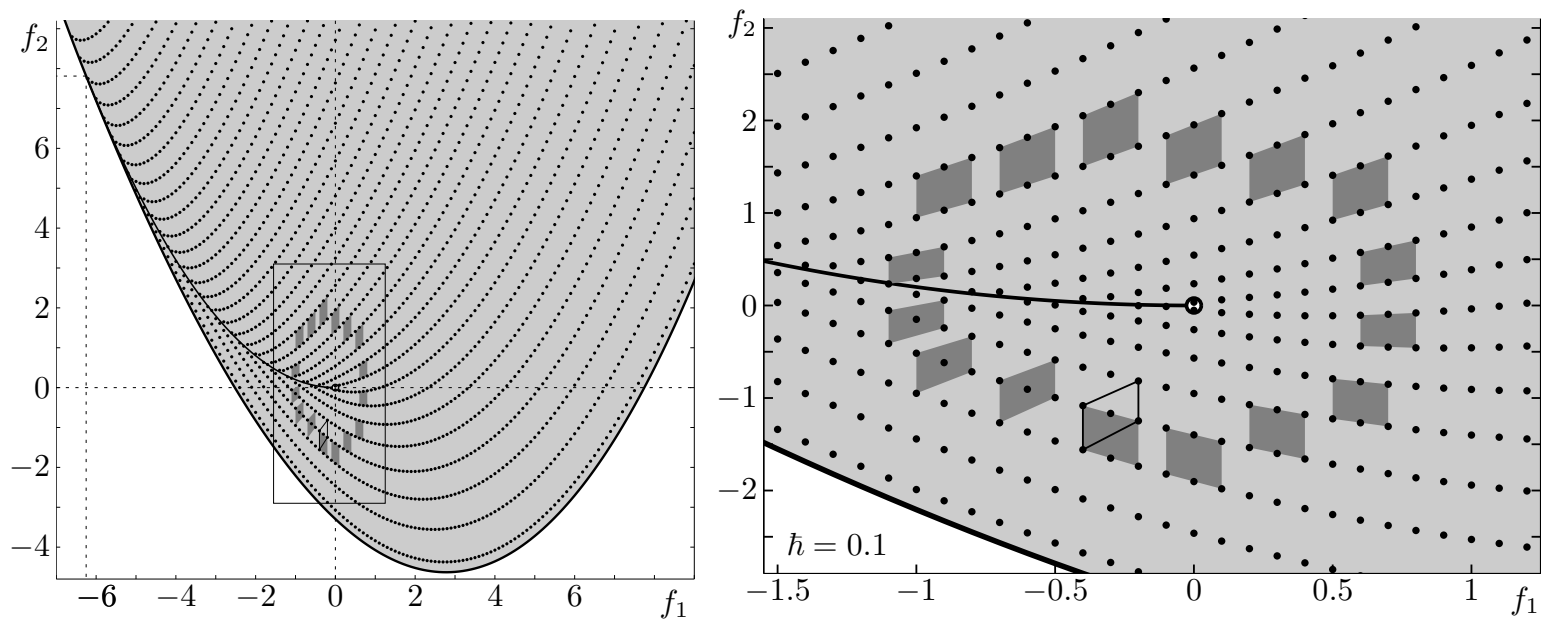
Construction of the $1:(-1)$ lattice defect starting from the regular Z^2 lattice. Dark grey quadrangles show the evolution of an elementary lattice cell along a closed path around the defect point.



Construction of 1 : 2 rational lattice defect.

Left: Elementary cell does not pass unambiguously.

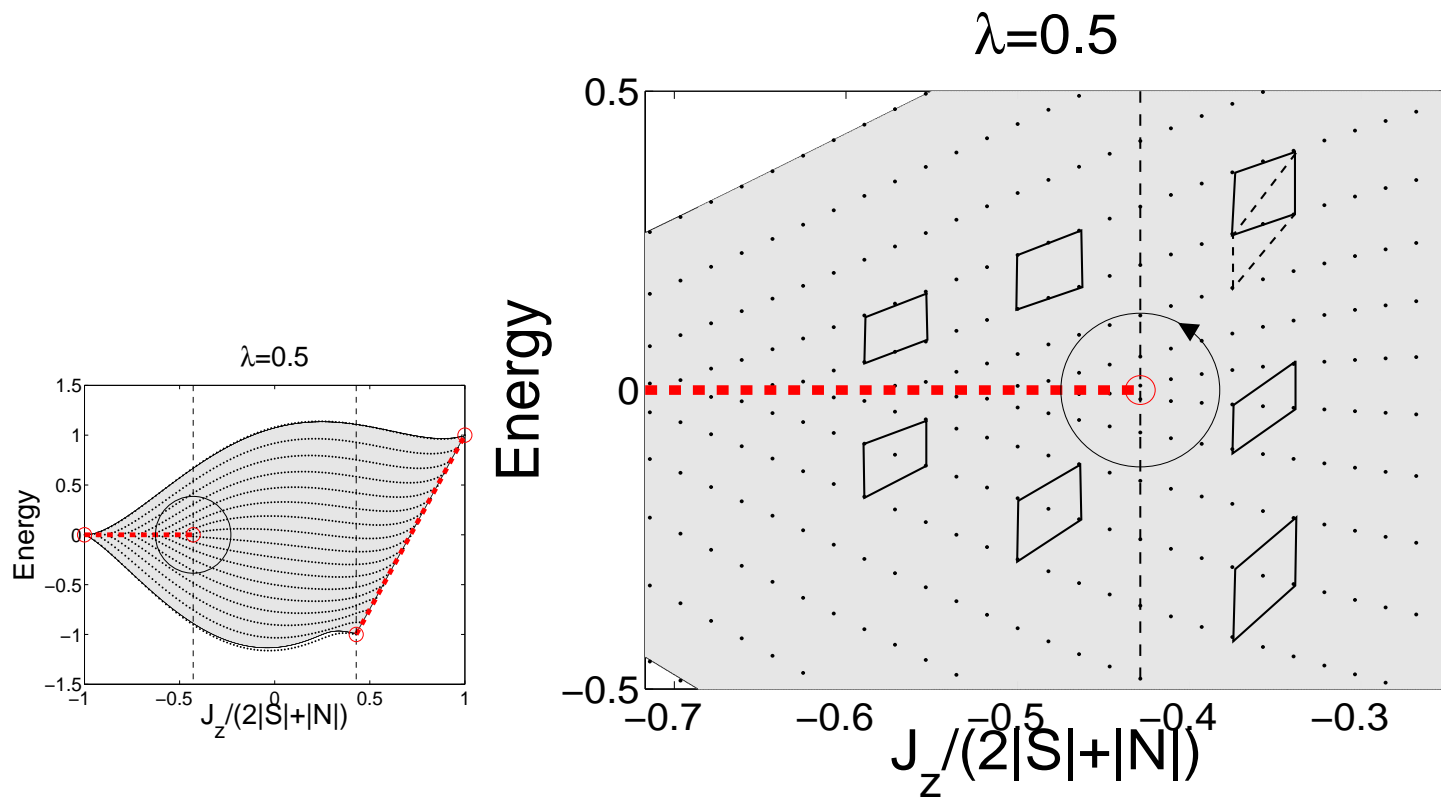
Right: Double cell passes.



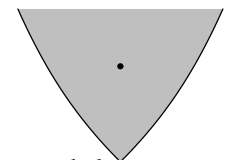
Quantum fractional monodromy for 1 : (-2) resonant oscillator system.

$$F_1 = \frac{\omega}{2}(p_1^2 + q_1^2) - \frac{2\omega}{2}(p_2^2 + q_2^2) + R_1(q, p), \quad (1)$$

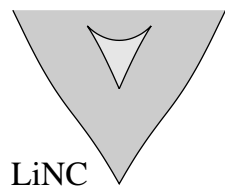
$$F_2 = \text{Im}[(q_1 + ip_1)^2(q_2 + ip_2)] + R_2(q, p). \quad (2)$$



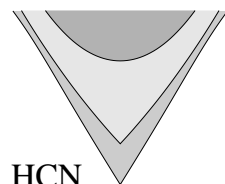
$$H_\lambda = \frac{1-\lambda}{|S|} S_z + \lambda \left(\frac{1}{|S||N|} S_z N_z + \frac{1}{2|S||N|^2} (N_-^2 S_+ + N_+^2 S_-) \right)$$



pendulum

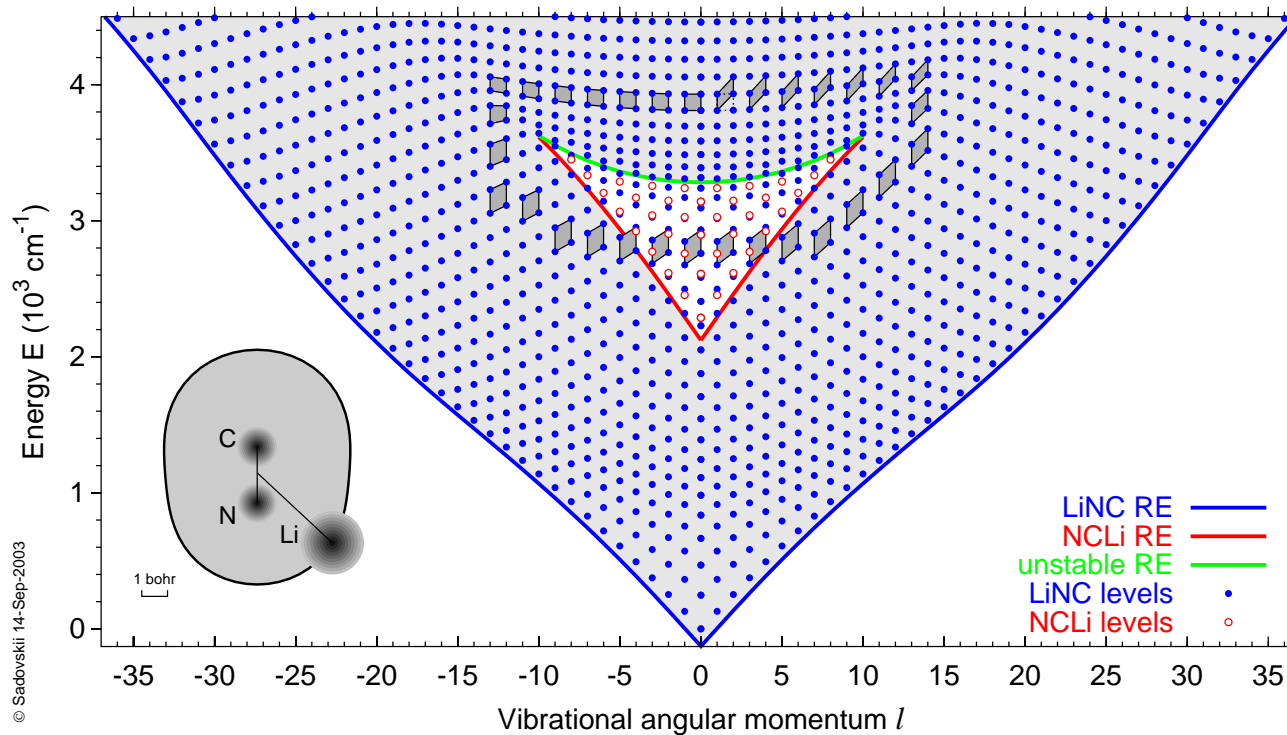


LiNC

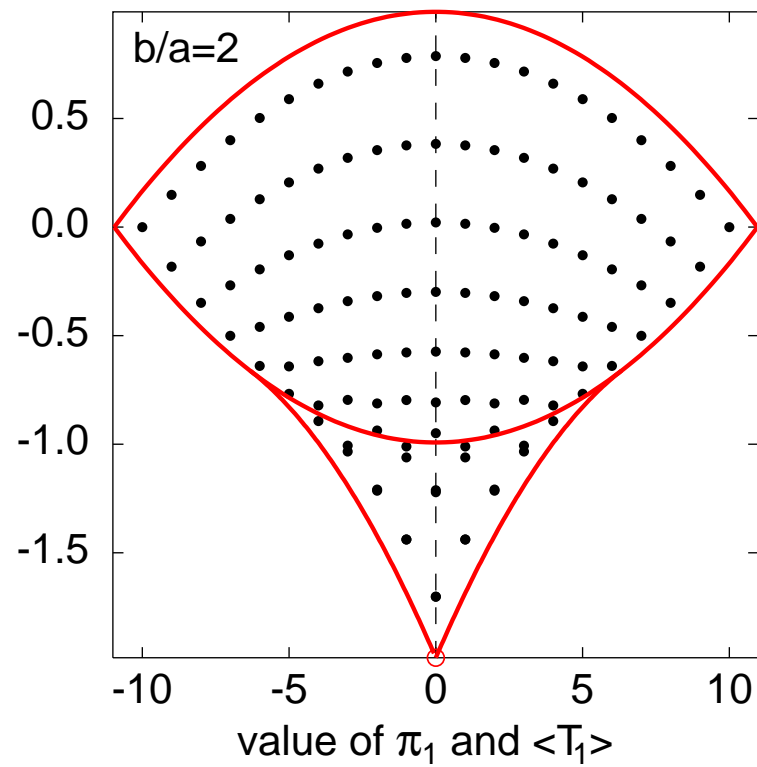
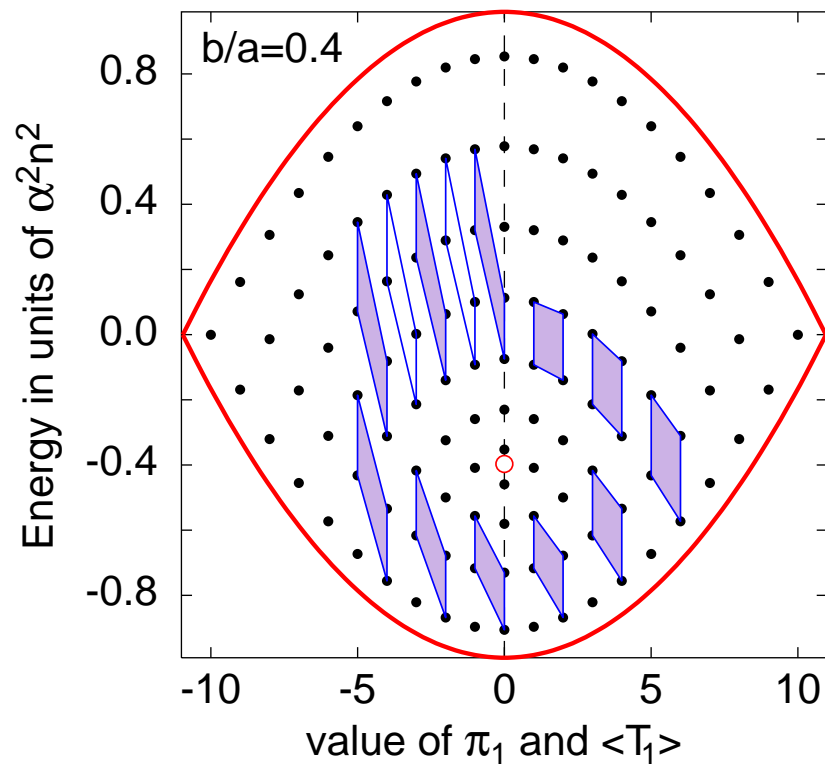


HCN

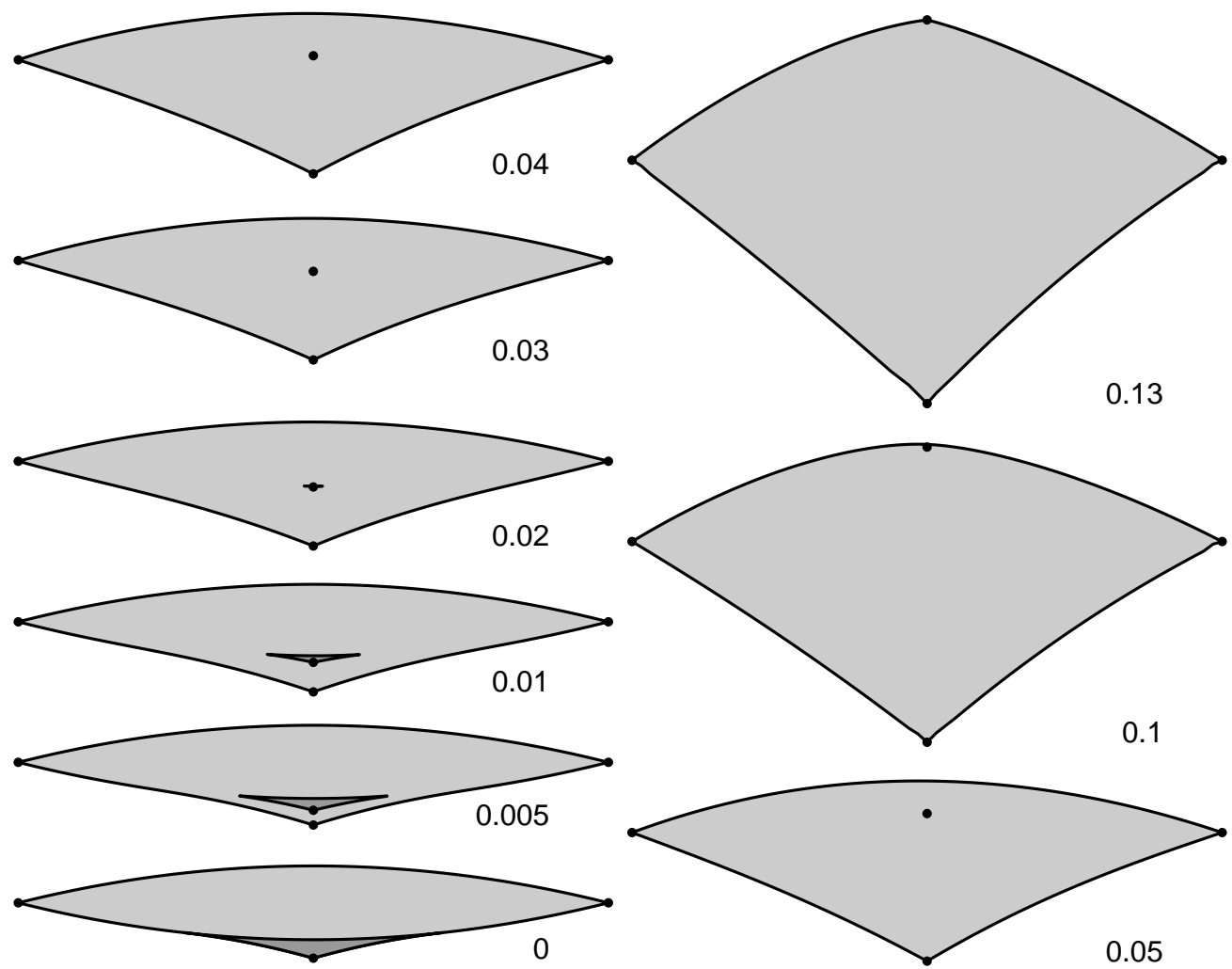
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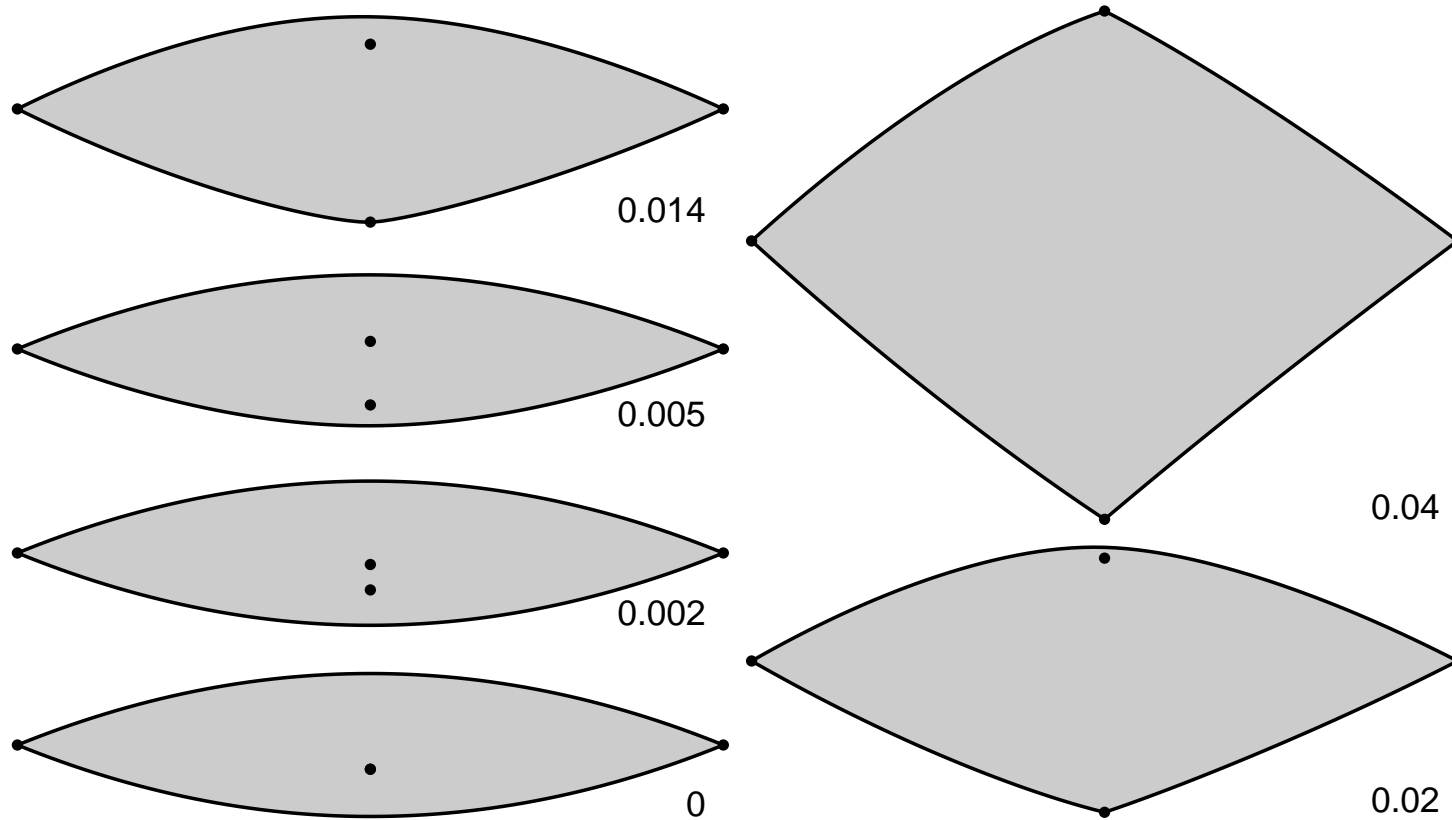
Nonlocal monodromy for LiCN type molecule or quadratic spherical pendulum.



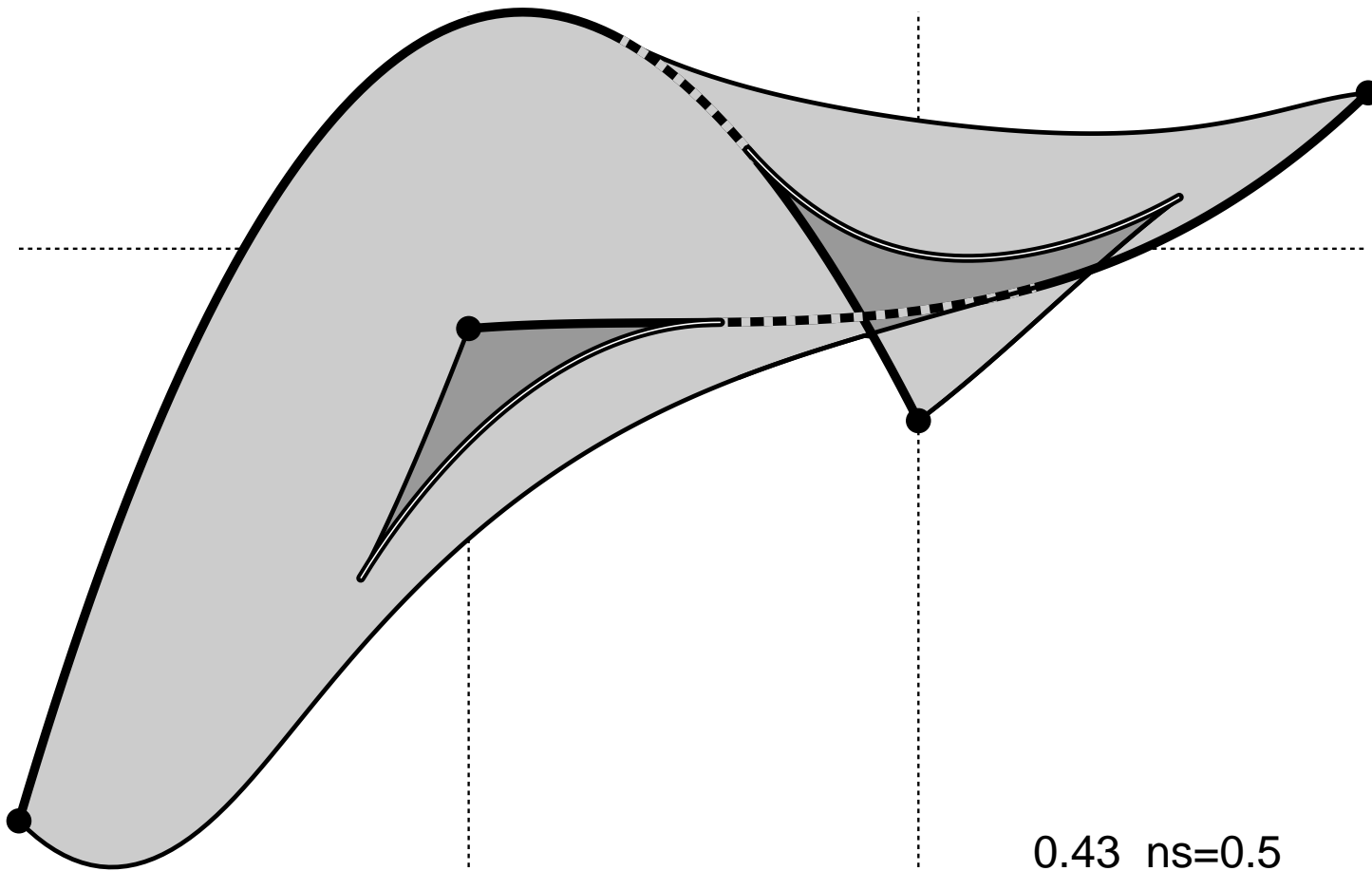
Hydrogen atom in orthogonal electric and magnetic fields.



Evolution of hydrogen atom in parallel fields near Zeeman limit.



Evolution of hydrogen atom (from orthogonal to parallel fields).



Hydrogen atom in some generic configuration of electric and magnetic fields.

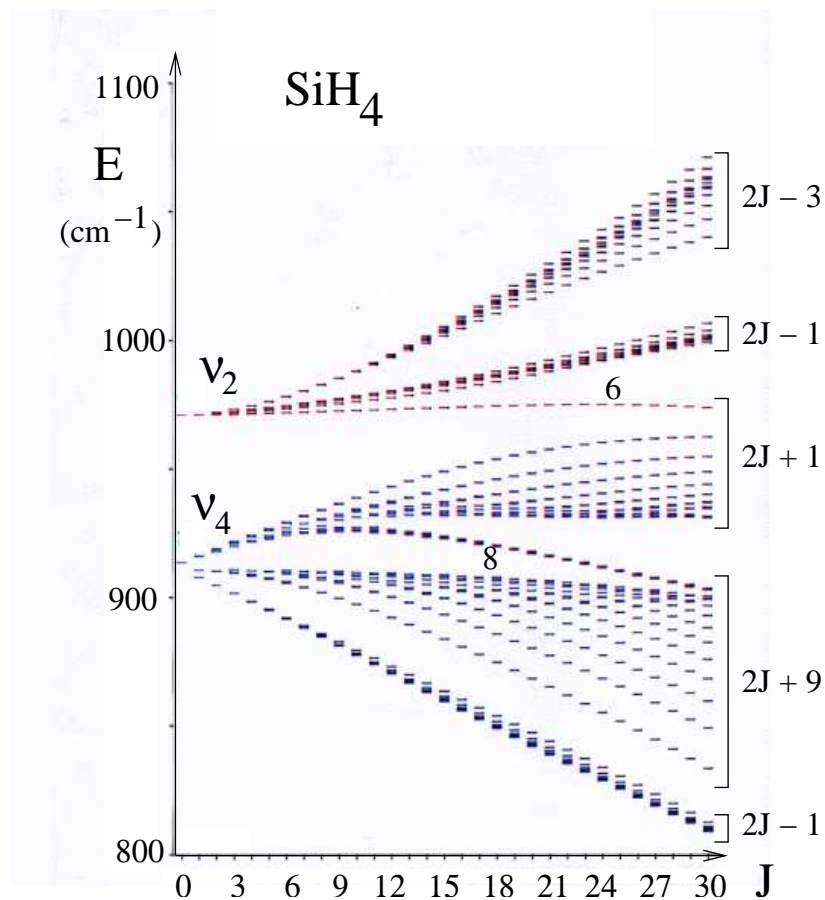


Fig.1 Reduced rovibrational energy as a function of rotational quantum number J for vibrational modes ν_4 (F_2 symmetry type) and ν_2 (E symmetry type) of SiH_4 tetrahedral molecule (T_d point symmetry group).

Table 3: Energy bands and corresponding Chern numbers for example shown in figure 1.

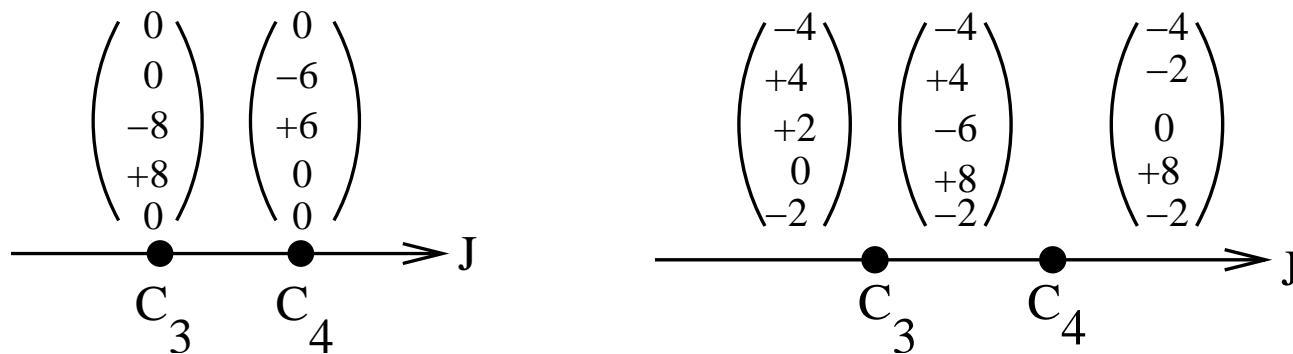
Band	$J \sim 8$	$J \sim 8$	$J \sim 30$	$J \sim 30$
	Numb. lev.	Chern numb.	Numb. lev.	Chern numb.
ν_2 (upper)	$2J - 3$	-4	$2J - 3$	-4
ν_2 (lower)	$2J + 5$	$+4$	$2J - 1$	-2
ν_4 (upper)	$2J + 3$	$+2$	$2J + 1$	0
ν_4 (middle)	$2J + 1$	0	$2J + 9$	$+8$
ν_4 (lower)	$2J - 1$	-2	$2J - 1$	-2

Dimension of matrix Hamiltonian - number of bands - rank of vector bundle.

Bands are isolated if there are no degeneracy points of eigenvalues.

Eigenline bundles are characterized by topological invariant - Chern number.

Degeneracy points are responsible for modification of band structure of the set of Chern numbers.



Schematic representation of the evolution of the band structure represented in Figure 1 as a function of one control parameter, the rotational quantum number J .
 Left - delta Chern associated with two, C_4 and C_3 , orbits of degeneracy points.
 Right - Chern numbers for isolated line bundles vs control parameter J .

Effective Hamiltonian written in terms of tensor products of rotational and vibrational irreducible (with respect to the O symmetry group) tensor operators :

$$\begin{aligned}
 H = & [V^{A_1} \otimes R^{A_1}]^{A_1} + [V^E \otimes R^E]^{A_1} \\
 & + [V^{F_1} \otimes R^{F_1}]^{A_1} + [V^{F_2} \otimes R^{F_2}]^{A_1} .
 \end{aligned} \tag{3}$$

Here V^Γ and R^Γ are vibration and rotation tensor operators, respectively, transforming according to irreducible representations $\Gamma = A_1, A_2, E, F_1, F_2$ of the symmetry group O .

Taking only leading contributions (the operators of lowest degree in $\{J_x, J_y, J_z\}$ variables) for rotational tensor operators and neglecting scalar J^2 dependence, we have the following explicit form of rotational contributions in the classical limit,

$$R^{A_1} = J_x^4 + J_y^4 + J_z^4; \quad (4)$$

$$R_1^E = 2J_z^2 - J_x^2 - J_y^2; \quad R_2^E = \sqrt{3}(J_x^2 - J_y^2); \quad (5)$$

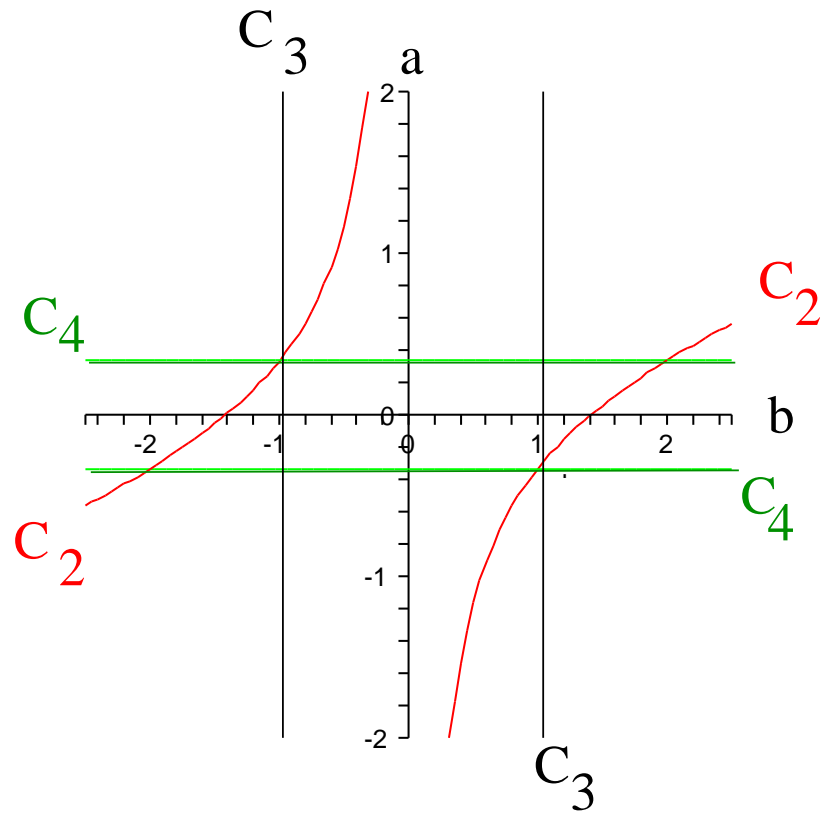
$$R_x^{F_1} = J_x; \quad R_y^{F_1} = J_y; \quad R_z^{F_1} = J_z; \quad (6)$$

$$R_x^{F_2} = J_y J_z; \quad R_y^{F_2} = J_z J_x; \quad R_z^{F_2} = J_x J_y. \quad (7)$$

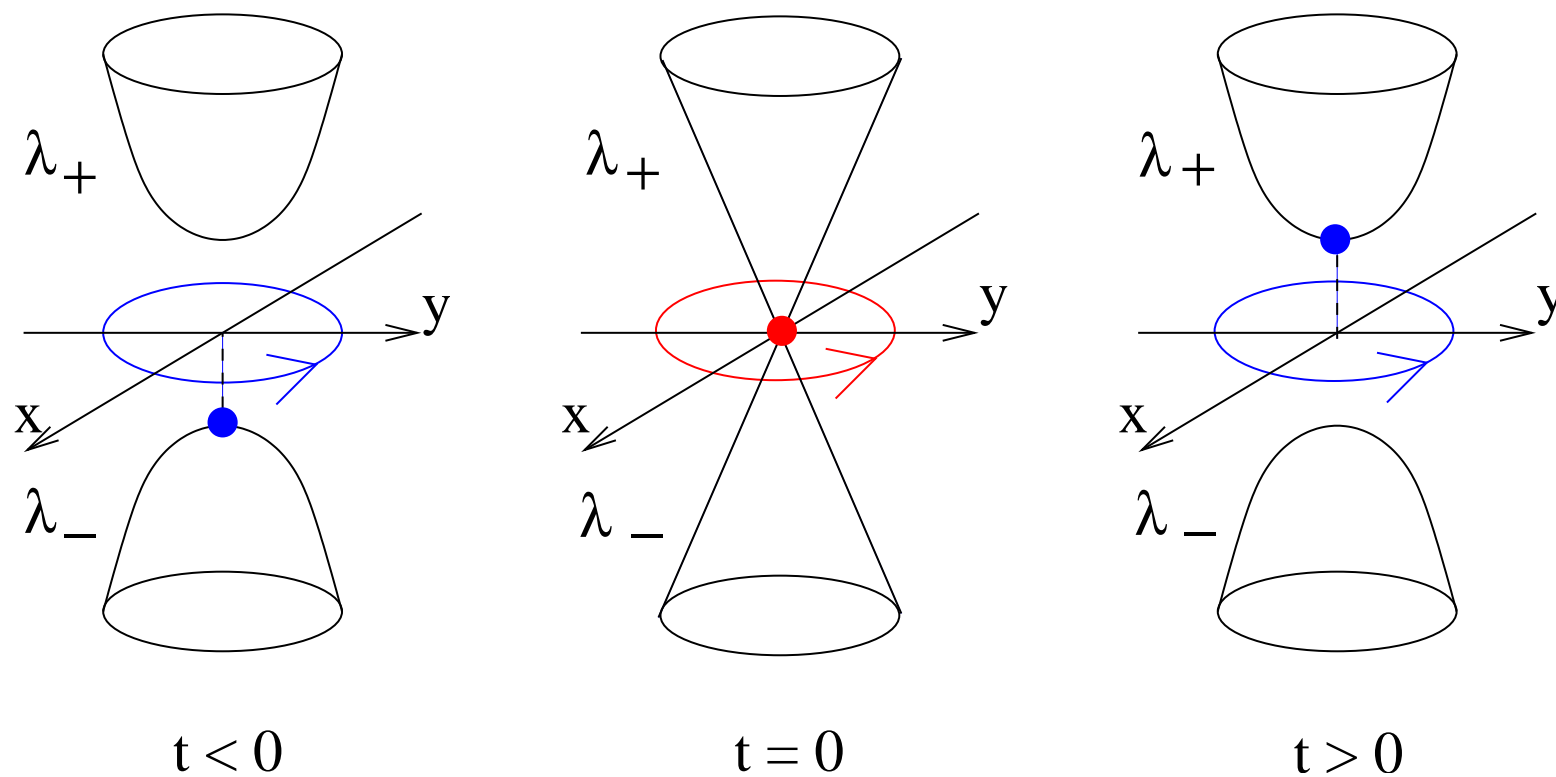
Model Hamiltonian for three vibrational states of F_2 symmetry

$$\begin{aligned}
 H = & \begin{pmatrix} 0 & iz & -iy \\ -iz & 0 & ix \\ iy & -ix & 0 \end{pmatrix} \\
 +a & \begin{pmatrix} y^2 + z^2 - 2x^2 & 0 & 0 \\ 0 & z^2 + x^2 - 2y^2 & 0 \\ 0 & 0 & x^2 + y^2 - 2z^2 \end{pmatrix} \\
 +b & \begin{pmatrix} 0 & xy & zx \\ xy & 0 & yz \\ zx & yz & 0 \end{pmatrix}.
 \end{aligned} \tag{8}$$

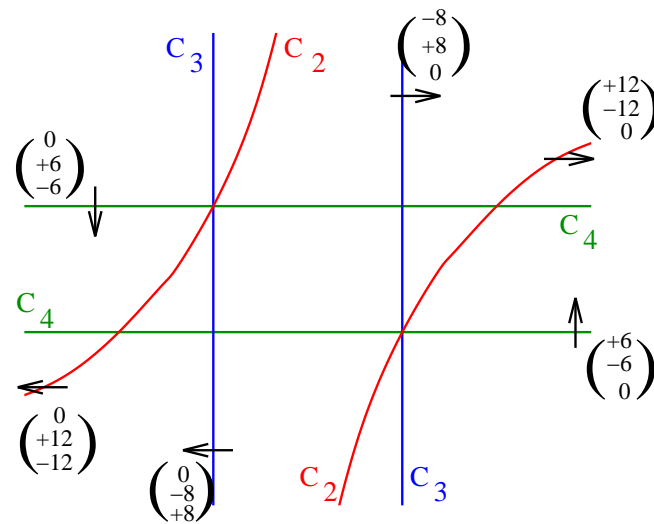
a, b - control parameters.



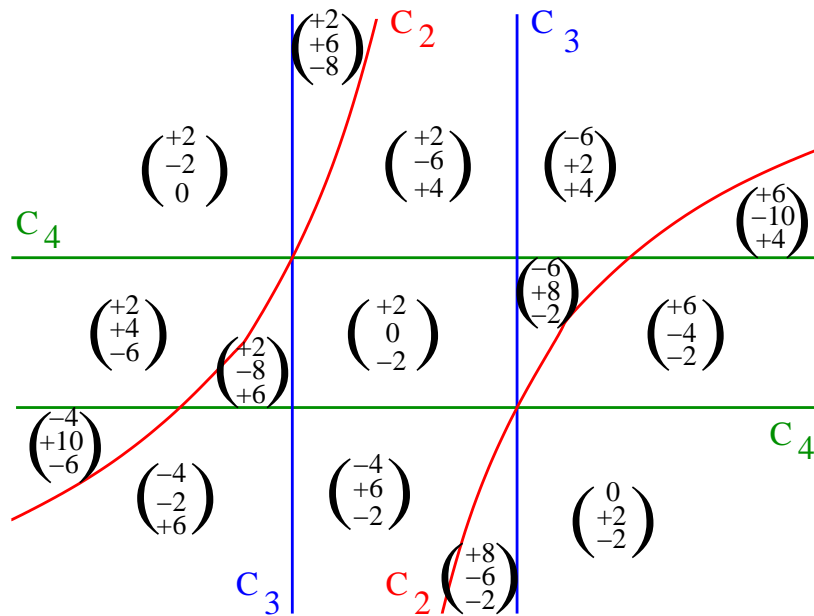
Degeneracy points (on C_2 , C_3 , C_4 orbits) in the space of control parameters (a, b) for the Hamiltonian (8).



Schematic representation of the evolution of eigenvalues of a local linearized model Hamiltonian in a two-level approximation along with variation of a control parameter t crossing the boundary of the iso-Chern domain. Exceptional points (blue points) in the chosen representation are shown for λ_+ and λ_- components.



Delta-Chern diagram for three state model (8) represented in the space of control parameters (a, b) . Each degeneracy line (the boundary of the iso-Chern domain) is associated with a three component column giving delta-Chern for each of three bands and with an arrow indicating the direction of the path in the control parameter space associated with the shown modifications of Chern numbers.



Iso-Chern diagram for three state model. Vertical (blue) lines represent boundaries with degeneracy points at C_3 positions. Horizontal (green) lines represent boundaries with degeneracy points at C_4 positions. Curved (red) lines represent boundaries with degeneracy points at C_2 positions. Each open iso-Chern domain is characterized by three Chern numbers associated with three bands arranged according to their energy. Upper, middle and lower numbers in each symbol give respectively Chern numbers for the band with higher, middle and lower energy.

Possible reorganization of bands for three vibrational states of F_i symmetry of the group O .

$$F_i \otimes (J) = (J + \Delta_{\max})_i \oplus (J + \Delta_{\text{middle}})_i \oplus (J + \Delta_{\min})_i, \quad (9)$$

where

$$\Delta_{\max} + \Delta_{\text{middle}} + \Delta_{\min} = 0, \quad (10)$$

and where $(J + \Delta_k)_i$, $k = \max, \text{middle}, \min$, denote for short $(J + \Delta_k) \otimes A_i$, $i = 1, 2$, with A_i referring to the representation of the O group.

