Journées Semi-Classiques Moléculaires

Manifestation of monodromy in molecular energy level spectra examples of HCN/CNH vs LiNC/NCLi and CO_2

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- to *San Vu Ngoc* for organizing this conference and invitation

Outline:

- Atomic and molecular systems with monodromy
- Floppy triatomic molecules as deformed spherical pendula
- 2D monodromy of the spherical pendulum and its deformations
- Shape corrections, monodromy of LiNC/NCLi, and analysis of HCN/CNH
- The elastic pendulum or the 1:1:2 resonant swing–spring
- Description based on classical singular reduction, classical monodromy
- The CO_2 molecule as quantum 1:1:2 resonant swing–spring
- 3D monodromy of 1:1:2 resonant swing–spring and of the CO_2 molecule
- Conclusions, perspectives and problems

Publications

http://purple.univ-littoral.fr/˜dima

M. Joyeux, D. A. Sadovskií and J. Tennyson, *Monodromy of the LiNC/NCLi molecule*, Chem. Phys. Lett. **382**(3-4), 439–442 (2003).

M. Joyeux, K. Efstathiou and D. A. Sadovskií, *Global bending quantum number and the absence of monodromy in the HCN↔CNH molecule*, Phys. Rev. A, **69**(3), 032504-1–15 (2004).

R. H. Cushman, H. Dullin, D. Holm, A. Giacobbe, M. Joyeux, D. A. Sadovskií, and B. I. Zhilinskií, *The CO_2 molecule as quantum realization of the 1:1:2 resonant swing–spring system with monodromy* Phys. Rev. Lett., in print, (2004)

Quantum systems with monodromy

are 2- and 3–body systems with certain similarities

in atoms:

Perturbed Keplerian systems: hydrogen atom in crossed electric and magnetic fields. *Cushman, Sadovskií, 1999*

Systems of two and three coupled angular momenta. *Sadovskií, Zhilinskií, 2000*

in molecules:

Two–center Kepler system: H_2^+. *Waalkens, Junge, Dullin, 2003*

Quantum analogues of Lagrange top: rigid symmetric top molecules in external electric fields. *Kozin, Roberts, 2003*

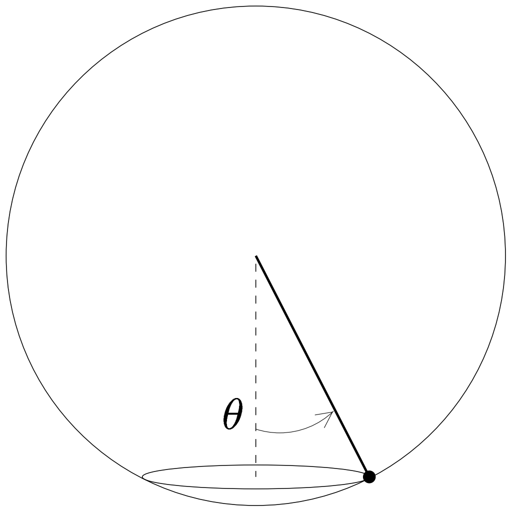
Rotating quasi-linear molecules (H_2O). *Child, Weston, Tennyson, 1999*

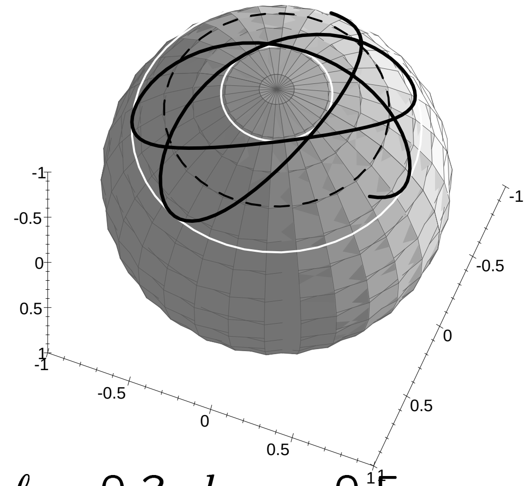
Analogues of 1:1:2 resonant swing-spring: CO_2, H-CX_3.
Cushman, Giacobbe, Joyeux, Sadovskií, Zhilinskií, <u>in progress, 2004</u>

Floppy triatomic molecules are among the first examples suggested at the Warwick meeting in 1997 after Cushman's talk on spherical pendulum.
Jacobson, Child, 2001; <u>our work in 2003</u>

Spherical pendulum

(Huygens long ago . . . Cushman 1983–97)



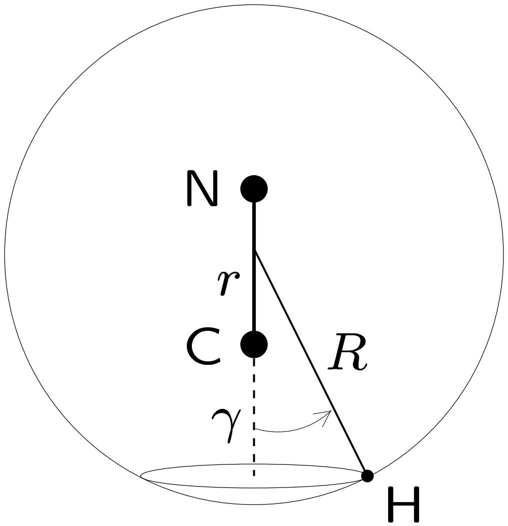


$\ell = 0.3$, $h = -0.5$

A particle moving on $\mathbb{S}^2$ in the linear potential $V(z) = z$ with one stable (lower) and one unstable (upper) equilibrium.

Symmetry: axial symmetry SO(2), time reversal, reflection σ_v

Floppy triatomic molecule



Many floppy molecules have *two* stable linear equilibria. To describe such systems we use *quadratic deformation*

$$V_c(z) = z - \tfrac{1}{2}cz^2$$

Other factors:

- shape
- swing-spring resonances
- overall rotation

Note that c in V_c defines the relative energies of the two stable linear equilibria A and B and the barrier X at $\ell = 0$,

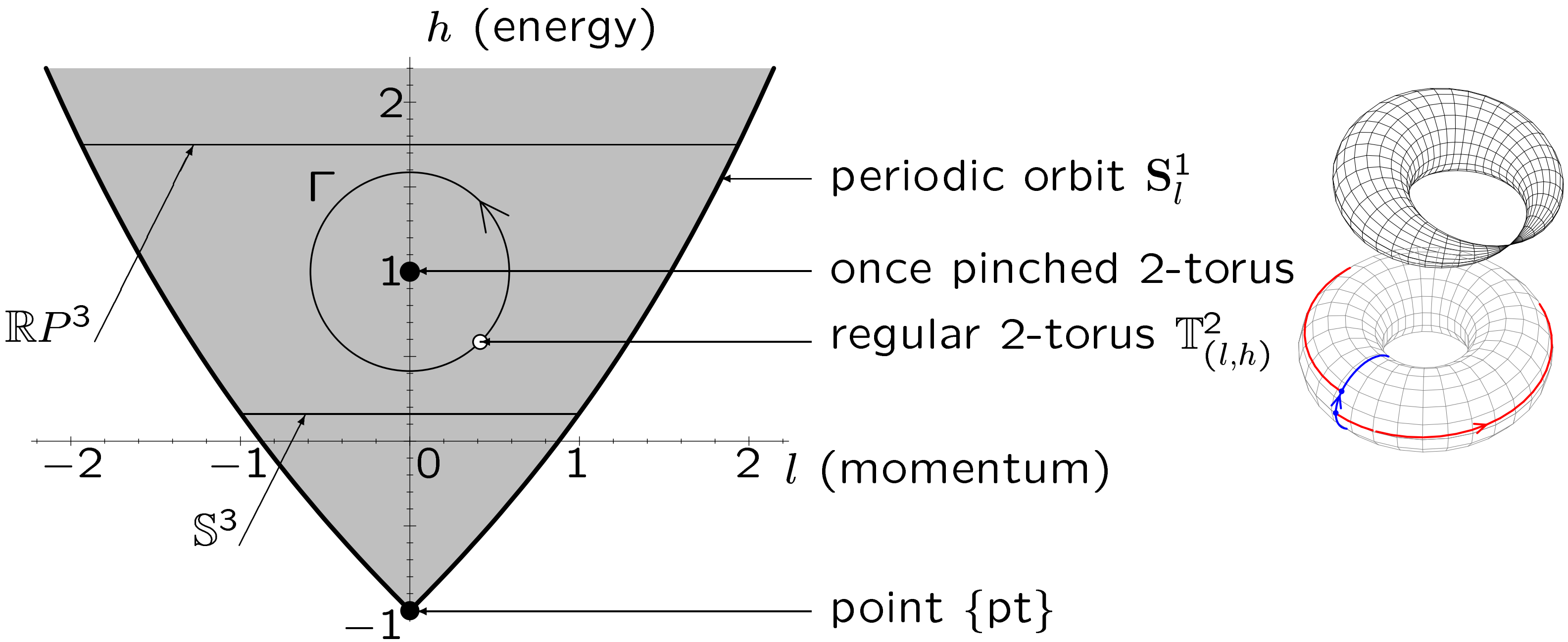
$$h_X > h_B > h_A, \quad (h_X - h_B)/(h_X - h_A) = (c-1)^2/(c+1)^2.$$

Symmetry: axial symmetry SO(2), time reversal, reflection σ_v

Image of the energy–momentum map

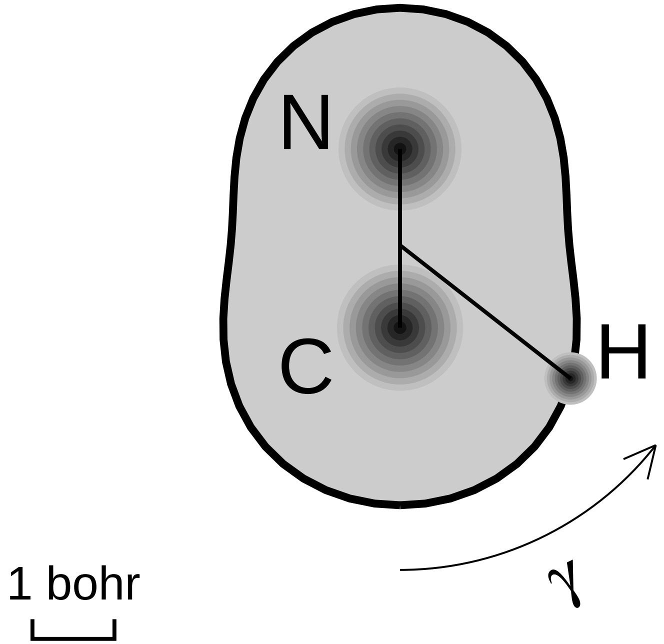
$$\mathcal{EM} : T\mathbb{S}^2 \to \mathbb{R}^2_{\ell,h} : (q,p) \to \Big(L(q,p), H(q,p)\Big) = (\ell, h)$$

of the spherical pendulum

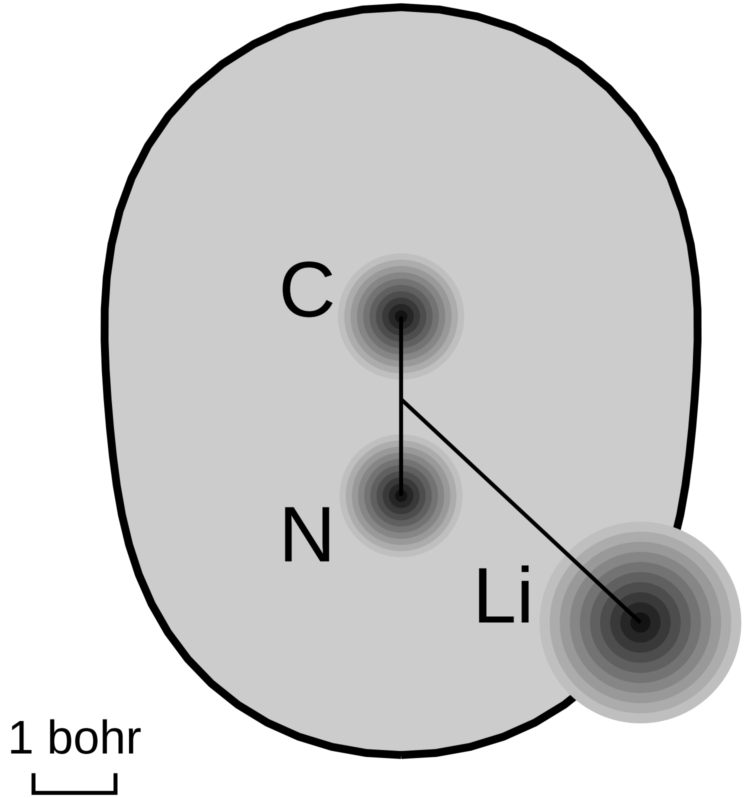


Shape correction $R_\epsilon(\gamma) = R_{\mathsf{max}}(1 - \epsilon \sin^2 \gamma)$

where $\epsilon \geq 0$ is the *asphericity parameter*



nonconvex
$\epsilon \approx 0.35$
$R = 4.35 \ldots 3.55 \ldots 4.80$



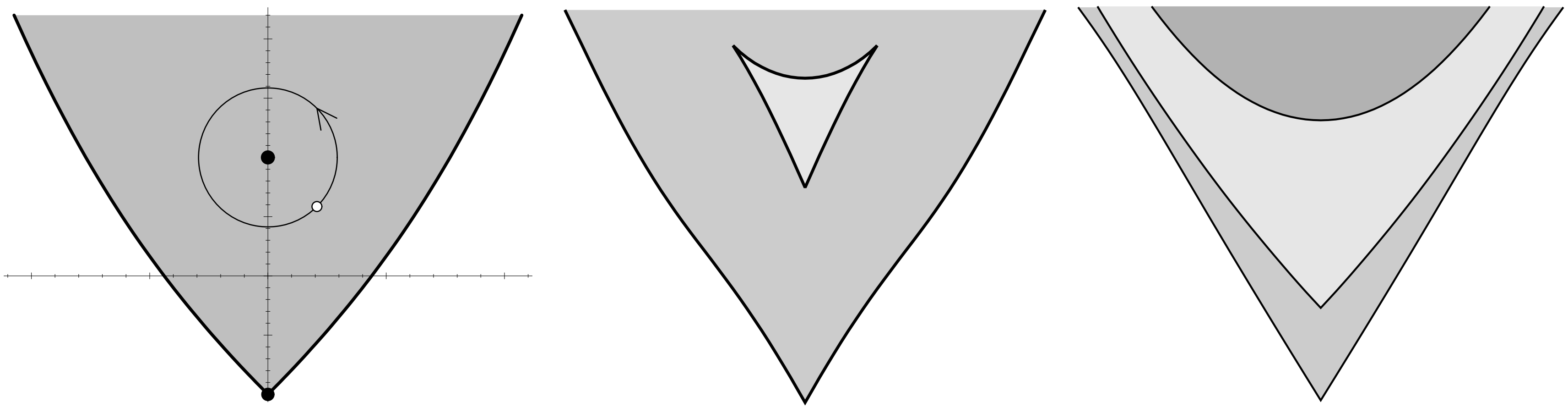
convex
$\epsilon \approx 0.26$
$R = 3.18 \ldots 2.04 \ldots 2.90$

Deformations in the image of the $\mathcal{EM}$ map

$$\left\{F(\gamma)=h, \frac{dF}{d\gamma}=0\right\} \quad \text{with } F(\gamma)=\frac{\ell^2}{2mR_\epsilon(\gamma)^2\sin^2\gamma}+V_c(\cos\gamma),$$

$$R_\epsilon(\gamma)=R_{\mathrm{max}}(1-\epsilon\sin^2\gamma), \quad V_c(z)=z-\tfrac{1}{2}cz^2, \quad z=\cos\gamma.$$

Solve for (h,ℓ) as functions of $\zeta=\cos\gamma$.



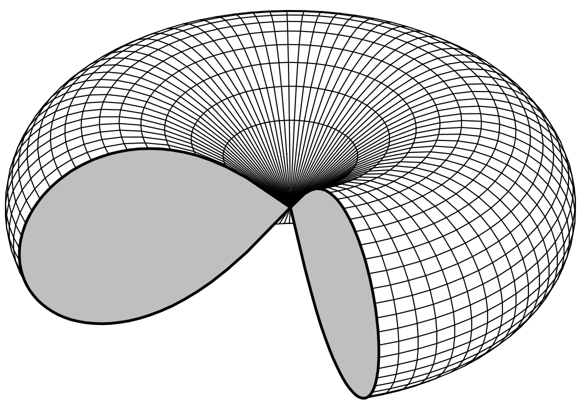
spherical pendulum	LiNC/NCLi	HCN/CNH
$c=\epsilon=0$	(convex)	(nonconvex)
	$c>1,\ \epsilon<\frac{1}{3}$	$c>1,\ \epsilon>\frac{1}{3}$

Gallery of singular fibers

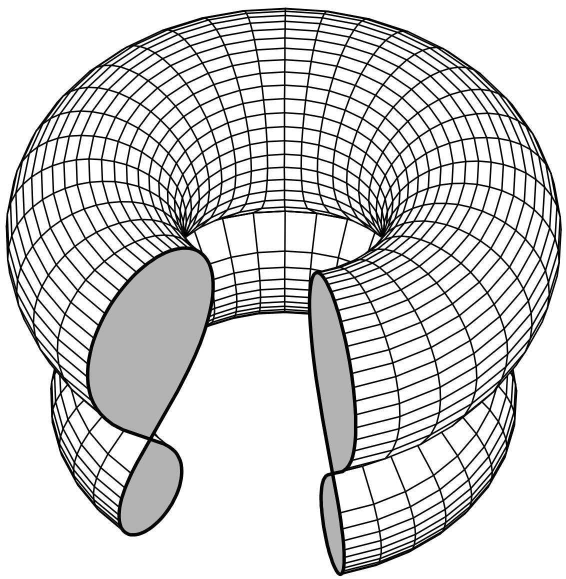
Values of the $\mathcal{E}\mathcal{M}$ map

isolated critical value	points on the critical cut	cusped points
when $c = \epsilon = 0$	when $c > 1$	when $c > 1$, $\epsilon < \frac{1}{3}$

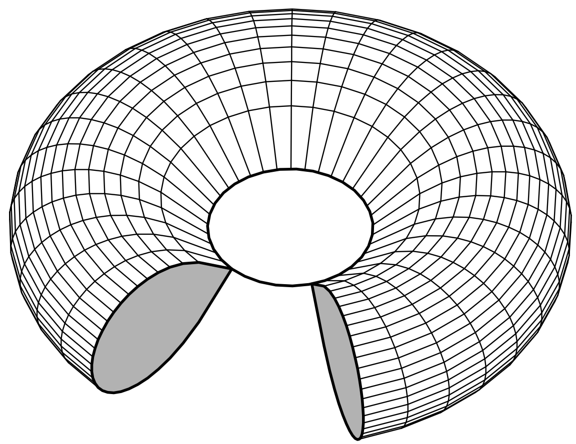
Inverse images



pinched torus

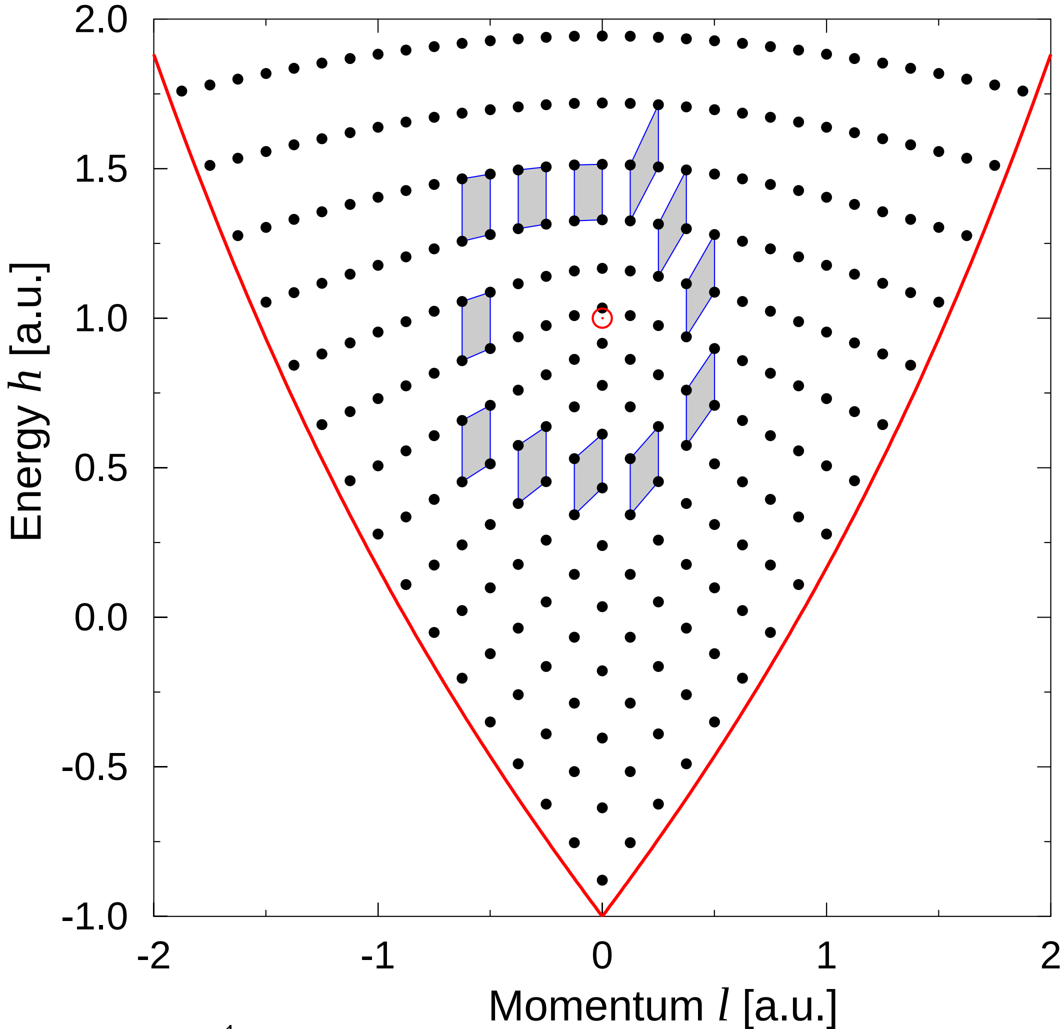


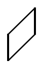
glued tori



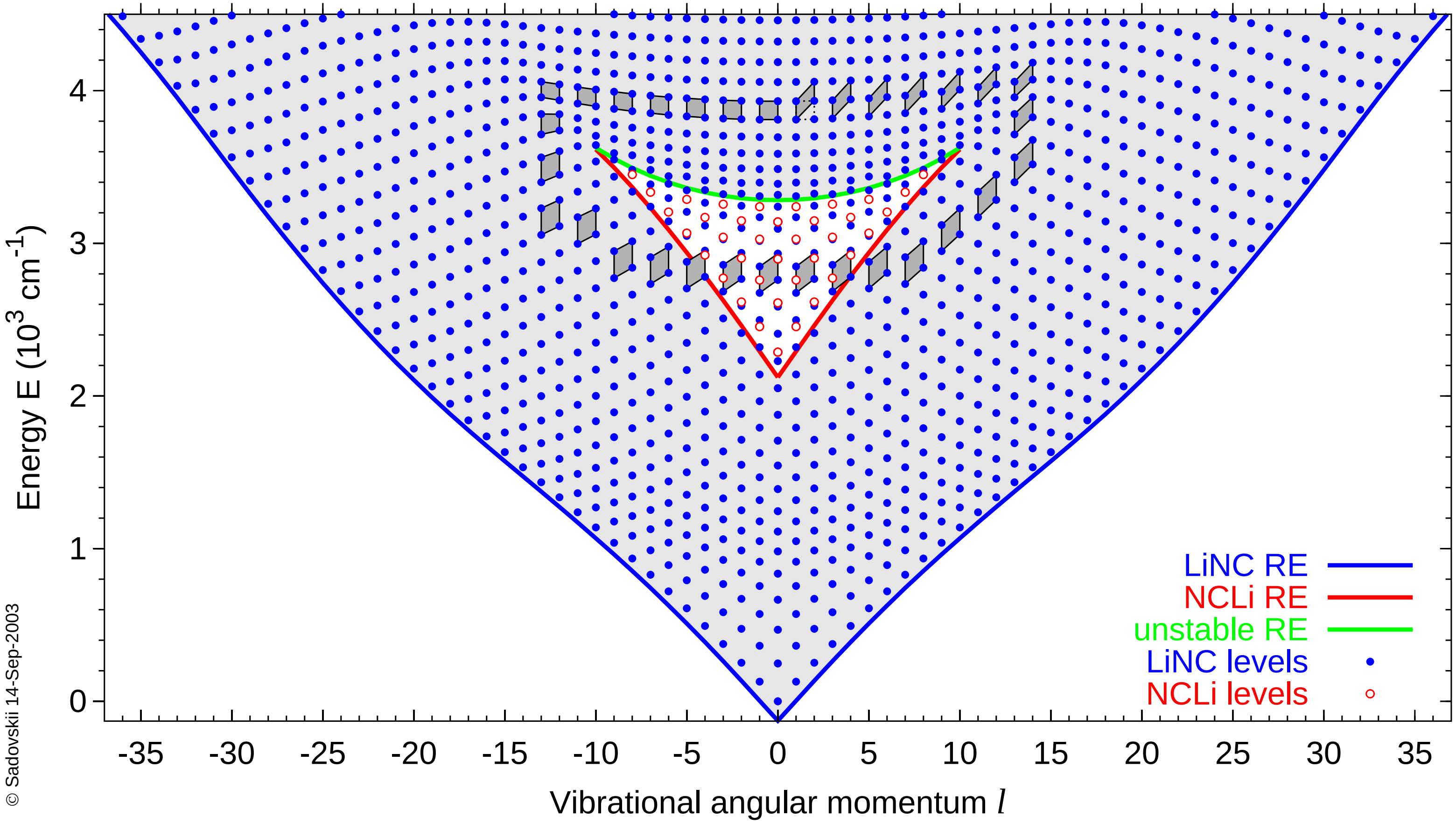
cusped torus

$\mathit{Mονοδρομία}$ $\begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$ in the spherical pendulum



The final cell  does *not* correspond to the original cell □

$M o \nu o \delta \rho o \mu \acute{\iota} \alpha \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$ in LiNC/NCLi



The final cell ▱ does *not* correspond to the original cell □

Filled and hollow circles show levels attributed to the LiNC and NCLi minimums; bold solid lines show energies of classical relative equilibria.

Comments on the study of LiNC/NCLi and computation details

The $\mathcal{EM}$ map of LiNC/NCLi has a two-leaf image with monodromy $\begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$ characteristic for convex systems ($\epsilon < \frac{1}{3}$) with $c > 1$.

The $\mathcal{EM}$ diagram of LiNC/NCLi is computed by *Marc Joyeux* using the potential in [R. Essers, J. Tennyson, P. E. S. Wormer, Chem. Phys. Lett. **89**, 223 (1982)].

Chemists give us an accurate 3D potential $V(r, R, \gamma)$ which they compute theoretically and adjust against known data.

The potential and kinetic energies of the system are first expanded in the neighborhood of the reaction path (or Minimum Energy Path, MEP).

<u>All terms in the kinetic energy which contain overall rotation are thrown out</u>.

The two stretch coordinates are defined as deviations

$$q_r = r - r_{\mathsf{MEP}}(\gamma) \quad \text{and} \quad q_R = R - R_{\mathsf{MEP}}(\gamma)$$

and then rescaled; the expansion is rewritten.

Since there is no resonances, oscillations in (q_r, q_R) are normalized.

$\mathcal{EM}$ diagram for HCN/CNH with $\nu_1 = \nu_3 = 0$

computed by *Marc Joyeux* using the potential in [J. Tennyson *et al*, JCP **115**, 3706 (2001)].

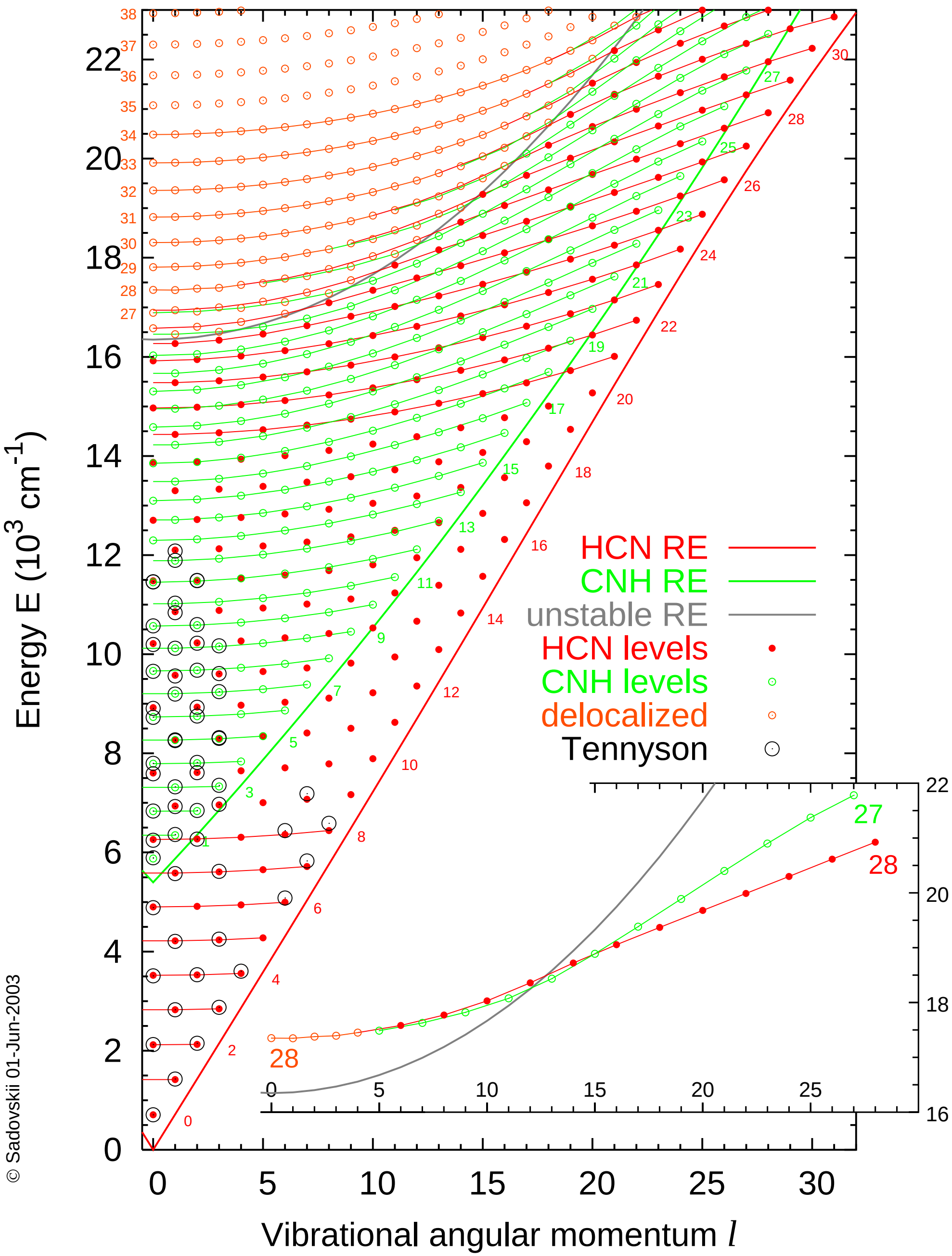
Bold solid lines show energies of classical rel. eq.; fine solid lines join states with the same quantum numbers n_{HCN}, n_{CNH}, or j, indicated the end of the respective sequences.

HCN/CNH is a nonconvex system ($\epsilon > \frac{1}{3}$, $c > 1$), it has a *three-leaf* image of the $\mathcal{EM}$ map without $\mu o \nu o \delta \rho o \mu \acute{\iota} \alpha$.

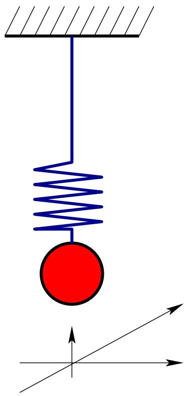
Global bending quantum number

$$\mathcal{J} = j = n_{\text{HCN}} = n_{\text{CNH}} + 1$$

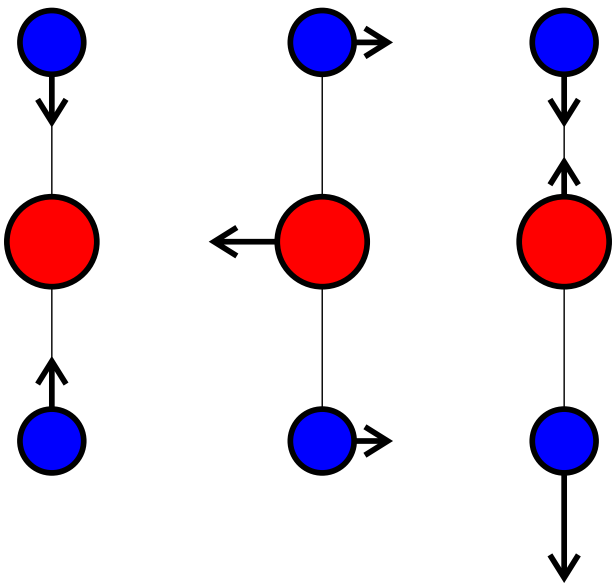
labels the full three-branch $\mathcal{J}$-multiplet contains $2\mathcal{J} + 1$ levels.



The 1:1:2 resonant swing–spring and the CO_2 molecule



Elastic pendulum in the field of gravity $V(z) = z$ with swinging in two equivalent directions (q_1, q_2) and springing of the pendulum q_3. Swinging and springing are in the 1:2 resonance.



The CO_2 molecule has four vibrational degrees of freedom: symmetric stretching mode $\nu_1(q_1)$ $\mathbf{1353.5}$ cm^{-1}, doubly degenerate bending mode $\nu_2(q_{2a}, q_{2b})$ $\mathbf{669.1}$ cm^{-1}, and asymmetric stretching $\nu_3(q_3)$ $\mathbf{2396.2}$ cm^{-1}. It also has two rotational degrees (with axes perpendicular to the molecule) described by the total angular momentum J.

Reduction of the 1:1:2 resonance with SO(2) symmetry

Molien generating function for the invariant polynomials in (q,p)

$$g(\lambda) = \frac{1+\lambda^3}{(1-\lambda^2)^3(1-\lambda^3)}$$

confirms the structure of the polynomial ring

$$\mathbb{R}(N,R,L,S) \bullet \{1,T\} = \mathbb{R}(N,R,L,S) \oplus \mathbb{R}(N,R,L,S)T,$$

whose generator invariants

$$N = \tfrac{1}{2}(q_1^2 + p_1^2 + q_2^2 + p_2^2 + 2q_3^2 + 2p_3^2),$$

$$R = \tfrac{1}{2}(q_1^2 + p_1^2 + q_2^2 + p_2^2), \qquad L = \tfrac{1}{2}(-q_1^2 - p_1^2 + q_2^2 + p_2^2),$$

$$S = (q_1p_2 + q_2p_1)q_3 - (q_1q_2 - p_1p_2)p_3 \qquad T = (q_1q_2 - p_1p_2)q_3 + (q_1p_2 + q_2p_1)p_3.$$

are bound by one relation (*sygyzy*)

$$2\Phi^{1:1:2}_{n,\ell} = T^2 + S^2 - (R-L)(R+L)(J-R) = 0, \quad n \geq R \geq |L| \geq 0.$$

The total symmetry group of these systems $\mathrm{SO}(2) \times C_s \times \mathcal{T}$:

$$\mathcal{T} : (N,R,L,S,T) \mapsto (N,-L,R,S,-T),$$

$$\sigma_v : (N,R,L,S,T) \mapsto (N,-L,R,S,T), \quad \mathcal{T}_s = \mathcal{T} \circ \sigma_v$$

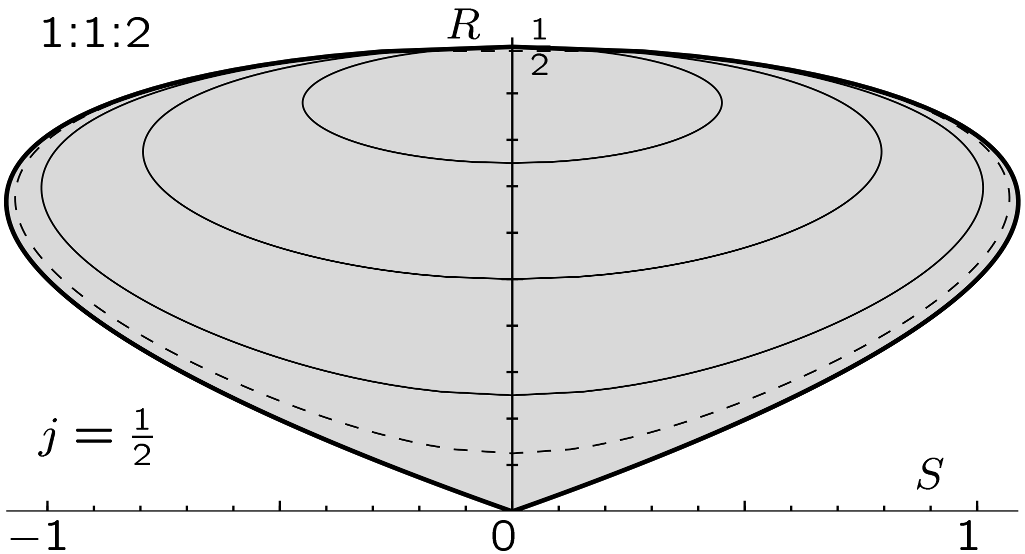
leads to a simpler *free* ring $\mathbb{R}(N,R,L^2,S)$. **Any Hamiltonian, and in particular the one obtained for CO_2 after normalization belongs to this ring**.

Reduced 1:1:2 resonant oscillator with $\mathrm{SO}(2)\times C_s\times\mathcal{T}$ symmetry

Fix the values *polyad integral* $N=n$ and *vibrational angular momentum* $L=\ell$

The *reduced Hamiltonian* $H_{n,\ell^2}(R,S)$ lives on the *reduced phase space* $P_{n,\ell}$. It is a polynomial in (R,S) whose coefficients depend on parameters (n,ℓ^2).

Here S describes main *Fermi resonance interaction*, and R gives *detuning*.

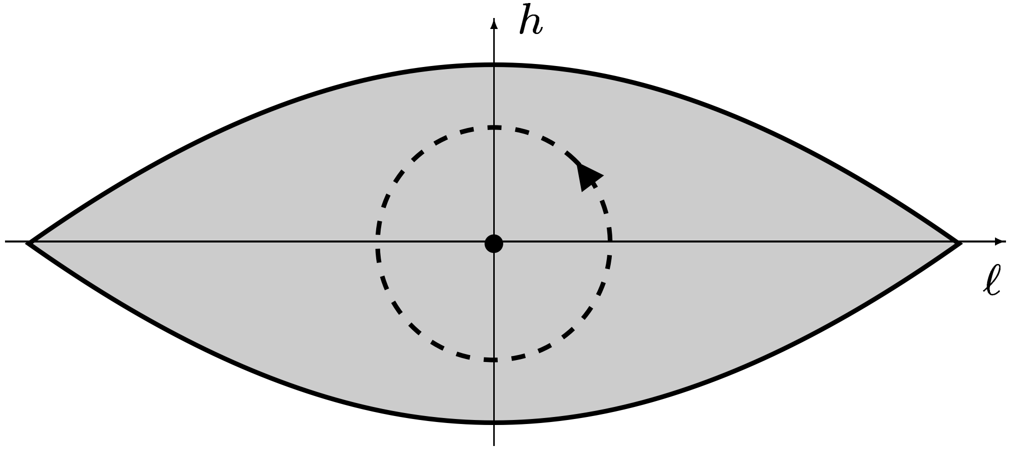


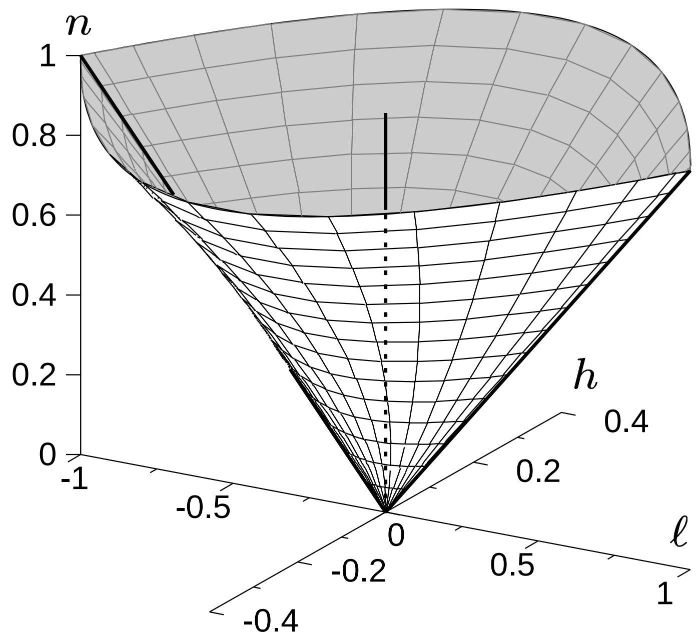
Reduced phase space can be embedded in the ambient space $\mathbb{R}^3$ with coordinates (R,S,T) using their sygyzy. The space $P_{n,0}$ is singular (a "turnips"), other spaces for $n>0$ and $\ell<|n|$ are diffeomorphic to $\mathbb{S}^2$. Equations of motion on these spaces are derived using the Poisson algebra which is generated by (R,S,T) and is "reminiscent" of so(3).

All we need to understand are intersections $H_{n,\ell^2}(R,S)\cap P_{n,\ell}$ and due to symmetry we can work in the $T=0$ plane

These intersections can be of three kinds: a regular point, a loop, and a singular loop for $\ell=0$. The later exists if the R term is small. They lift to a relative equilibrium, which is an $S^1\times S^1$ or in the limiting case $|\ell|=n$ and $\ell=0$ just an S^1 orbit, a regular $\mathbb{T}^3$, or a singular 3D variety "pinched-curled" torus, respectively.

The range of the $\mathcal{EM}$ map of the 1:1:2 resonant swing–spring



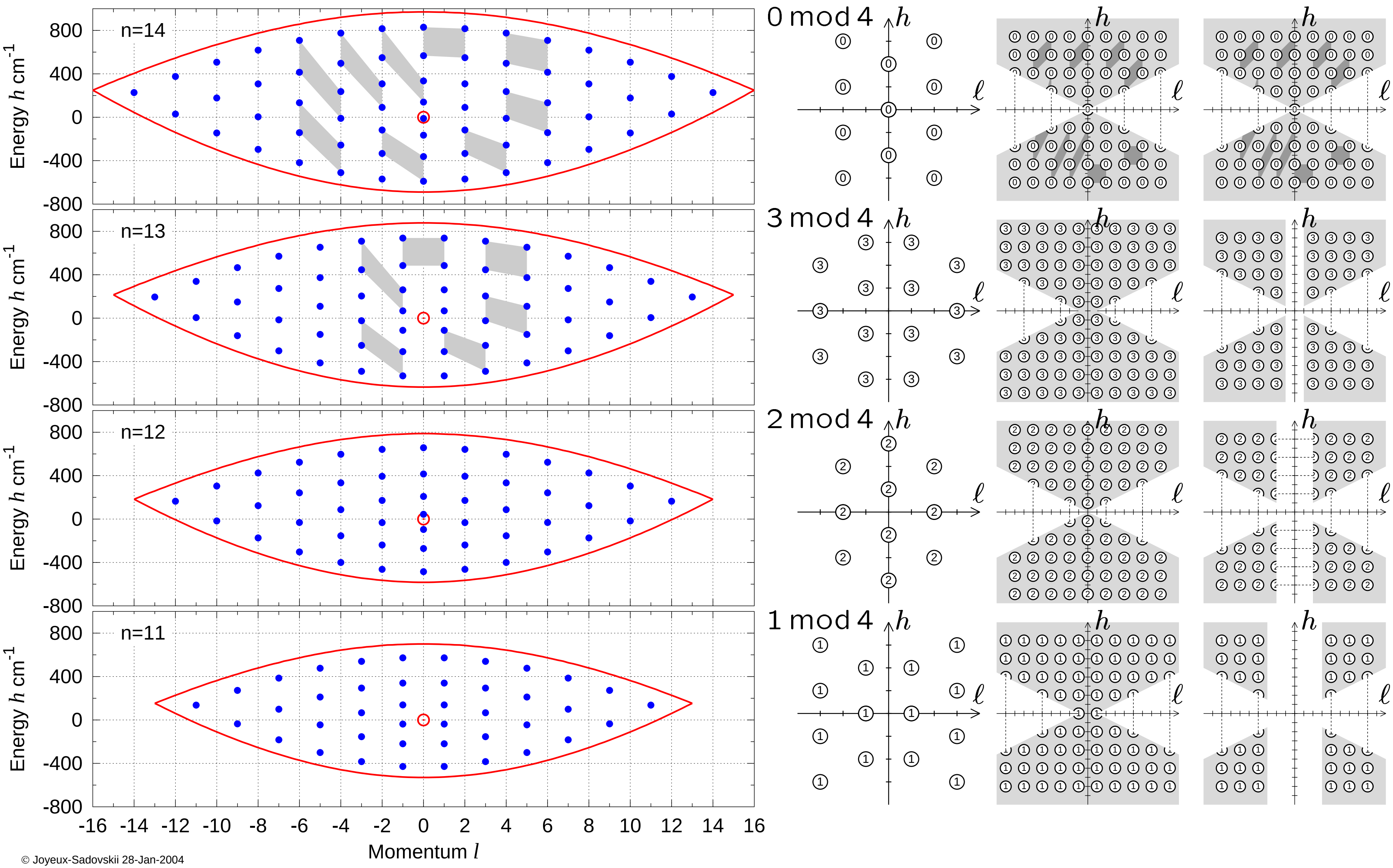


Note the singular thread $h = \ell = 0$ in the domain of regular $\mathcal{EM}$ values, which represent the pinched-curled 3-tori. We compute monodromy along the contour which goes around this thread. Two other singular threads on the surface represent S^1 orbits with $|\ell| = n$.

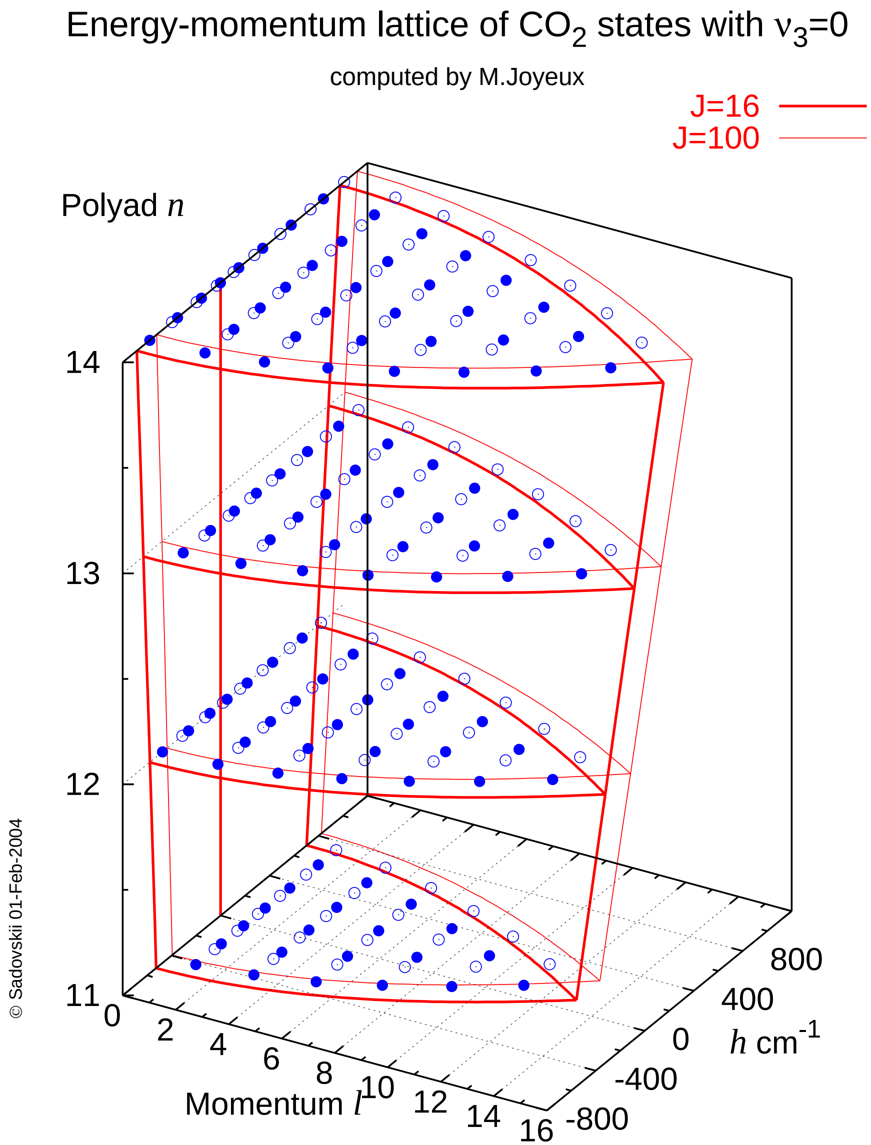
Since the R term in CO_2 is very small we can expect that at sufficiently large n the picture will be only slightly deformed in the case of the molecule. It turns out that it has this image already for $n > 2$, i.e., for the quantum ground state.

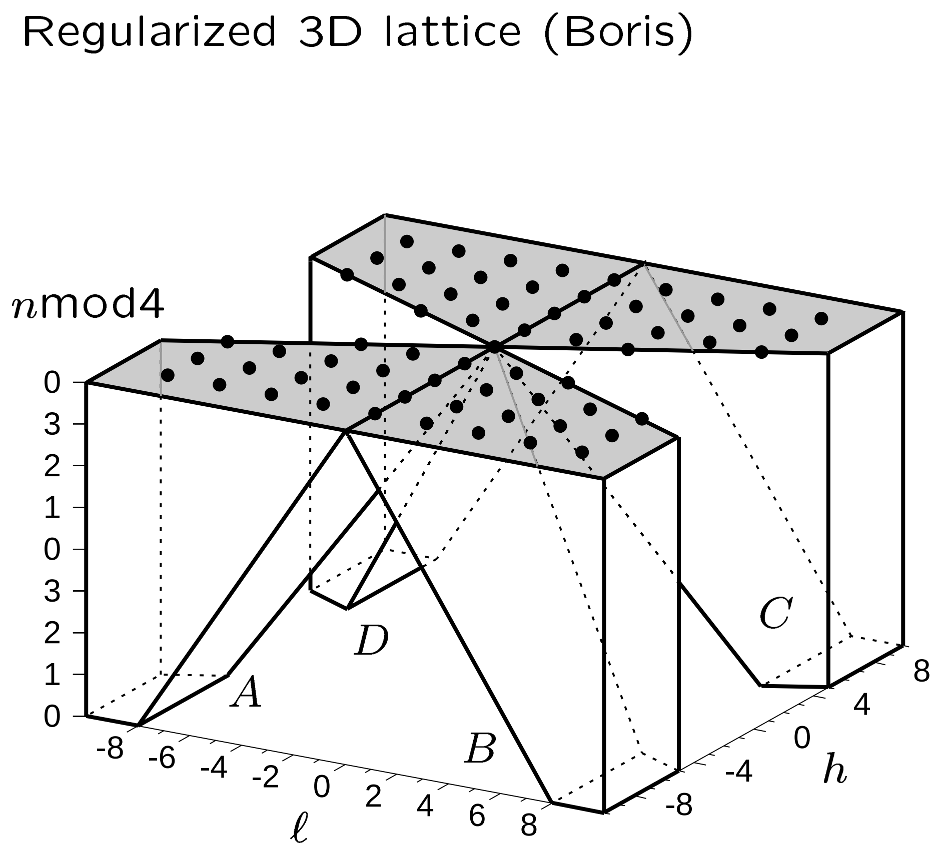
$\mathcal{EM}$ lattice of the CO_2 molecule and its reconstruction in 2D

(data by Marc Joyeux — ideas and cardboard models by Boris Zhilinskií)



3D quantum $\mathcal{EM}$ lattice





The 3×3 monodromy matrix $M \in \mathsf{SL}(3, \mathbb{Z})$

Computing the 3×3 monodromy matrix becomes *un jeux d'enfant*: it is a product of matrices each representing crossing a particular cut, for example if we start with a unit cell in part A and go counterclockwise

$$A \to B \to C \to D \to A$$

then

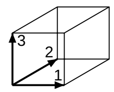
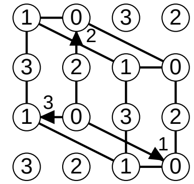
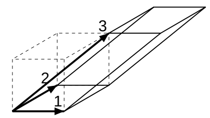
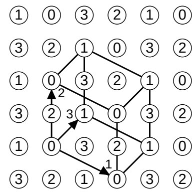
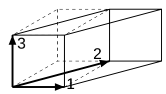
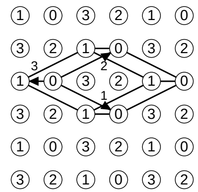
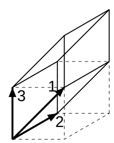
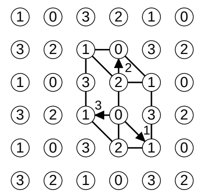
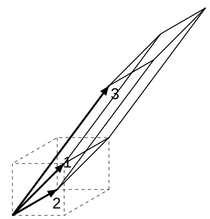
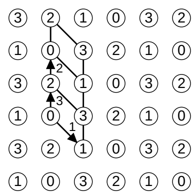
$$M = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 2 & 1 & -1 \\ 0 & 0 & 1 \end{pmatrix}.$$

We should pay attention to the sequence in which the cuts are crossed. Furthermore, for each particular cell the matrix M is, of course, different:

$$M' = A^{-1} M A$$

We should therefore analyze the *classes* of $\mathsf{SL}(3, \mathbb{Z})$.

Elementary cells in the unit cell basis of the regularized 3D $\mathcal{EM}$ lattice (a) and in the A quadrant of the initial 3D $\mathcal{EM}$ lattice (b)

cell	A	shape^a	shape^b	$A^{-1}\,M\,A$
α	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$			$\begin{pmatrix}1&0&0\\2&1&-1\\0&0&1\end{pmatrix}$
β	$\begin{pmatrix}1&0&1\\0&1&1\\0&0&1\end{pmatrix}$			$\begin{pmatrix}1&0&0\\2&1&1\\0&0&1\end{pmatrix}$
γ	$\begin{pmatrix}1&1&0\\0&1&0\\0&0&1\end{pmatrix}$			$\begin{pmatrix}-1&-2&1\\2&3&-1\\0&0&1\end{pmatrix}$
δ	$\begin{pmatrix}1&0&0\\0&1&0\\1&0&1\end{pmatrix}$			$\begin{pmatrix}1&0&0\\1&1&-1\\0&0&1\end{pmatrix}$
κ	$\begin{pmatrix}1&0&1\\0&1&1\\1&0&2\end{pmatrix}$			$\begin{pmatrix}1&0&0\\1&1&0\\0&0&1\end{pmatrix}$

General discussion

- We hope that our method will be of some help to chemists—but then it is about time they start learning, as it seems the best way to look at many things.
- Monodromy is the simplest kind of singularity which leads to the nontrivial consequences both in classical and quantum dynamics. A more general approach calls for analysis of other singularities.
- Normalization permits to apply this analysis to KAM systems.
- Monodromy is not uncommon. We now know many important systems with monodromy, especially of the simplest 2D type and variations on the theme.
- Dynamical study of quantum monodromy and implications in other branches of physics remain essentially unexplored.
- Relation to other Boris' hot topics: diabolic points, fractional monodromy, density of states diagrams

Results on quantum swing–spring and concluding remarks

- The 1:1:2 resonant swing–spring is the first understood case of essentially three-dimensional though still “simple” monodromy.
- The CO_2 molecule is a perfect quantum realization of this system. Since CO_2 is very well studied and is well accessible experimentally, we can think seriously of experimental studies of monodromy and related quantum dynamics.
- The elementary cell method of Zhilinskií combined with his lattice regularization (reconstruction) ideas seems to be the most adequate way to analyze quantum monodromy in two-, three- and probably higher dimensions.
- Much of the mathematical theory of 3D lattice defects, classes of $SL(2,\mathbb{Z})$ and correspondence between defects and singularities of Hamiltonian systems remains to be developed.