Symmetry and Perturbation Theory 2001
special session
dedicated to the memory of *Louis Michel*

Normal forms, geometry, and dynamics of atomic and molecular systems with symmetry

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Summary:
We show how general ideas of Michel, Zhilinskií, Zak, and others on the application of topology, group theory, and commutative algebra in the analysis of symmetric dynamical systems can be concretized for Hamiltonian dynamical systems with symmetries. Particular examples include perturbed Kepler systems (such as hydrogen atom in external fields) and molecular rotation-vibration systems. We consider reduction of continuous dynamical symmetries using normal forms and study singular reduction, geometry, and Poisson structure of reduced systems using polynomial invariants. Particular attention is paid to further analysis of residual continuous and discrete symmetries of the reduced system and to characterization of relative equilibria.

Outline:

- Introductory example:
  Hénon-Heiles oscillator
- Reduction of n-oscillator systems:
  dynamical symmetry, reduced phase space, integrity basis
- Hydrogen atom-in-fields systems
  - Classification
  - Reduced phase space (RPS)
  - Extra symmetries
  - Group action, orbifold
  - Integrity basis
  - Applications
- Rotation-vibration systems:
  F_2 mode of tetrahedral molecule A_4
  vibrations of ozone O_3

Publications

http://pca3.univ-littoral.fr/~sadovski

D. A. Sadovskií and B. I. Zhilinskií, *Group theoretical and topological analysis of localized vibration-rotation states*, Phys. Rev. A **47**(4) 2653–71 (1993).

D. A. Sadovskií, N. G. Fulton, J. R. Henderson, J. Tennyson, and B. I. Zhilinskií, *Nonlinear normal modes and local bending vibrations of H_3^+ and D_3^+*, J. Chem. Phys. **99**(2) 906–18 (1993).

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D. A. Sadovskií and B. I. Zhilinskií, *Counting levels within vibrational polyads. Generating function approach*, J. Chem. Phys. **103**(24), 10520–36 (1995).

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R. H. Cushman and D. A. Sadovskií, *Monodromy in perturbed Kepler systems: hydrogen atom in crossed fields*, Europhys. Lett., **47**(1), 1–7 (1999); Physica D **142**, 166-96 (2000).

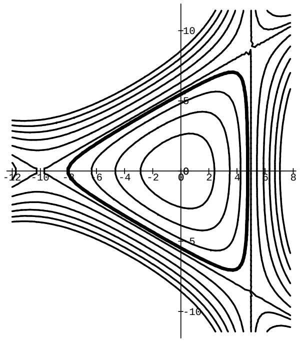
D. A. Sadovskií and B. I. Zhilinskií, *Monodromy, diabolic points, and angular momentum coupling*, Phys. Lett. A **256**(4) 235–44 (1999)

1:1 oscillator with C_3 symmetry:

E modes of H_3^+, A_4 and AB_4

Hénon-Heiles oscillator :

$$H = \frac{1}{2}(q_x^2 + p_x^2) + \frac{1}{2}(q_y^2 + p_y^2) + \epsilon\left(\frac{1}{3}q_x^3 - q_x q_y^2\right)$$



Hénon-Heiles potential calculated for $\epsilon = 0.1$ and $E/E_{\text{saddle}} = 0.2, 0.45, 0.7, \mathbf{0.9}, 1, 1.2, \ldots$

Integrity basis for the Hénon-Heiles problem

reduced phase space RPS $= CP_1 \sim S_2$

angular momentum representation
for two oscillators $z_\alpha = q_\alpha + ip_\alpha$

$$\mathbf{J} = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \frac{1}{4}\begin{pmatrix} z_x\bar{z}_y + z_y\bar{z}_x \\ iz_x\bar{z}_y - iz_y\bar{z}_x \\ z_x\bar{z}_x - z_y\bar{z}_y \end{pmatrix}$$

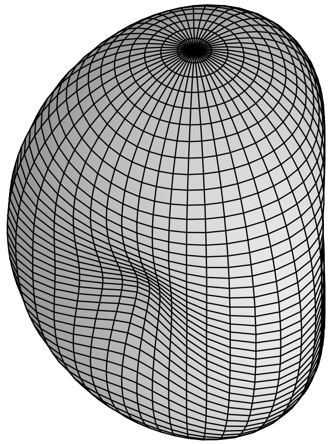
generating function

$$g(E \oplus A_2 \to A_1; \lambda) = \frac{1}{(1-\lambda^2)(1-\lambda^3)}$$

invariants of the $S_1 \wedge D_3 \wedge \mathcal{T}$ action

$$\begin{aligned} n &= 2J = \frac{1}{2}\rho^2 = \frac{1}{2}(\bar{z}_x z_x + \bar{z}_y z_y) \\ \mu &= J_2^2 \\ \xi &= \frac{1}{2}J_3(3J_1^2 - J_3^2) \end{aligned}$$

Relative equilibria of the normal mode E
as stationary points of $H_{\text{n.f.}}$



time reversal : $(x, y, z) \to (x, y, -z)$

scaled polynomial coordinates on RPS $= S_2$

$$\begin{aligned} |\mathbf{J}| \to Jn^{-1} &= \frac{1}{2} \\ \mu \to \mu n^{-2} &= \cos(\theta)^2/4 \\ \xi \to \xi n^{-3} &= -\sin(\theta)^3\cos(3\varphi)/16 \end{aligned}$$

Normal form for the Hénon-Heiles problem

$$\begin{aligned} n &- \epsilon^2 n^2\left(\frac{5}{12} - \frac{7}{3}\mu\right) \\ &- \epsilon^4 n^3\left(\frac{67}{432} + \frac{7}{36}\mu - \frac{56}{9}\xi\right) + \ldots \end{aligned}$$

	n	$\epsilon^2 n^2$	$\epsilon^4 n^3$	$\epsilon^6 n^4$	$\epsilon^8 n^5$
1	1	$-\frac{5}{12}$	$-\frac{67}{432}$	$-\frac{42229}{155520}$	$-\frac{15624833}{18662400}$
μ		$\frac{7}{3}$	$-\frac{7}{36}$	$-\frac{76447}{6480}$	$-\frac{11656729}{2332800}$
ξ			$\frac{56}{9}$	$\frac{2093}{135}$	$\frac{353843}{8100}$
μ^2				$\frac{115171}{1944}$	$\frac{2217943}{233280}$
$\mu\xi$					$\frac{6701639}{4050}$

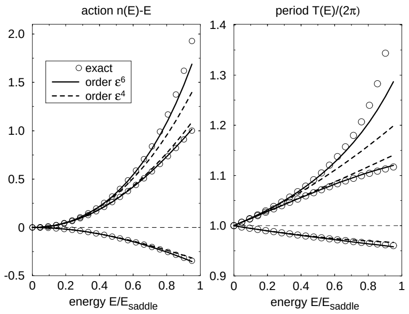
Stationary points of the normal form of the Hénon-Heiles problem

point	$\mathfrak{g}$	ξ	μ	θ	φ
$\Pi_{7,8}$	C_3	0	1/4	0	–
$\Pi_{1,2,3}$	C_2	−1/16	0	$\pi/2$	0, $\pm 2\pi/3$
$\Pi_{4,5,6}$	C_2'	1/16	0	$\pi/2$	π, $\pm\pi/3$

energy at the stationary points

$\mathfrak{g}$	energy in units of n with $\tau = n^2\epsilon$
C_3	$1 + \frac{1}{6}\tau - \frac{11}{54}\tau^2 + \frac{1171}{2430}\tau^3 - \frac{217567}{145800}\tau^4$
C_2	$1 - \frac{5}{12}\tau - \frac{235}{432}\tau^2 - \frac{38585}{31104}\tau^3 - \frac{2663129}{746496}\tau^4$
C_2'	$1 - \frac{5}{12}\tau + \frac{101}{432}\tau^2 + \frac{108467}{155520}\tau^3 + \frac{35328559}{18662400}\tau^4$

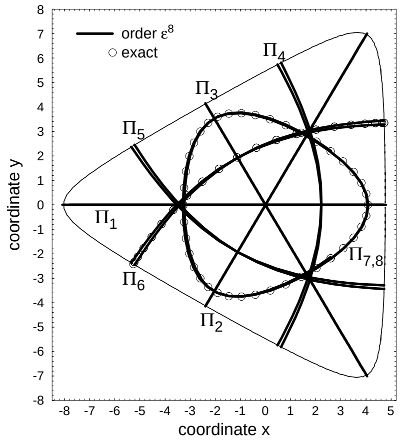
Action $n(E)$ and period $T(E)$ in the Hénon-Heiles problem at three stationary points



energy in units relative to the barrier

solid and dashed lines show ε^6 and ε^4 order normal form approximations

Nonlinear normal modes of the Hénon-Heiles oscillator calculated from the ϵ^8 and normal form



energy at 90% of E_{saddle}

Generalization:

Local description of Hamiltonian dynamical systems near a stable equilibrium

Consider k oscillator with 1:1:$\cdots$:1 resonance,

$$H = H_0 + \ldots = \tfrac{1}{2} z\bar{z} + \ldots, \quad z_\alpha = q_\alpha + ip_\alpha$$

The flow φ of the vector field X_{H_0}

$$\varphi : R_1 \times C_k \to C_k : (t, z) \to \exp(it)\, z.$$

defines *oscillator symmetry* S_1 which acts on the phase space C_k with coordinates $(z, \bar{z})$

The above action of S_1 is *free*, the reduced phase space is a complex projective space CP_{k-1}. Basic invariants of this action are

$$\begin{aligned} n_\alpha &= \tfrac{1}{2} z_\alpha \bar{z}_\alpha, \\ s_\alpha &= \tfrac{1}{2}(z_\beta, \bar{z}_\beta) \cdot (z_\gamma, \bar{z}_\gamma), \\ t_\alpha &= \tfrac{i}{2}(z_\beta, \bar{z}_\beta) \wedge (z_\gamma, \bar{z}_\gamma). \end{aligned}$$

This construction goes back to Weyl.

Molien generating function

for oscillator symmetry S_1

Consider S_1 action with matrix

$$U_t = \text{diag}(\underbrace{e^{it}, \ldots, e^{it}}_{k \text{ times}}, \underbrace{e^{-it}, \ldots, e^{-it}}_{k \text{ times}}),$$

apply Molien theorem

$$g(\lambda) = \frac{1}{2\pi}\int_0^{2\pi} \frac{dt}{\det(1 - \lambda U_t)},$$

take the Cauchy integral for $\theta = \exp(it)$,

$$g(\lambda) = \frac{1}{2\pi i}\oint_{|\theta|=1} \frac{\theta^{k-1} d\theta}{(1-\lambda\theta)^k(\theta-\lambda)^k},$$

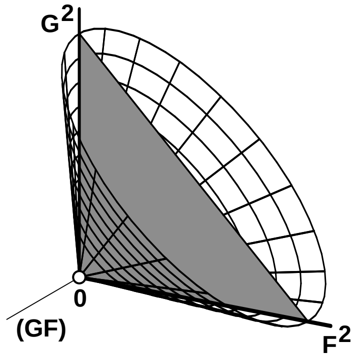
derive Molien generating function

$$g(\lambda) = \frac{1}{(k-1)!}\frac{\partial^{k-1}}{\partial\theta^{k-1}}\frac{\theta^{k-1}}{(1-\lambda\theta)^k}\Big|_{\theta=\lambda},$$

where in particular

$$\begin{aligned} g_{C_1/S_1}(\lambda) &= 1/(1-\lambda^2), \\ g_{C_2/S_1}(\lambda) &= (1+\lambda^2)/(1-\lambda^2)^3, \\ g_{C_3/S_1}(\lambda) &= (1+4\lambda^2+\lambda^4)/(1-\lambda^2)^5, \\ g_{C_k/S_1}(\lambda) &= \sum_{s=0}^{k-1}\binom{k-1}{s}^2 \lambda^{2s}/(1-\lambda^2)^{2k-1}. \end{aligned}$$

Classification of different problems with hydrogen atom in electric $\mathbf{F}$ and magnetic $\mathbf{G}$ fields



Symmetry of problems with hydrogen atom in electric F and magnetic G fields

no fields $O(3) \wedge \mathcal{T}$ $G^2 = F^2 = 0$ point O
Stark effect $C_{\infty v} \wedge \mathcal{T}$ $G^2 = 0,\ F^2 > 0$ ray OF^2
Zeeman effect $C_{\infty h} \wedge \mathcal{T}_s$ $G^2 > 0,\ F^2 = 0$ ray OG^2
parallel fields $C_\infty \wedge \mathcal{T}_s$ $G^2 > 0,\ F^2 > 0, \quad (\mathbf{GF})^2 = G^2F^2$ conical surface
orthogonal fields $G_4 = \{I, \sigma, \mathcal{T}_s, \mathcal{T}_2\}$ $G^2 > 0,\ F^2 > 0, \quad (\mathbf{GF}) = 0$ plane G^2OF^2
generic configuration $\mathcal{T}_s$ $G^2 > 0,\ F^2 > 0, \quad (\mathbf{GF}) \neq 0,\ (\mathbf{GF})^2 < G^2F^2$ interior of the cone

Parallel field problem:

Principal integral of motion n, $n^2 = L^2 + K^2$, strict integral of motion L_z

Reduced phase space $\Sigma = S_2 \otimes S_2$

Integrity basis:

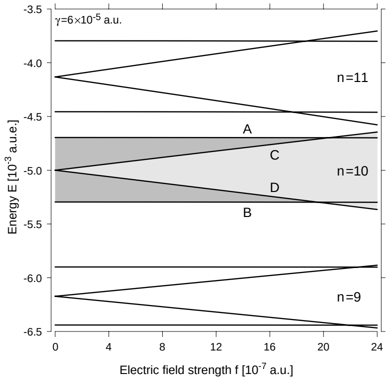
$$\begin{aligned} \mu &= L_z/n, \\ \nu &= K_z/n, \\ \xi &= (L^2 - K^2)/n^2 \end{aligned}$$

n-normalized n.f. expression for energy

$$\begin{aligned} \tilde{E} &= G\mu + 3F\nu - \frac{1}{4}G^2\xi \\ &\quad + \frac{1}{8}(9F^2 + G^2)\mu^2 + \frac{1}{8}(3F^2 - 5G^2)\nu^2 \\ &\quad + \frac{1}{8}(3G^2 - 17F^2)\mu\nu \end{aligned}$$

The n-shell approximation

for the parallel field problem:



neighboring n-shells (quantum multiplets)

Relative equilibria

of the parallel field problem:

Betti numbers for $\Sigma_4 = S_2 \otimes S_2$:

$$b_0 = b_4 = 1, \quad b_1 = b_3 = 0, \quad b_2 = 2$$

Euler characteristics of Σ_4 equals 4

Morse inequalities tell us that
the *simplest* Morse function on Σ_4 has

1 max, 1 min, and 2 $(++--)$ saddles

these stationary points can be placed on the four critical orbits of the action of $C_\infty \wedge \mathcal{T}_s$

orbit	ν	μ	ξ	nonlinear normal mode
A	0	$+1$	$+1$	circle around field axis
B	0	-1	$+1$	circle around field axis
C	$+1$	0	-1	linear up field axis
D	-1	0	-1	linear down field axis

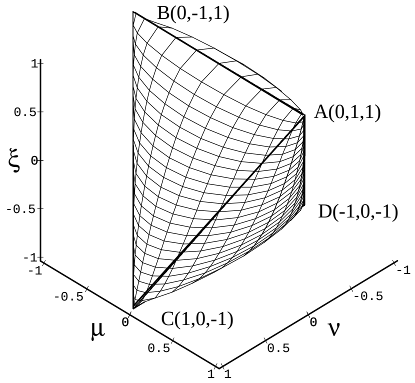
The orbifold $\mathfrak{O}$

of the parallel field problem:

$$|\xi| \le 1, \quad |\mu| \le 1, \quad |\nu| \le 1$$

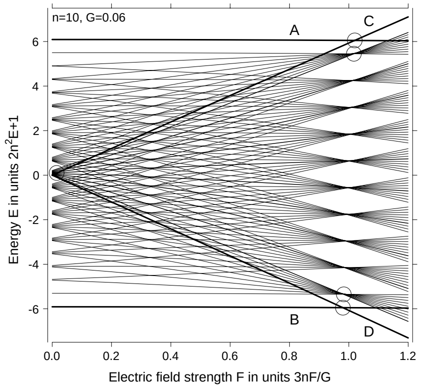
$$\sigma = \mathbf{e}_z \cdot (\mathbf{L} \wedge \mathbf{K})/n^2$$

$$4\sigma^2 = 1 - \xi^2 - 2(1-\xi)\mu^2 - 2(1+\xi)\nu^2 \ge 0$$



The Collapse of the n-shell structure

in the parallel field problem:

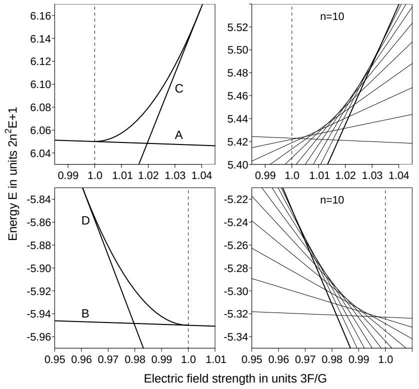


Bifurcations in the collapse region

of the parallel field problem:

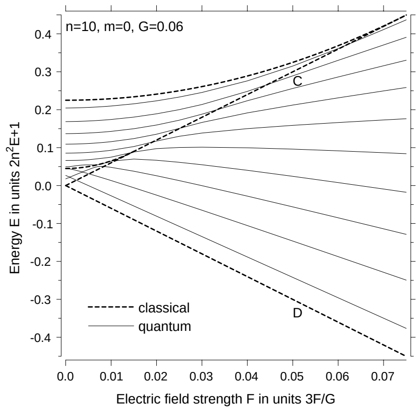
$\approx \delta_C$	$\approx \delta_A$	$\approx \delta_B$	$\approx \delta_D$
$\frac{2G}{3} + \frac{G^2}{72}$	$\frac{G^2}{8} - \frac{G^3}{16}$	$-\frac{G^2}{8} + \frac{G^3}{16}$	$-\frac{2G}{3} + \frac{G^2}{72}$

classical vs quantum

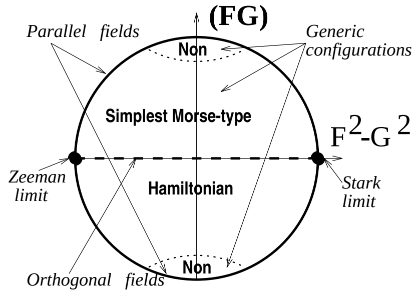


Relative equlibria near the Zeeman limit

of the double reduced parallel field problem with $L_z = 0$



Where to look for bifurcations?



Applications of invariant theory

Q. How to work with the space $S_2 \times S_2$? How to study the Hamiltonian flow and the group actions and to express the reduced Hamiltonian $H_{\text{n.f.}}$ on it?

A. Use polynomial invariants $\mathbf{K}$, $\mathbf{L}$, n, and ζ.

Q. But these invariants are algebraically related, the ring generated by $\mathbf{K}$ and $\mathbf{L}$ (restricted to $\zeta = 0$ and $n =$ const is *not* free!

A. Construct the *integrity basis* for this ring.

Molien generating function for invariants of the combined action of Keplerian (n) and KS (ζ) symmetry

$$g(\lambda)_{C_4/T_2} = \frac{1 + 2\lambda^2 + \lambda^4}{(1-\lambda^2)^6}.$$

indicates that there are *six* main and *three* auxiliary (numerator) integrity basis polynomials which we can choose to be

auxiliary (ϕ) K_p, L_p, $K_p^2 - L_p^2$,
main (θ) K_e, L_b, K_b, L_e, n, ζ .

We use integrity basis

1. to express any invariant polynomial and in particular the reduced Hamiltonian $H_{\text{n.f.}}$ in the form

$$H_{\text{n.f.}} = \mathcal{P}(\theta) + \sum_i \phi_i \mathcal{P}_i(\theta)$$

with $\mathcal{P}(\theta)$ arbitrary polynomials in main invariants K_b, K_e, L_b, L_e, n, and ζ. We subsequently restrict to $\zeta = 0$ and consider n as a constant.

2. to represent the reduced phase space $S_2 \times S_2$ using its maps with coordinates K_b, K_e, L_b, L_e. The *signs* of auxiliary polynomials ϕ_i distinguish different maps.

3. to study the group action on $S_2 \times S_2$ as action on the invariants and on the maps.

Hydrogen atom in crossed fields

F electric field along q_e
G magnetic field along q_b
C effective charge of the nucleus
L angular momentum of the electron

Hamiltonian function in 3D (q_b, q_e, q_p)

$$H = \frac{1}{2}\mathbf{p}^2 - \frac{C}{r} + F q_e + \frac{1}{2} G L_b + \frac{1}{8} G^2 (q_e^2 + q_p^2)$$

Hamilton function in the KS space

$$\begin{aligned} H &= \frac{1}{2}(p^2 + q^2) \\ &\quad + \frac{1}{3} f (q_2 q_1 - q_4 q_3) q^2 + \frac{1}{2} g (q_2 p_3 - q_3 p_2) q^2 \\ &\quad + \frac{1}{8} g^2 (q_2^2 + q_3^2)(q_1^2 + q_4^2) q^2 \\ &= \frac{4}{\omega}, \end{aligned}$$

Regularization of the Kepler problem using Kustaanheimo-Stiefel transformation:

$$M_{\text{KS}} = \begin{pmatrix} q_1 & -q_2 & -q_3 & q_4 \\ q_2 & q_1 & -q_4 & -q_3 \\ q_3 & q_4 & q_1 & q_2 \\ q_4 & -q_3 & q_2 & -q_1 \end{pmatrix},$$

coordinates in the initial 3D space:

$$(q_b, q_e, q_p, 0)^T = M_{\text{KS}}(q_1, q_2, q_3, q_4)^T$$

$$r = q_b^2 + q_e^2 + q_p^2 = q_1^2 + q_2^2 + q_3^2 + q_4^2$$

momenta in the initial 3D space:

$$(p_b, p_e, p_p, \Pi)^T = \frac{1}{2r} M_{\text{KS}}(p_1, p_2, p_3, p_4)^T$$

where we impose an extra restriction

$$\zeta \overset{\text{def}}{=} -2r\Pi = q_1 p_4 - q_4 p_1 + q_3 p_2 - q_2 p_3 = 0$$

Parameterization

4D oscillator frequency $\omega = \dfrac{2\sqrt{-2E}}{C}$

scaled field parameters:

$$g = G\left(\frac{2}{\omega C}\right)^2, \quad f = 3F\left(\frac{2}{\omega C}\right)^3$$

uniform field parameters:

$$F = \frac{1}{3} F_s \frac{S}{C}\left(\frac{\omega C}{2}\right)^4, \quad G = G_s \frac{S}{C}\left(\frac{\omega C}{2}\right)^3$$

formal smallness parameters:

$$S = C\left(\frac{2}{\omega C}\right)^3 \sqrt{G^2 + \left(3F\frac{2}{\omega C}\right)^2} \approx \tau = n\frac{\omega}{2} S$$

Upper limit of the smallness parameter

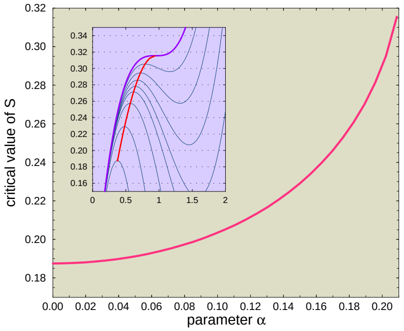
Stark ionization along
$q_1 = q_2 = 0, \quad q_3 = q_4 = \sqrt{\rho/2}$

$$\frac{1}{2}\rho - \frac{1}{6}\rho^2 F_s \left(S\frac{\omega}{2}\right) + 1/32 \rho^3 G_s^2 \left(S\frac{\omega}{2}\right)^2 = \frac{4}{\omega}$$

the critical smallness parameter S_{saddle}

$$\begin{aligned} S &= -\frac{(4F_s - \sqrt{43F_s^2 - 27})}{729(F_s - 1)^2 (F_s + 1)^2} \\ &\quad \times (70F_s^2 - 4F_s\sqrt{43F_s^2 - 27} - 54) \\ &\approx \tfrac{3}{16} - \tfrac{75}{256}(F_s - 1) + \tfrac{9579}{16384}(F_s - 1)^2 \ldots \end{aligned}$$

Critical value of the uniform field amplitude of the orthogonal electric and magnetic fields



$$F_s = \cos\alpha\pi, \quad G_s = \sin\alpha\pi, \quad S_{\text{crit}} \approx \frac{3}{16} + \cdots$$

Keplerian reduction
(first normal form)

The principal integral of motion

$$2n = \frac{1}{2}(p_1^2 + p_2^2 + p_3^2 + p_4^2 + q_1^2 + q_2^2 + q_3^2 + q_4^2)$$

The KS restriction integral

$$\zeta = q_1 p_4 - q_4 p_1 + q_3 p_2 - q_2 p_3 = 0$$

The reduced phase space Σ with $n = \text{const}$ can be described by two vectors: the angular momentum $\mathbf{L}$ and the Runge-Lentz vector $\mathbf{K}$

$$n^2 = \mathbf{K}^2 + \mathbf{L}^2, \quad \mathbf{K} \cdot \mathbf{L} = 0$$

the topology of the RPS is $S_2 \times S_2$

Action $R_4(q)|\text{SO}(2)$ generated by ζ

$$U_{\phi_\zeta} = \begin{pmatrix} \cos\phi_\zeta & 0 & 0 & -\sin\phi_\zeta \\ 0 & \cos\phi_\zeta & \sin\phi_\zeta & 0 \\ 0 & -\sin\phi_\zeta & \cos\phi_\zeta & 0 \\ \sin\phi_\zeta & 0 & 0 & \cos\phi_\zeta \end{pmatrix},$$

Action $R_8(q,p)|S_1 \otimes S_1$ generated by n and ζ

$$U_{\phi_n \phi_\zeta} = \text{diag}\left(\frac{\phi}{\theta}, \phi\theta, \frac{\theta}{\phi}, \frac{1}{\phi\theta}, \frac{\phi}{\theta}, \phi\theta, \frac{\theta}{\phi}, \frac{1}{\phi\theta}\right).$$

with $\exp(i\phi_n) \to \phi, \quad \exp(i\phi_\zeta) \to \theta$ and

$$\begin{aligned} X &= \det\left[1 - \lambda U_{\phi_n \phi_\zeta}\right], \\ &= \left[\frac{(\theta - \lambda\phi)(1 - \lambda\phi\theta)(\phi - \lambda\theta)(\theta\phi - \lambda)}{\theta^2\phi^2}\right]^2. \end{aligned}$$

Molien generating function for invariants

$$\begin{aligned} g(\lambda)_{C_4/T_2} &= \frac{1}{2\pi}\int_0^{2\pi} \frac{1}{2\pi}\int_0^{2\pi} \frac{d\phi_n d\phi_\zeta}{X}, \\ &= \frac{1}{2\pi i}\oint_{|\phi|=1} \frac{1}{2\pi i}\oint_{|\theta|=1} \frac{d\phi\, d\theta}{X\phi\theta}, \\ &= \frac{1 + 2\lambda^2 + \lambda^4}{(1 - \lambda^2)^6}. \end{aligned}$$

Reduced phase space

$$\Sigma = S_2 \times S_2, \quad n = \text{const}, \quad \zeta = 0$$

$$n^2 = \mathbf{K}^2 + \mathbf{L}^2, \quad \mathbf{K}\cdot\mathbf{L} = 0$$

Angular momentum components:

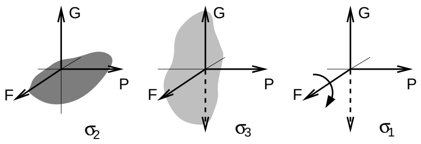
$$\begin{aligned} L_b &= \frac{1}{2}(q_2p_3 - q_3p_2 + q_1p_4 - q_4p_1) \\ L_e &= \frac{1}{2}(q_2p_4 + q_3p_1 - q_1p_3 - q_4p_2) \\ L_p &= \frac{1}{2}(q_1p_2 + q_3p_4 - q_2p_1 - q_4p_3) \end{aligned}$$

Laplace-Runge-Lentz vector components:

$$\begin{aligned} K_b &= \frac{1}{4}(p_2^2 + q_2^2 + q_3^2 + p_3^2 - q_1^2 - p_1^2 - q_4^2 - p_4^2) \\ K_e &= \frac{1}{2}(p_4p_3 - q_2q_1 - p_1p_2 + q_4q_3) \\ K_p &= -\frac{1}{2}(q_3q_1 + p_1p_3 + q_4q_2 + p_4p_2) \end{aligned}$$

Symmetry group G_4

of the orthogonal field problem



$$G_4 = \{I, \sigma, T_s = T\circ\sigma', T_2 = T\circ C_2\}$$

σ	reflection in the ep plane
T	time reversal
C_2	rotation around axis e
σ'	reflection in the eb plane

Molien generating function for invariants

$$g_{C_4/T_2\wedge G_4}(\lambda) = \frac{1 + 4\lambda^4 + 3\lambda^8}{(1-\lambda^2)^3(1-\lambda^4)^3}.$$

Action of G_4

on the generators of the polynomial ring

	I	$C_*\circ\sigma^{(eb)}$	$\sigma^{(ep)}$	$C_*\circ C_2^{(e)}$
n	+	+	+	+
ζ	+	+	−	−
K_e	+	+	+	+
K_b	+	+	−	−
K_p	+	−	+	−
L_e	+	+	−	−
L_b	+	+	+	+
L_p	+	−	−	+

Integrity basis polynomials

main K_e, L_b, K_b^2, L_e^2

n, ζ^2

auxiliary K_bL_e, $K_p^2 - L_p^2$, $K_bL_e(K_p^2 - L_p^2)$,

ζK_b, ζL_e,

$\zeta K_b(K_p^2 - L_p^2)$, $\zeta L_e(K_p^2 - L_p^2)$

Keplerian ("first") normal form

for the orthogonal fields problem

$$\begin{aligned} H_{\text{n.f.}} &= 4/\omega \\ H_{\text{n.f.}} &= 2n\left(1 + \frac{\tau}{2}H_1 + \frac{\tau^2}{4}H_2 + \frac{\tau^3}{32}H_3 + \ldots\right) \end{aligned}$$

$$\begin{aligned} H_1 &= -G_sL_b - F_sK_e \\ H_2 &= -\left(3L_b^2 - 2K_e^2 + 3K_b^2 + 2L_e^2 + 2(L_p^2 - K_p^2) - 3\right)G_s^2/4 \\ &\quad -(7K_eL_b - L_eK_b)F_sG_s/3 \\ &\quad -(51K_e^2 - 9L_e^2 + 17)F_s^2/36 \\ H_3 &= -L_b(6L_e^2 - 6K_e^2 + 9K_b^2 + 5L_b^2 + 6(L_p^2 - K_p^2) - 9)G_s^3 \\ &\quad -K_e(125 - 43L_e^2 + 125K_e^2)F_s^3/9 \\ &\quad +(-45K_eL_e^2 + 45K_e^3 - 65K_eK_b^2 + 117K_e \\ &\quad -147L_b^2K_e - 45K_e(L_p^2 - K_p^2) + 48L_b(L_eK_b))F_sG_s^2/6 \\ &\quad +(3K_b^2L_b + 87L_e^2L_b - 615K_e^2L_b - 3L_b^3 - 232L_b \\ &\quad -3L_b(L_p^2 - K_p^2) + 108K_e(L_eK_b))F_s^2G_s/18 \end{aligned}$$

Relative equilibria

in the crossed fields problem

Stationary points of the first normal form:

position on $S_2 \times S_2$ and action n

	symmetry G_4
K_e	$\mp F_s - \tau F_sG_s^2(4G_s^2 - 3)/12$
	$\mp \tau^2F_sG_s^2(-103G_s^2 - 60G_s^4 + 40G_s^6 + 21)/144$
L_b	$\pm G_s - \tau G_sF_s^2(4G_s^2 - 3)/12$
	$\mp \tau^2G_sF_s^2(80G_s^6 - 104G_s^4 - 230G_s^2 + 51)/288$
$\frac{1}{2}n\omega$	$1 \mp S/2 + S^2(3G_s^4 - 20G_s^2 + 35)/36$

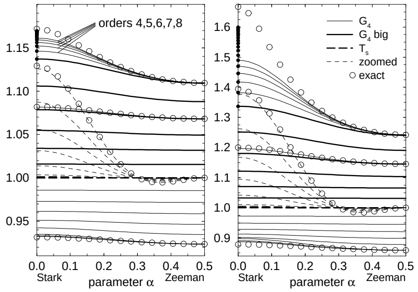
	symmetry T_s
K_e	$-\tau F_sG_s^2(4G_s^2 + 1)/12$
L_b	$-\tau G_sF_s^2(4G_s^2 + 1)/12$
K_b	$\pm G_s$
	$\mp \tau^2G_sF_s^2(80G_s^6 + 72G_s^4 - 146G_s^2 + 13)/288$
L_e	$\mp F_s$
	$\mp \tau^2F_sG_s^2(6 - 77G_s^2 + 28G_s^4 + 40G_s^6)/144$
$\frac{1}{2}n\omega$	$1 - S^2F_s^2(3G_s^2 - 2)/36$

period of orbits: $T = \pi(\omega/2)d(nS)/dS$

Action and period

of the nonlinear normal modes

of the Rydberg electron in the crossed fields



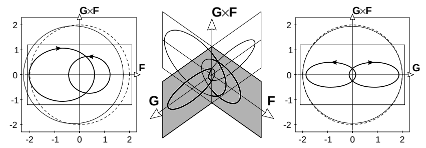
normal form prediction of order ϵ^3

for $S = 0.03, 0.06, 0.09, 0.12, 0.15, 0.18$

3D image of the nonlinear normal modes

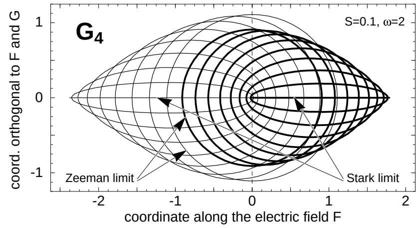
of the Rydberg electron in crossed fields

$S = 0.2$ and $F_s = \cos(\pi/3)$ ($\alpha = 1/3$)



nonlinear normal modes of symmetry G_4

$S = 0.1$ and $F_s = \cos(\alpha\pi)$ with $\alpha = 0\ldots1/2$

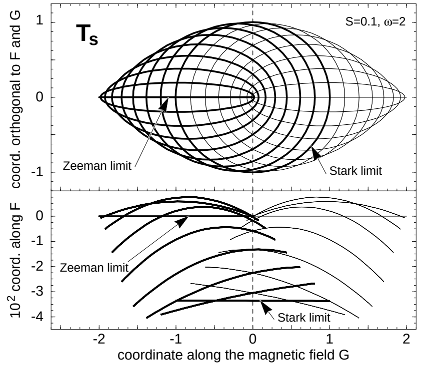


normal form prediction of order ϵ^3

nonlinear normal modes of symmetry T_s

of the Rydberg electron in crossed fields

$S = 0.1$ and $F_s = \cos(\alpha\pi)$ with $\alpha = 0\ldots1/2$



normal form prediction of order ϵ^3

Dynamical S_1 symmetry
of the first n. f. of the crossed fields system

Approximate integral of motion

$$T_1 = G_s L_b + F_s K_e = -\frac{1}{2} H_1 = c$$

Molien function for $C_4/S_1 \times S_1 \times S_1$

$$g(\lambda) = \frac{1+\lambda^4}{(1-\lambda^2)^4(1-\lambda^4)}$$

so(4) generators of the polynomial ring

$$\mathbf{T} = \begin{pmatrix} G_s L_b + F_s K_e \\ G_s L_e - F_s K_b \\ L_p \end{pmatrix}, \quad \mathbf{V} = \begin{pmatrix} F_s L_e + G_s K_b \\ G_s K_e - F_s L_b \\ K_p \end{pmatrix}$$

Integrity basis polynomials

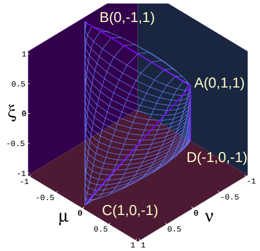
main $n,\ \zeta,\ T_1 = c,\ \pi_1 = V_1,$
$\pi_2 = T_2^2 + T_3^2 - V_2^2 - V_3^2$

auxiliary $\pi_3 = 2(T_2 V_3 - T_3 V_2)$

Relation between invariants

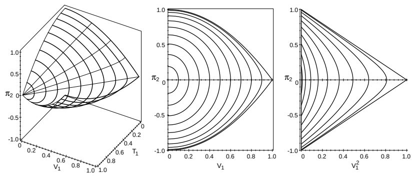
$$\pi_2^2 + \pi_3^2 = [(n-c)^2 - \pi_1^2][(n+c)^2 - \pi_1^2] \geq 0$$

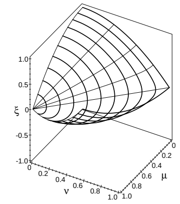
Orbit space
of the S_1 action on $S_2 \otimes S_2$



$$\begin{aligned} \pi_3 &\geq 0 \\ \xi &= \mathbf{T}^2 - \mathbf{V}^2 \\ \mu &= T_1 \\ \nu &= V_1 \\ |\xi| &\leq 1, \\ |\mu| &\leq 1, \\ |\nu| &\leq 1 \\ n &\to 1 \end{aligned}$$

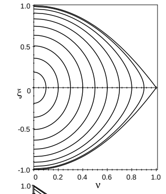
$T_1 = c$ sections of the orbit space are images of the second reduced phase spaces $P_{n,c}$



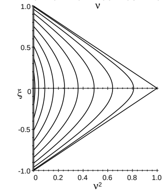


Orbifold $(S_2 \otimes S_2)/S_1$ represented in the co-ordinates

$$\begin{aligned} \pi_4 &= T_1 = c \ (\text{cf } \mu = L_z), \\ \pi_1 &= V_1 \ (\text{cf } \nu = K_z), \\ \pi_2 &= \mathbf{T}^2 - \mathbf{V}^2 - (T_1^2 - V_1^2) \end{aligned}$$



The image of second reduced phase spaces with $0 \leq \mu \leq 1$ and $\sigma = (\mathbf{T} \wedge \mathbf{V}).\mathbf{e}_1 = 0$



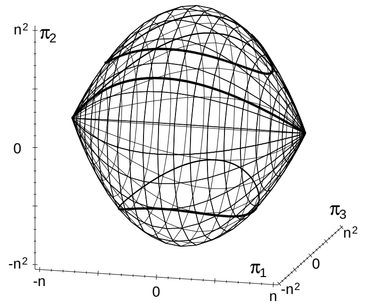
Second reduced phase spaces with reduced $Z_2 \times Z_2$ symmetry

Second reduced phase space $P_{n,c}$

is defined in the ambient space R_3 by

$$\pi_2^2 + \pi_3^2 = [(n-c)^2 - \pi_1^2][(n+c)^2 - \pi_1^2]$$

for c=0 this is *not* a smooth sphere S_2 but a *singular* space with two conical points at $V_1 = \pm n$



Second reduced Hamiltonian
of the crossed fields system

Molien function for invariants of the $Z_2 \times Z_2 = G_4$ action

$$g(\lambda) = \frac{1+\lambda^4}{(1-\lambda^2)^2(1-\lambda^4)^3}$$

$Z_2 \times Z_2$-symmetrized integrity basis

main: $n, \quad T_1 = c, \quad \zeta^2, \quad V_1^2, \quad \pi_2$

auxiliary: ζV_1

<u>Conclusion</u> : second normal form $H_{\text{s.n.f.}}$ is a function of $V_1^2 = \pi_1^2$ and π_2.
To the lowest order this function is

$$H_{\text{s.n.f.}} = a\pi_2 - b\pi_1^2 = \text{const}(n, c, \tau)$$

where in our particular case

$$a = G_s^2, \quad b = \frac{1}{2} - G_s^2 - G_s^4$$

<u>Higher orders of the second normal form</u>

main: $n, \quad \zeta^2 \to 0, \quad \mu = T_1 = \pi_4 = c,$
$\boxed{\nu^2 = V_1^2 = \pi_1^2, \quad \xi = \pi_2}$

auxiliary: $\zeta\nu \to 0$

$$\begin{aligned} H_{\text{s.n.f.}} &= c + \frac{\tau}{4}\mathcal{H}_1 + \frac{\tau^2}{144} c \mathcal{H}_2 + \cdots \\ &= \frac{\tau}{72}(6G_s^4 + 38G_s^2 - 17) + \frac{2}{\tau} - \frac{2S}{\tau^2} \end{aligned}$$

such that

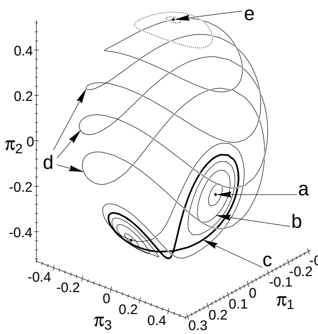
$$\begin{aligned} \mathcal{H}_1 = \ & \\ & (G_s^4 + 2G_s^2 - 1/2)\nu^2 + G_s^2 \pi_2 \\ & + (6G_s^4 - 20G_s^2 + 17)c^2/6 \\ \mathcal{H}_2 = \ & \\ & (-51G_s^8 + 90G_s^6 - 13G_s^4 + 152G_s^2 - 43)\nu^2 \\ & - (6G_s^4 + 8G_s^2 - 68)G_s^2 \pi_2 \\ & - (17G_s^8 - 34G_s^6 - 69G_s^4 + 220G_s^2 - 125)c^2 \\ & + (9G_s^8 - 16G_s^6 + 89G_s^4 - 288G_s^2 + 125) \end{aligned}$$

Dynamics on the second reduced space
of the crossed fields system

Poisson structure on the ambient space

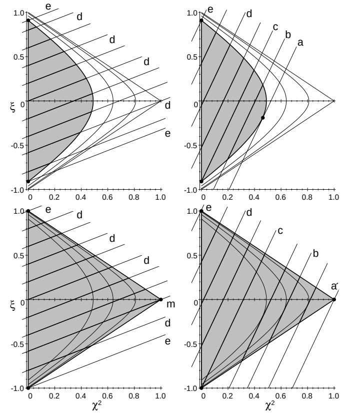
$$\begin{aligned} \{\pi_1, \pi_2\} &= 4\pi_3 \\ \{\pi_3, \pi_1\} &= \pi_2 \\ \{\pi_2, \pi_3\} &= 2\pi_1(n^2 + \pi_2 + c^2 - \pi_1^2) \end{aligned}$$

Constant energy level sets of $H_{\text{s.n.f.}}$ for $c \neq 0$



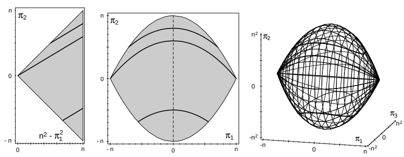
Qualitative analysis of the second reduced Hamiltonian
$H_{\text{s.n.f.}}$
of the crossed fields system

orbit space representation
of the constant level sets

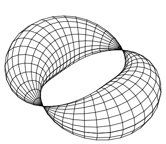


Reconstruction of the dynamically invariant sets in the case with monodromy
for the crossed fields system

from orbit space to $P_{n,c}$ and then to $S_2 \times S_2$



it follows that the singular fiber is a *doubly pinched torus* in $S_2 \times S_2$, a heteroclinic connection of stable and unstable manifolds of two fixed points

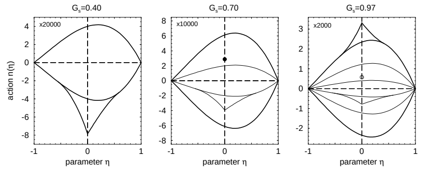


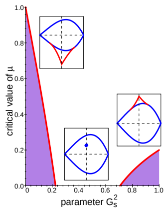
a system with such singular fiber has monodromy

Manifestation of monodromy in the energy momentum map
of the crossed fields system

three different dynamical regimes :

$$a/b < -1, \quad |a/b| < 1, \quad a/b > 1$$



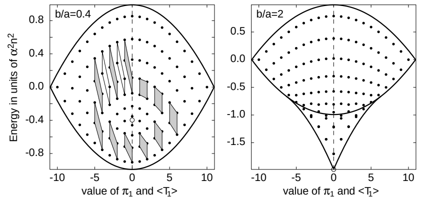


When $|a/b| < 1$, i.e., when

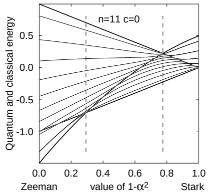
$$G_s^2 \in \left(\frac{\sqrt{6}}{2} - 1, \frac{\sqrt{2}}{2}\right)$$

the isolated critical point corresponds to the pinched torus and the system has monodromy.

Quantum monodromy
quantum levels form a regular *lattice* in the domain of the regular values of the energy momentum map



in the case with monodromy (left) this lattice has a point defect



we can now change the ratio of the two fields and "tune" the crossed fields system with $c = 0$ into the monodromy domain

vibrational polyads of molecules:

- triply degenerate vibration of tetrahedral or octahedral molecules A_4, AB_4, etc
- molecules with approxiamate 1:1:1 resonance, such as ozone O_3

Basic invarinats of the 1:1:1 oscillator symmetry serve as dynamical variables on the reduced phase space CP_2

$$\begin{aligned}
n_f &= \frac{1}{2}(z_1\bar{z}_1 + z_2\bar{z}_2 + z_3\bar{z}_3) \\
x_3 &= \frac{1}{2}(z_1\bar{z}_1 - z_2\bar{z}_2), \quad n_3 = \frac{1}{2}(z_3\bar{z}_3) \\
s_1 &= \frac{1}{2}(z_2\bar{z}_3 + z_3\bar{z}_2), \quad t_1 = \frac{1}{2}(z_2\bar{z}_3 - z_3\bar{z}_2)i \\
s_2 &= \frac{1}{2}(z_1\bar{z}_3 + z_3\bar{z}_1), \quad t_2 = \frac{1}{2}(z_3\bar{z}_1 - z_1\bar{z}_3)i \\
s_3 &= \frac{1}{2}(z_1\bar{z}_2 + z_2\bar{z}_1), \quad t_3 = \frac{1}{2}(z_1\bar{z}_2 - z_2\bar{z}_1)i
\end{aligned}$$

integrity basis for 1:1:1 systems

Generating function for invariants

$$g_{C_3/S_1}(\lambda) = (1 + 4\lambda^2 + \lambda^4)/(1 - \lambda^2)^5$$

suggests the choice of integrity basis

$$\underbrace{\mathcal{R}(n, x_3, s_1, s_2, s_3)}_{\text{main}} \times \underbrace{\{1, n_3, n_3^2, t_1, t_2, t_3\}}_{\text{auxiliary}}$$

Relation between the generators (sygyzies):

$$\begin{aligned}
t_1^2 + s_1^2 - 4n_3n_2 = 0, &\quad t_1t_2 - s_1s_2 + 2s_3n_3 = 0, \\
&\quad s_2t_3 + s_3t_2 + 2n_1t_1 = 0, \\
t_2^2 + s_2^2 - 4n_3n_1 = 0, &\quad t_1t_3 - s_1s_3 + 2s_2n_2 = 0, \\
&\quad s_1t_3 + s_3t_1 + 2n_2t_2 = 0, \\
t_3^2 + s_3^2 - 4n_1n_2 = 0, &\quad t_2t_3 - s_2s_3 + 2s_1n_1 = 0, \\
&\quad s_1t_2 + s_2t_1 + 2n_3t_3 = 0,
\end{aligned}$$

with

$$n_1 = \tfrac{1}{2}(n - n_3 + x_3), \quad n_2 = \tfrac{1}{2}(n - n_3 - x_3).$$

Poisson algebra
of dynamical invariants of the 1:1:1 system

	s_1	s_2	s_3	n_3	t_1	t_2	t_3
x_3	$-t_1$	$-t_2$	$2t_3$	0	s_1	s_2	$-2s_3$
s_1		$-t_3$	t_2	t_1	$2x_1$	$-s_3$	s_2
s_2			$-t_1$	$-t_2$	s_3	$2x_2$	$-s_1$
s_3				0	$-s_2$	s_1	$2x_3$
n_3					s_1	$-s_2$	0
t_1						t_3	$-t_2$
t_2							t_1

symmetrized integrity basis
F_2-mode system of tetrahedral molecules

Generating function for $S_1 \times T_d$ invariants

$$\frac{1 + 2\lambda^3 + 3\lambda^4 + 3\lambda^5 + 2\lambda^6 + \lambda^9}{(1 - \lambda^2)^2(1 - \lambda^3)(1 - \lambda^4)}$$

Generating function for $S_1 \times T_d \times \mathcal{T}$ invariants (i.e., with reversal symmetry added)

$$\frac{1 + \lambda^3 + \lambda^4 + \lambda^5 + \lambda^6 + \lambda^9}{(1 - \lambda^2)^2(1 - \lambda^3)(1 - \lambda^4)}.$$

suggests four main integrity basis invariants

$$\begin{bmatrix}110\\110\end{bmatrix}, \quad \begin{bmatrix}200\\020\end{bmatrix}, \quad \begin{bmatrix}111\\111\end{bmatrix}, \quad \begin{pmatrix}400\\022\end{pmatrix},$$

and five nontrivial numerator invariants

$$\begin{pmatrix}300\\120\end{pmatrix}, \begin{pmatrix}301\\121\end{pmatrix}, \begin{pmatrix}410\\032\end{pmatrix}, \begin{pmatrix}411\\033\end{pmatrix}, \begin{pmatrix}702\\144\end{pmatrix} - \begin{pmatrix}612\\054\end{pmatrix}.$$

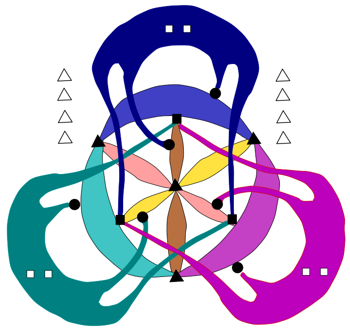
where

$$\begin{bmatrix}abc\\pqr\end{bmatrix} = z_1^a z_2^b z_3^c \bar{z}_1^p \bar{z}_2^q \bar{z}_3^r + \left\{ \begin{matrix}\text{column}\\ \text{permutations}\end{matrix} \right\},$$

and

$$\begin{pmatrix}abc\\pqr\end{pmatrix} = \begin{bmatrix}abc\\pqr\end{bmatrix} + \begin{bmatrix}pqr\\abc\end{bmatrix}.$$

Group action:
orbits of the O (or T_d) group action on CP_2



critical orbits of the $T_d \times \mathcal{T}$ group action on the vibrational reduced phase space CP_2

orbit	$\frac{x_3}{N_f}$	$\frac{s_1}{N_f}$	$\frac{s_2}{N_f}$	$\frac{s_3}{N_f}$	$\frac{n_3}{N_f}$	$\frac{t_1}{N_f}$	$\frac{t_2}{N_f}$	$\frac{t_3}{N_f}$	stabilizer
• $A^{(2)}$	0	0	0	-1	0	0	0	0	C_s^{xy}
	0	0	0	1	0	0	0	0	
	$\frac{1}{2}$	0	-1	0	$\frac{1}{2}$	0	0	0	
	$\frac{1}{2}$	0	1	0	$\frac{1}{2}$	0	0	0	
	$-\frac{1}{2}$	1	0	0	$\frac{1}{2}$	0	0	0	
	$-\frac{1}{2}$	-1	0	0	$\frac{1}{2}$	0	0	0	
▲ $A^{(3)}$	0	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	0	0	0	$C_3^{[111]}$
	0	$\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{2}{3}$	$\frac{1}{3}$	0	0	0	
	0	$-\frac{2}{3}$	$\frac{2}{3}$	$-\frac{2}{3}$	$\frac{1}{3}$	0	0	0	
	0	$-\frac{2}{3}$	$-\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	0	0	0	
△ $B, C^{(3)}$	0	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$C_3^{[111]}$
	0	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	
	0	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	
	0	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	
■ $A^{(4)}$	0	0	0	0	1	0	0	0	S_4^z
	1	0	0	0	0	0	0	0	S_4^x
	-1	0	0	0	0	0	0	0	S_4^y
□ $B, C^{(4)}$	0	0	0	0	0	0	0	1	S_4^z
	$-\frac{1}{2}$	0	0	0	$\frac{1}{2}$	1	0	0	S_4^x
	$\frac{1}{2}$	0	0	0	$\frac{1}{2}$	0	1	0	S_4^y

Dynamics on invariant subspaces $CP_1 \sim S_2$ of CP_2

C_2 invariant CP_1 subspace of CP_2

$$(Y_1, Y_2, Y_3) = \left(\frac{s_3}{2}, \frac{t_3}{2}, \frac{x_3}{2}\right).$$

Poisson algebra restricted to the subspace

$$\{Y_\alpha, Y_\beta\} = \epsilon_{\alpha\beta\gamma} Y_\gamma,$$

with Casimir

$$Y_1^2 + Y_2^2 + Y_3^2 = \left(\frac{n}{2}\right)^2.$$

C_s^{xy} invariant sphere S_2 of CP_2

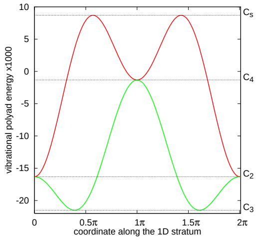
$$(X_1, X_2, X_3) = \left(\frac{t_1 - t_2}{2\sqrt{2}}, \frac{s_1 + s_2}{2\sqrt{2}}, \frac{2s_3 - N_f}{2}\right) = \left(\frac{\tau}{\sqrt{2}}, \frac{\sigma}{\sqrt{2}}, \frac{2\eta - 1}{2}\right) N_f,$$

which form another so(3) algebra,

$$X_1^2 + X_2^2 + X_3^2 = \left(\frac{n}{2}\right)^2, \quad \{X_i, X_j\} = \epsilon_{ijk} X_k.$$

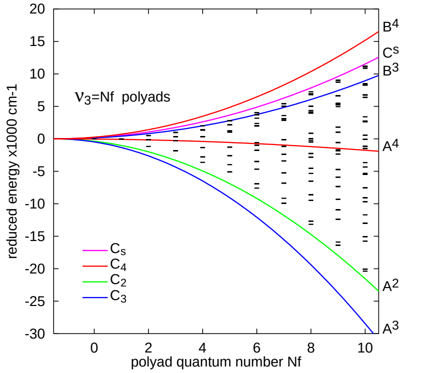
Relative equilibria on non-critical orbits C_s invariant subspace of CP_2

Normal form $H_{\mathrm{n.f.}}$ with $n = 10$ in the model for a tetrahedral molecule P_4 restricted to the C_s invariant sphere in the CP_2 space;



relative equilibria and polyads:

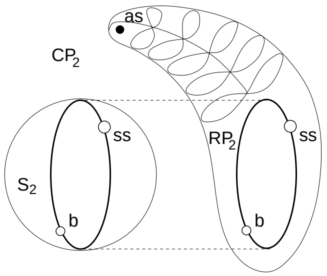
model normal form prediction for the polyads of the $\nu_3^{F_2}$ mode of P_4



critical and noncritical points of the $T_d \times \mathcal{T}$ action on CP_2

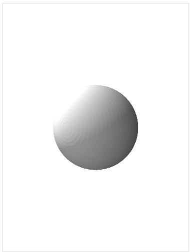
three-mode system of ozone O_3

Stratification of the reduced phase space CP_2 caused by the action of $Z_2 \times Z_2$



second reduction for ozone

stratification of the polyad sphere S_2 under the action of $Z_2 \times Z_2$ and second normal form H_{n,n_s} for the 1:1 stretching polyad of ozone with $n_s = n = 6$



Energy of relative equilibria, polyad structure, and quantum levels of ozone