An Update on the Theory of Rotational Energy Surfaces

I.S.M.S. 2019 : Rotational Structure / Frequencies

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Overview

-- Semiclassical Basics
-- The Asymmetric Top
-- Harter's R.E.S. Theory
-- A Few Elliptic Integrals
-- New Results Showcase
-- Summary & Prospectus

Find Mathematica source code for **HEllipticPFDE** and **DihedralPFDE** at Wolfram Demonstrations Project.

(cf. [!])

(HElliptic|Dihedral)PFDE

Input:
Hamiltonian Surface

Throughput:
Equations of Motion
Period Integrands
dt(E), dt(E)', dt(E)'' . . .
Degree Bounds
Hermite Reduction Matrices

Output:
An O.D.E. for T(E). w/ certificate function G.

(cf. [CreativeTelescoping])

Semiclassical Basics

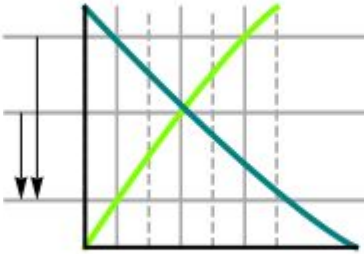
Quantization & Tunnel Splitting:

$$S(E_n) = (n + \delta)h$$

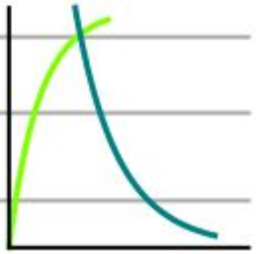
$$n \in \mathbb{N}, \quad \delta = 1/2$$

$$\Delta_n = \left(T(E_n) e^{\frac{1}{2}\tilde{S}(E_n)}\right)^{-1}$$

(cf. [S.C.])

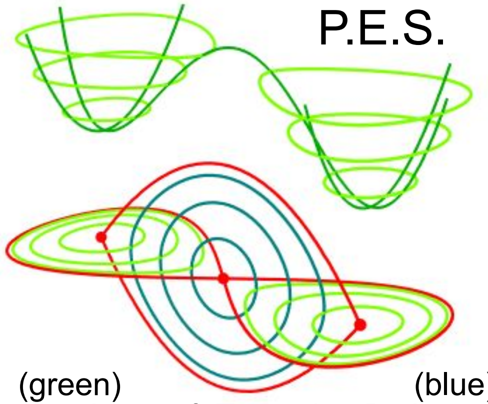


Action, S(E)



Period, T(E)

Energy, E



(green) (blue)
Oscillation Loops & Tunneling Paths,
or, the skeleton of a Riemann torus.

$$\texttt{HEllipticPFDE}\left[p^2 + q^2 - \frac{1}{4}q^4\right] \implies 3T + \partial_E\left(16E(E-1)\partial_E T\right) = 0$$

$$T = \partial_E S = \pi\, {}_2F_1(1/4, 3/4, 1, E), \qquad \tilde{T} = \partial_E \tilde{S} = (\sqrt{2}/2)\pi\, {}_2F_1(1/4, 3/4, 1, 1-E)$$

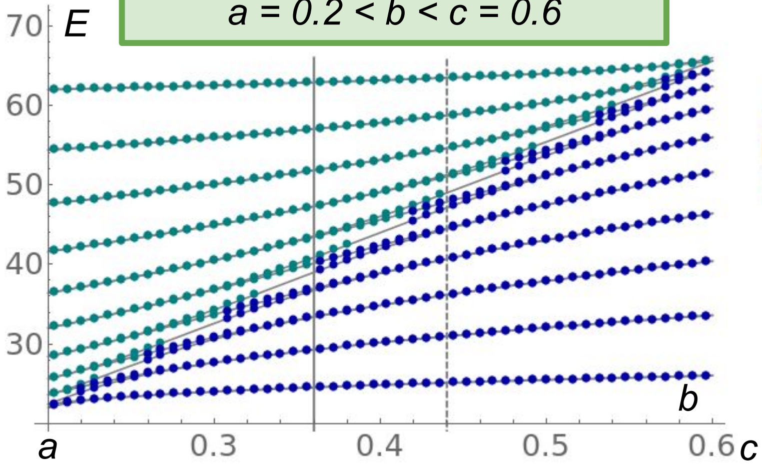
-- Born-Oppenheimer: potential theory works for molecules,
vibrations and rotations occur semi-classically.

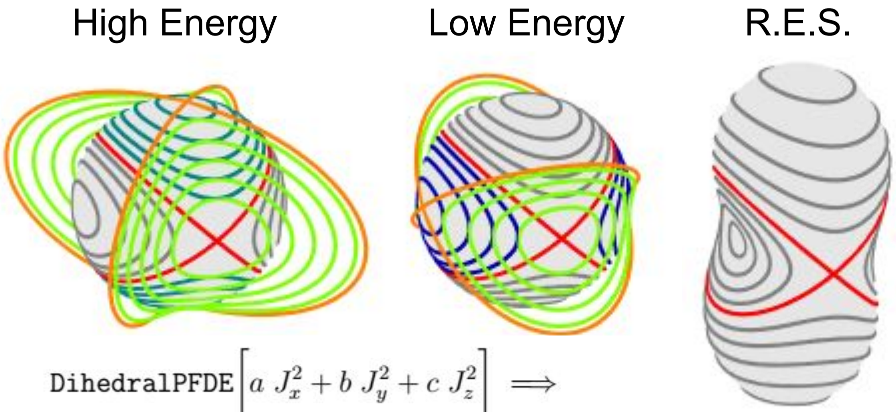
-- Schrödinger Eq. + W.K.B. approx. + topology determines:
quantization, energy levels, tunnel splittings.

Wick Rotation:
p → i p
permutes real &
complex periods.

Integrating the Asymmetric Top

Asymmetric Top E. Levels
a = 0.2 < b < c = 0.6





$$\texttt{DihedralPFDE}\left[a\,J_x^2 + b\,J_y^2 + c\,J_z^2\right] \Longrightarrow$$

$$(a+b+c-3E)T + \partial_E(4(a-E)(b-E)(c-E)\partial_E T) = 0$$

-- Precession period first derivative of action. Actions are solid angles.
-- According to O.D.E.: only two period integrals, similar to quartic example.
-- Semi-classical formulas are the same, up to a few minor amendments.
-- **How can we adapt theory to account for centrifugal distortion?**

Try:
Jz → i Jz
or
Jx → i Jx

W.G. Harter's R.E.S. Theory

-- Starts with Hamiltonian for
rigid body rotation
+ centrifugal distortion.

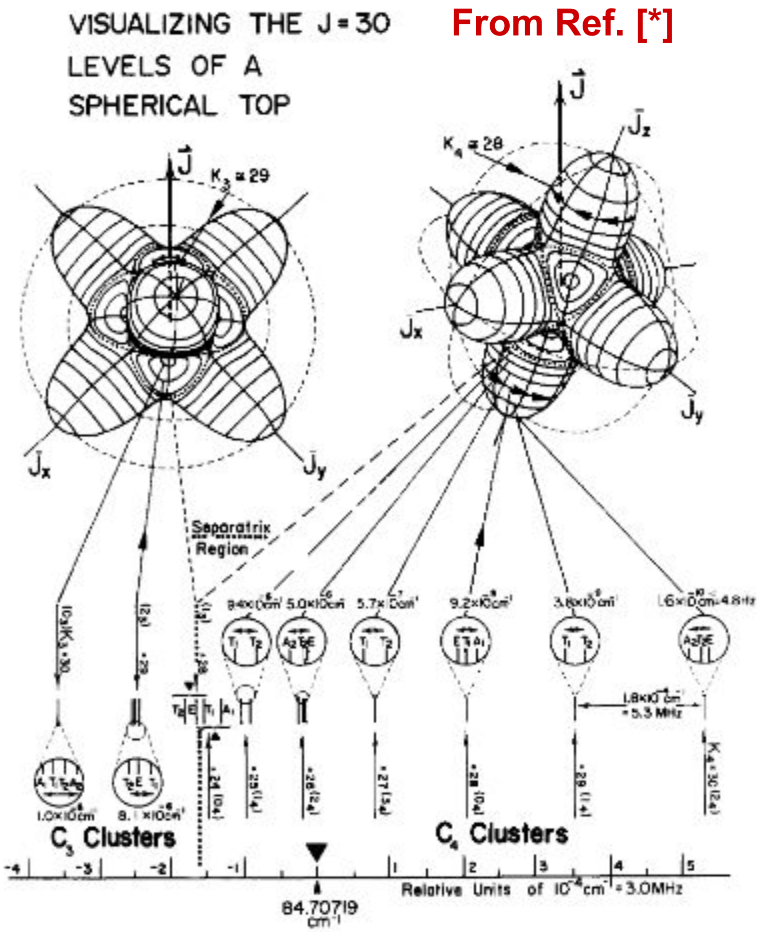
-- "*p dq*" becomes "*Jz dφ*" and
action integrals ***do not***
have turning points.

-- Complex topology allows
more tunneling, implies
a larger splitting matrix.

-- Even a "two integral model"
allows non-trivial spectra.

**-- Period integrals not
entirely characterized.**

**-- Tunneling prescription
ignores homology.**



Curves with Hypergeometric T(E)

See also, S. Ramanujan: “Modular Equations and Approximations to π”.

$$(k-1)T + \partial_E(k^2 E(E-1)\partial_E T) = 0, \qquad k = 2, 3, 4, 6.$$

$$4(k-1)E\,T + \partial_E(k^2 E(E^2-1)\partial_E T) = 0, \qquad k = 3, 4, 6.$$

Analyzing the Goursat Sphere Curves

DihedralPFDE $\left[4\left((J_xJ_y)^2+(J_yJ_z)^2+(J_zJ_x)^2\right)\right] \implies 9(5E-4)\,T+\partial_E(16E(E-1)(3E-4)\partial_E T)=0$ ← **octahedral**

DihedralPFDE $\left[J_z^6-5(J_x^2+J_y^2)J_z^4+5(J_x^2+J_y^2)^2J_z^2-2(J_x^4-10J_x^2J_y^2+5J_y^4)J_xJ_z\right] \implies 5(21E-5)\,T+\partial_E(4E(E-1)(27E+5)\partial_E T)=0$

Energy Levels: $H = 2(J_x^4 + J_y^4 + J_z^4)$, $J = 30$

n_4	$E(QM)$	$E(SC)$	$\Delta(QM)$	$\Delta(SC)$
30	1.879	1.875	3.370×10^{-8}	3.189×10^{-8}
29	1.653	1.649	1.221×10^{-6}	1.220×10^{-6}
28	1.461	1.459	1.955×10^{-5}	1.992×10^{-5}
27	1.303	1.300	1.810×10^{-4}	1.870×10^{-4}
26	1.174	1.172	1.047×10^{-3}	1.103×10^{-3}
25	1.076	1.072	2.989×10^{-3}	4.076×10^{-3}
24	1.001	1.004	6.449×10^{-3}	6.969×10^{-3}
n_3	$E(QM)$	$E(SC)$	$\Delta(QM)$	$\Delta(SC)$
30	0.744	0.749	2.232×10^{-4}	2.156×10^{-4}
29	0.883	0.889	2.580×10^{-3}	2.767×10^{-3}
28	0.985	0.989	8.425×10^{-3}	9.504×10^{-3}

Scale: $2/3 < E(n_3) < 1$, $1 < E(n_4) < 2$

$$S_4(E) = \frac{\pi}{4}\left(E + \frac{9}{32}E^2 + \frac{135}{1024}E^3 + \frac{4941}{65536}E^4 + \frac{201933}{4194304}E^5 + \dots\right)$$

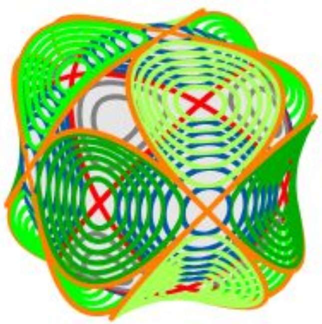
$$\widetilde{S}_4(E) = s_0 + s_1\frac{4}{\pi}S_4(E) + s_2\left(\ln(E)\frac{4}{\pi}S_4(E) - E + \frac{11}{64}E^2 + \dots\right)$$

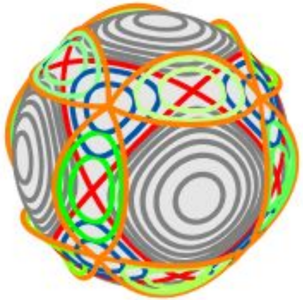
$$S_3(E) = \frac{3\pi}{8}\left(E + \frac{9}{16}E^2 + \frac{81}{128}E^3 + \frac{3969}{4096}E^4 + \frac{57591}{32768}E^5 + \dots\right)$$

$$\widetilde{S}_3(E) = \frac{\pi}{2\sqrt{2}}\left(\left(\frac{1}{3} - E\right) + \frac{9}{32}\left(\frac{1}{3} - E\right)^2 + \frac{459}{1024}\left(\frac{1}{3} - E\right)^3 + \dots\right)$$

$s_0 \approx 1.09861$, $s_1 \approx -0.62774$, $s_2 \approx 0.25000$.

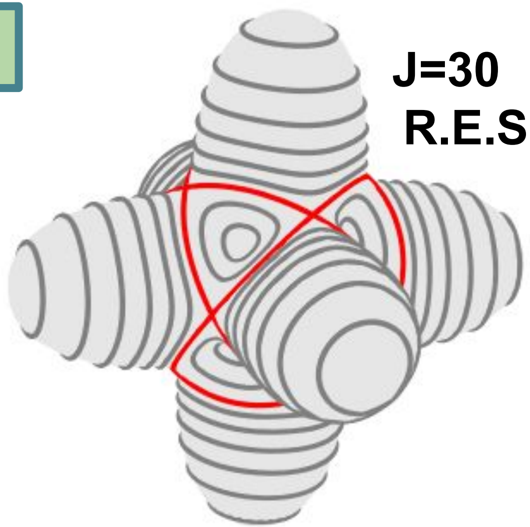
High-E Tunneling





Low-E Tunneling

J=30
R.E.S.



S.C. Algorithm

-DihedralPFDE	0.1s
-Build all S(E)	1.6s
-Root Solve: En -Evaluate: Δn	0.3s
TOTAL TIME	2.0s

Summary and Prospectus

--R.E.S Theory now working with periods from O.D.E.s.
--Some Octahedral and Icosahedral calculations are trivially easy.
--Possibilities of **DihedralPFDE** not yet exhausted, more soon.
--New algorithms fast enough for parameter extraction.
--Tunneling integrals increasingly well understood via geometry.

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[R.E.S.]

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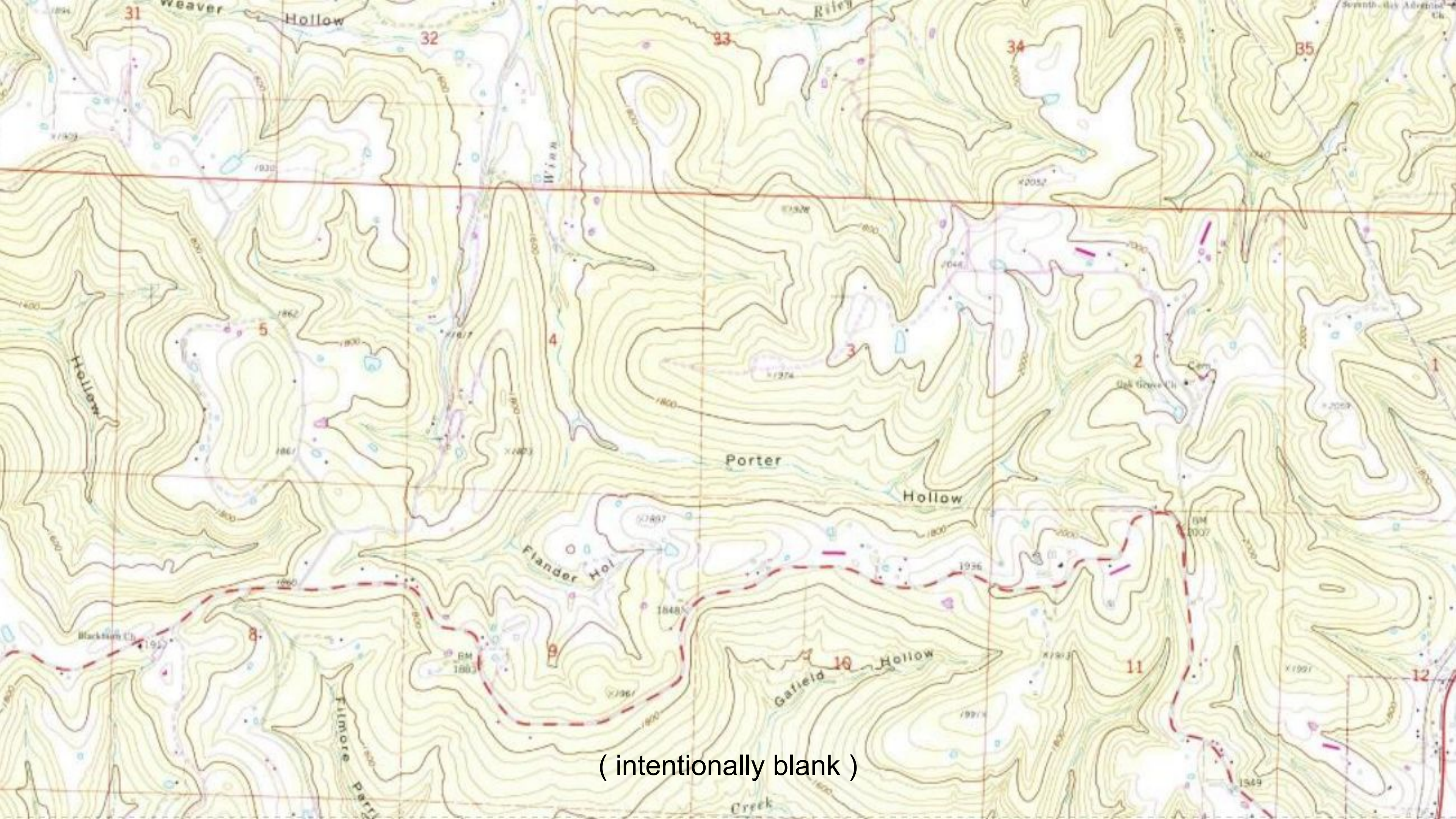

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