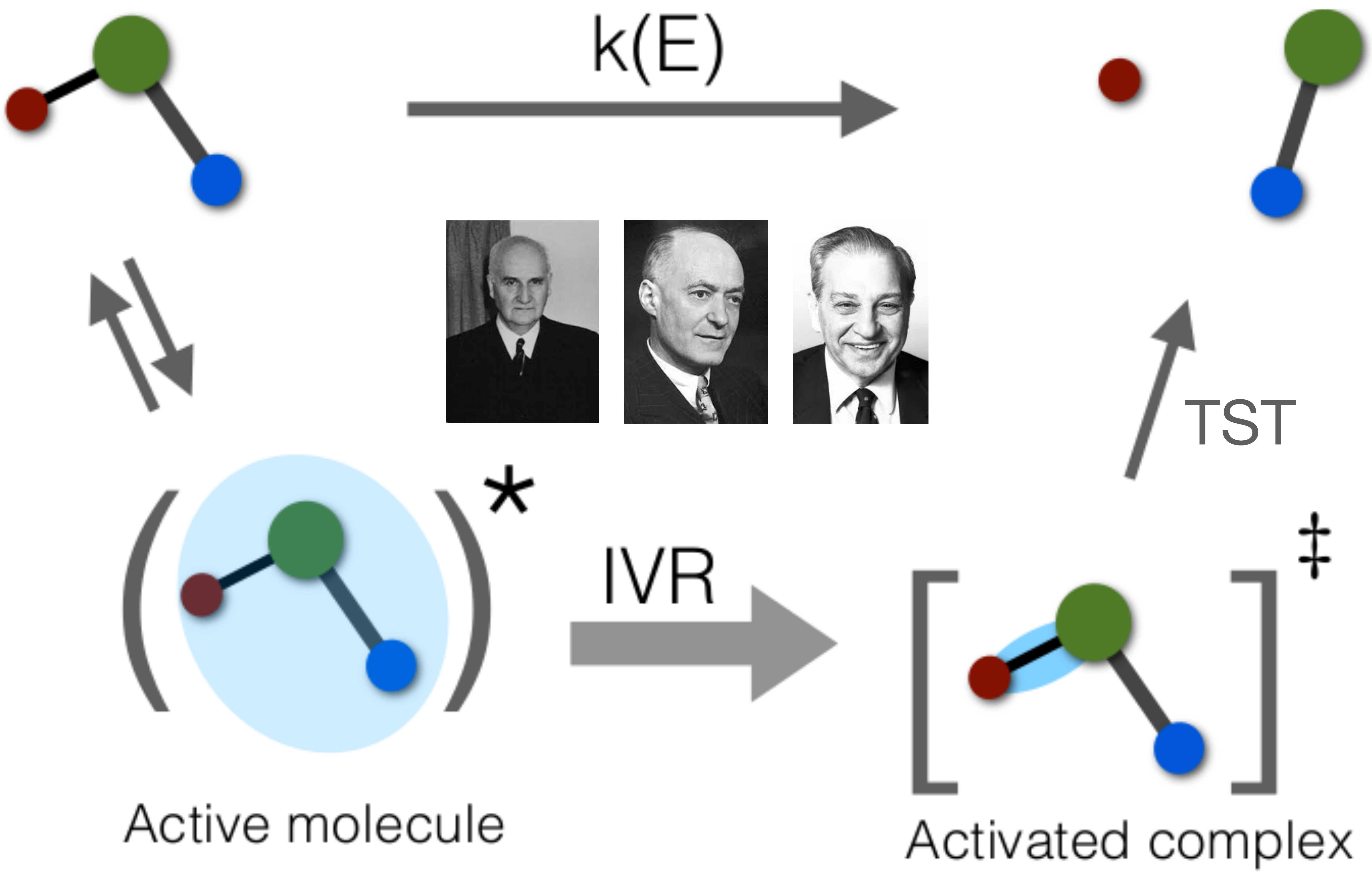
On the dynamical origins of nonstatisticality

To flow or not to flow…

Srihari Keshavamurthy, Chemistry, IIT Kanpur

Unimolecular reactions ~ 1950s

Hinshelwood-Lindemann-Marcus



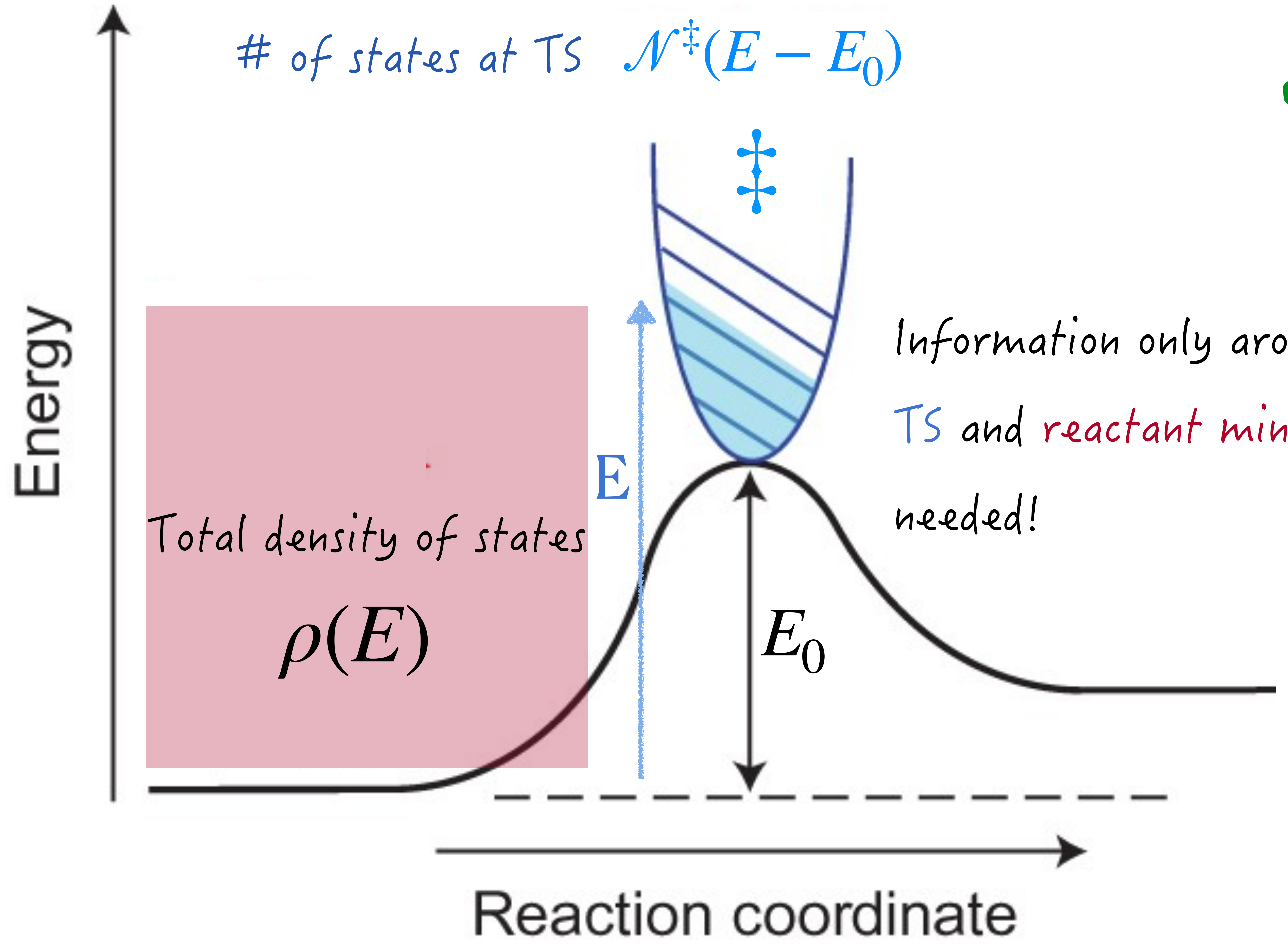
$$\tau^{\ddagger}_{rxn} \gg \tau_{\mathrm{IVR}}$$

RRKM

Dynamics

(FPUT)

$$k(E) \approx \frac{\mathcal{N}^{\ddagger}(E - E_0)}{2\pi\hbar\rho(E)}$$



Information only around TS and reactant minima needed!

If RRKM then:

$$\frac{N(t)}{N(0)} = e^{-k(E)t}$$

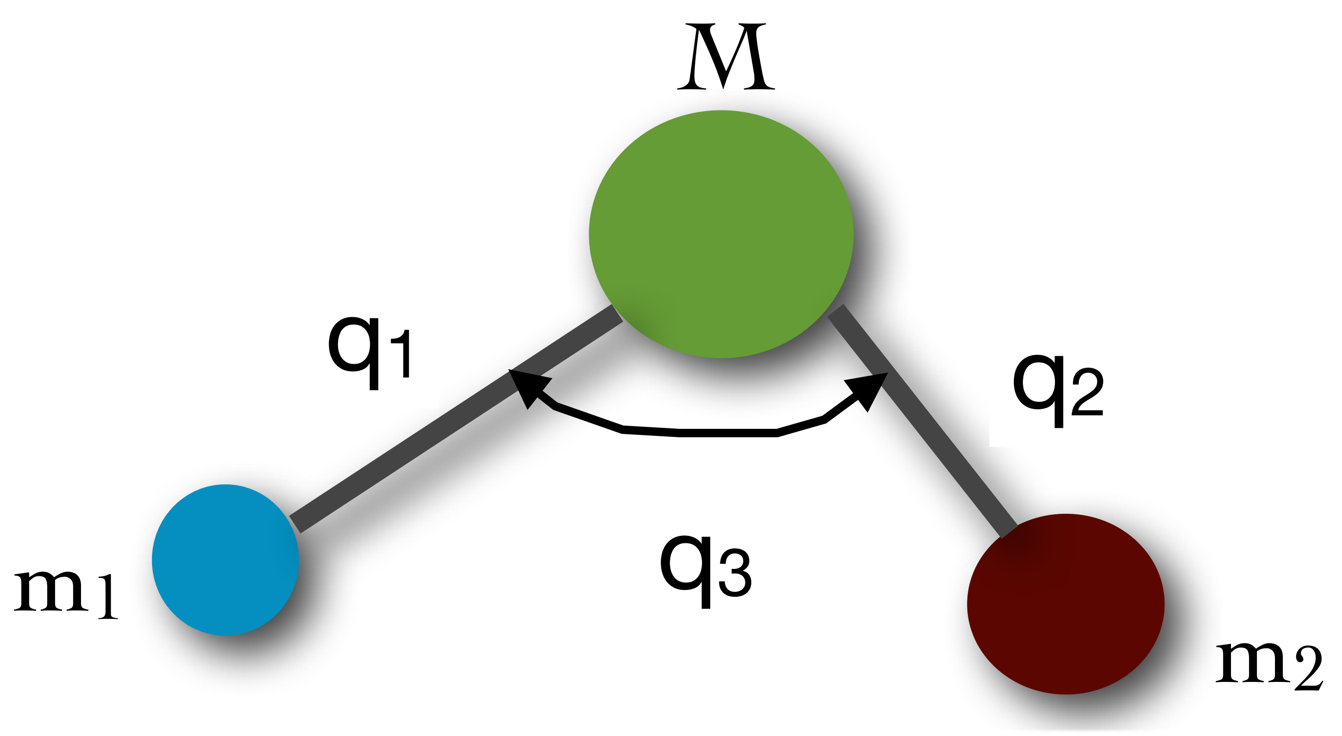
Exponential survival probability

Subtleties…

Ignore !?

Model Hamiltonian

D L Bunker, J. Chem. Phys. (1962)



$$H(\mathbf{p},\mathbf{q}) = \sum_{k=1}^{3}\left[\frac{1}{2}G_{kk}^{(0)}p_k^2 + V_k(q_k)\right] + \sum_{k<l=1}^{3} G_{kl}^{(0)}p_k p_l$$

$$V_k(q_k) = D_k\left[1 - e^{-\alpha_k(q_k - q_k^0)}\right]^2$$

$$V_3(q_3) \sim \omega_3(q_3 - q_3^0)^2$$

Zeroth-order Hamiltonian

Integrable

Coupling

$\epsilon \neq 0$; Non-integrable

Modes 1 and 2 (stretches) anharmonic (nonlinear); <u>dissociation</u> for E > D_{low}

Mode 3 (bending) is harmonic ; <u>cannot dissociate</u>

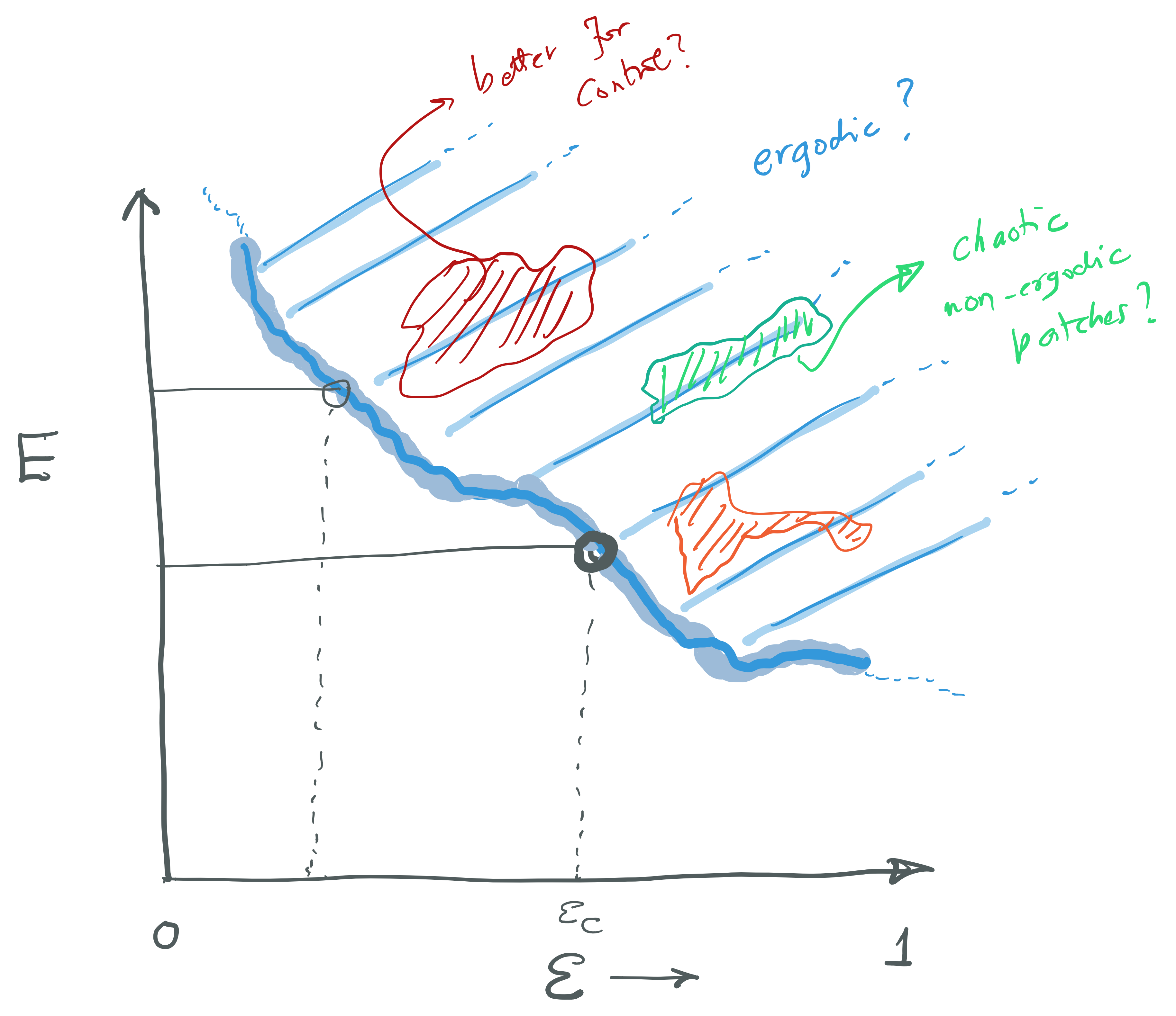
NB: Inspired by Bunker's model Hamiltonian $G_{ij}(\mathbf{q}) \rightarrow G_{ij}^{(0)}$

Question…

(necessary & sufficient)

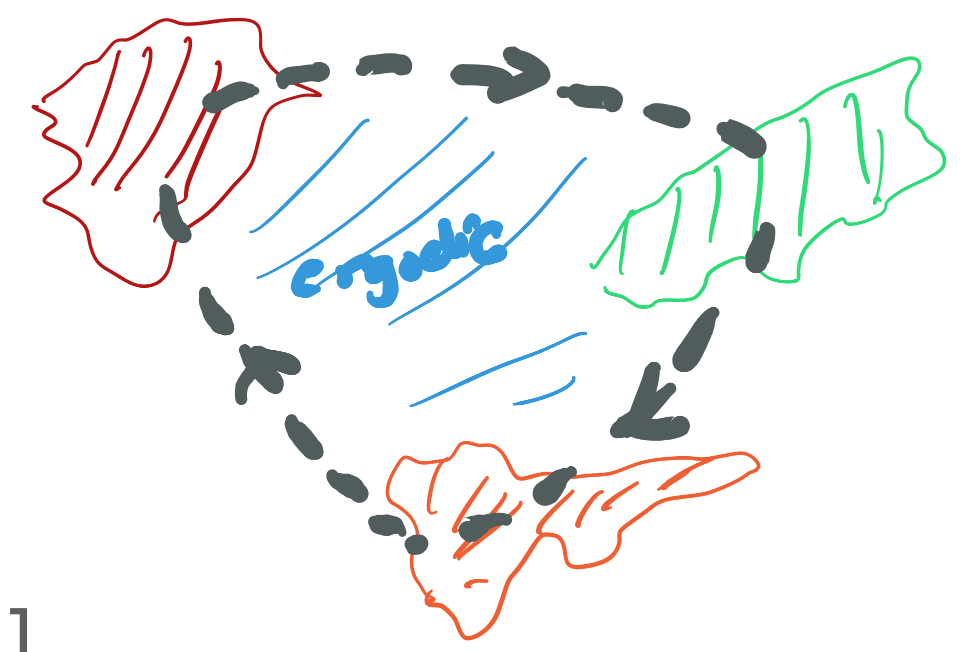
$$H(\mathbf{p},\mathbf{q}) = \sum_{k=1}^{3}\left[\frac{1}{2}G^{(0)}_{kk}p_k^2 + V_k(q_k)\right] + \epsilon \sum_{k<l=1}^{3} G^{(0)}_{kl}p_k p_l$$

Given Hamiltonian parameters,
can one predict/estimate ε_{crit} for which RRKM valid?



Classical - Oxtoby and Rice, J. Chem. Phys. 65, 1676 (1976)

Quantum - Local Random Matrix Theory, Bose Statistics Triangle Rule:
Logan, Wolynes, Leitner, Gruebele, …

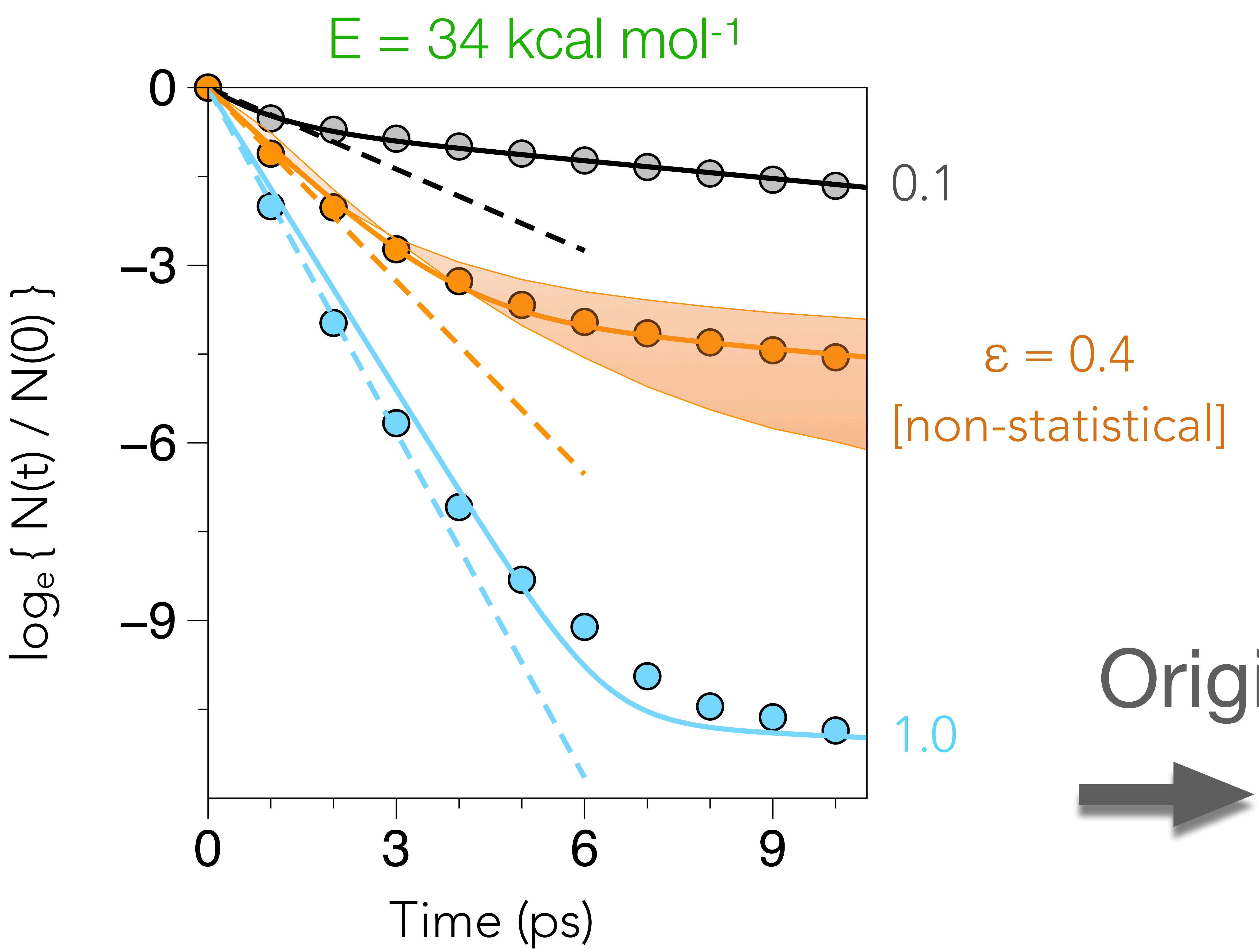


$$\epsilon^{\mathrm{QM}}_{\mathrm{crit}} \sim \epsilon^{\mathrm{CM}}_{\mathrm{crit}} \;\; ?$$

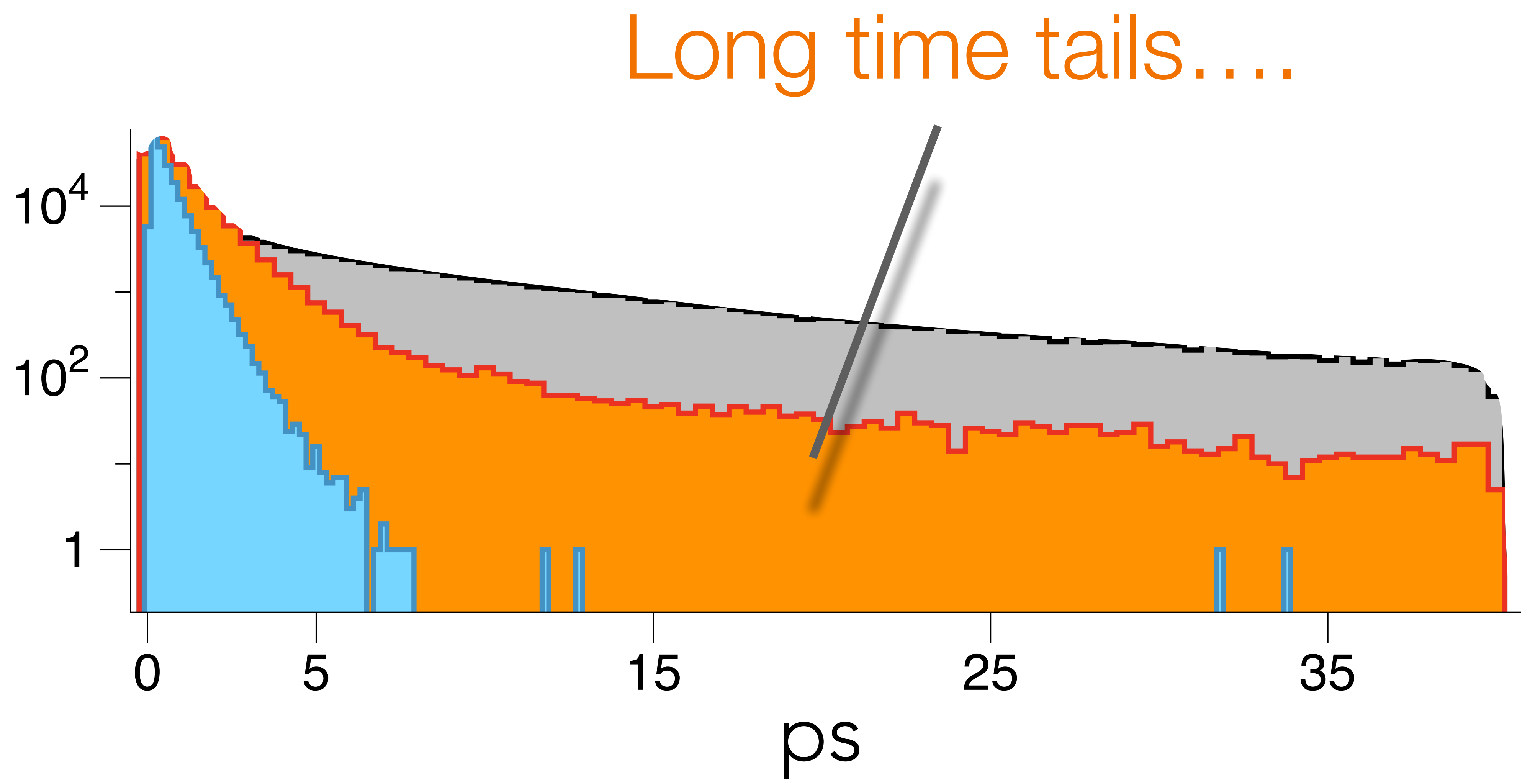
[Tunnelling, coherence, entanglement,…]

Specific Bunker model

Model #6 ~ ozone D = 24 kcal mol^{-1}



[~ 200000 trajectories, time ~ 40 ps]



Lifetime distribution

Origin of the slower timescales?

→ Need to identify the <u>coupling vibration resonances</u>

$$Q_1 Q_2 Q_3^2$$

QM

ladder ops.

CM

adia. angle

Momentum coupling in bond coordinates

$a \leftrightarrow \sqrt{J}\, e^{i\theta}$

Heisenberg

For e.g. $a_1^\dagger a_2^\dagger a_3^2 + H.c.$ $\longrightarrow$ $J_3\sqrt{J_1 J_2}\cos(\theta_1+\theta_2-2\theta_3)$

Fermi Resonances

Nonlinear Resonances

$|v_1,v_2,v_3\rangle \leftrightarrow |v_1\pm1, v_2\pm1, v_3\mp2\rangle$

$|\underline{v}\rangle$ $\qquad$ $|\underline{v}'\rangle$

$\frac{d}{dt}(\theta_1+\theta_2-2\theta_3)\approx 0$

"locked, in phase"

degenerate $E^{HO}_{\underline{v}} \approx E^{HO}_{\underline{v}'}$

$\Rightarrow \omega_1+\omega_2-2\omega_3 \approx 0$

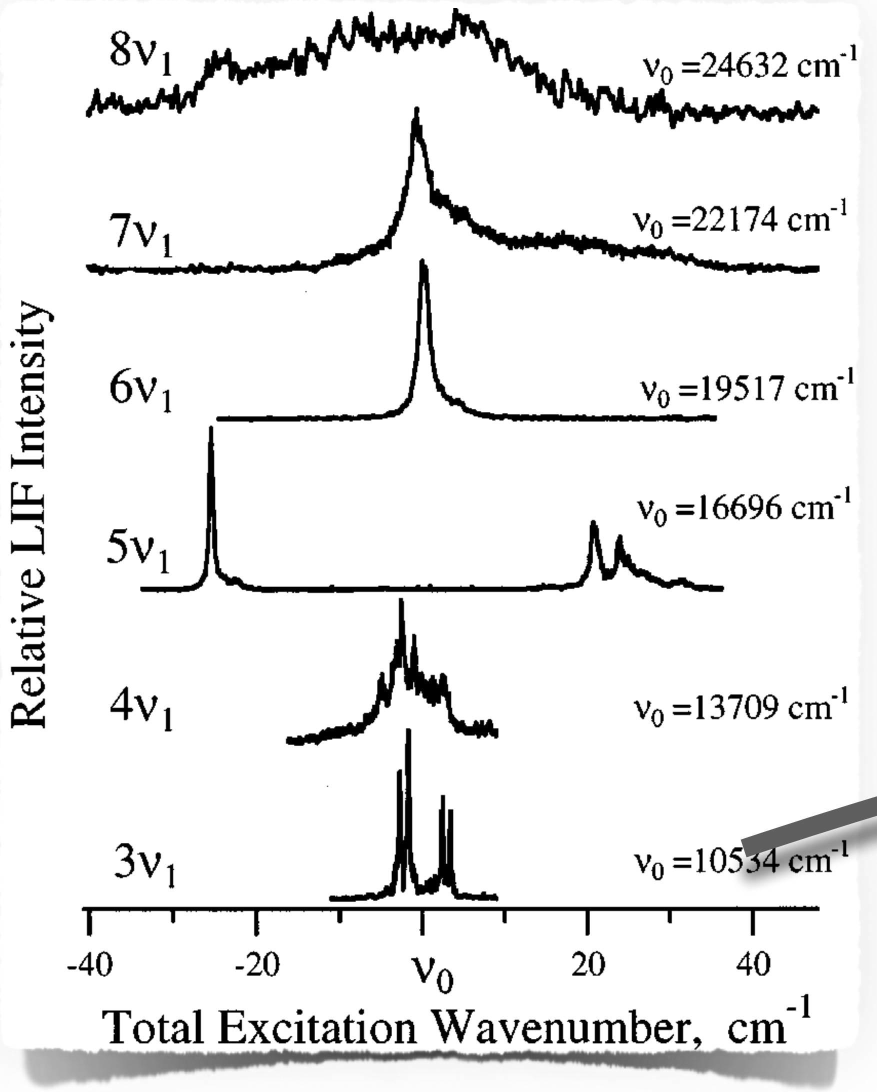
$\Omega_1+\Omega_2-2\Omega_3 \approx 0$

Slow: cannot be averaged away!

anharmonicity : $f_{QM}(\underline{v},\underline{v}')\approx 0$

$f_{CM}(\underline{J},\underline{J}') \approx 0$

Correspondence!



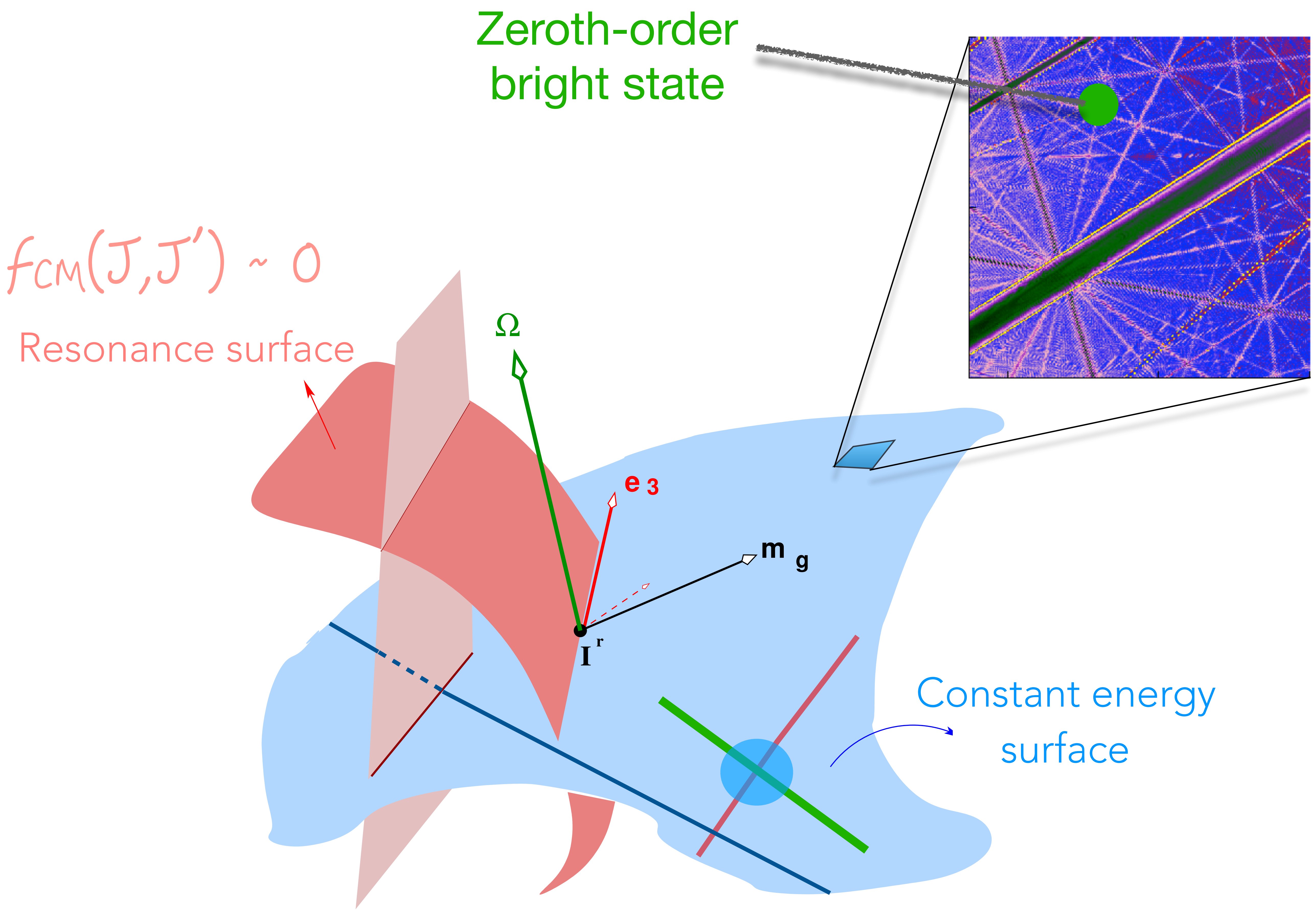
$$\boxed{J_k \longleftrightarrow \left(v_k + \tfrac{1}{2}\mu_k\right)\hbar}$$

Depend on E

"nonlinear"

The Arnold web

“IVR traffic routes”…



Rich “Geography” of the Arnold web ~ *IVR pathways*

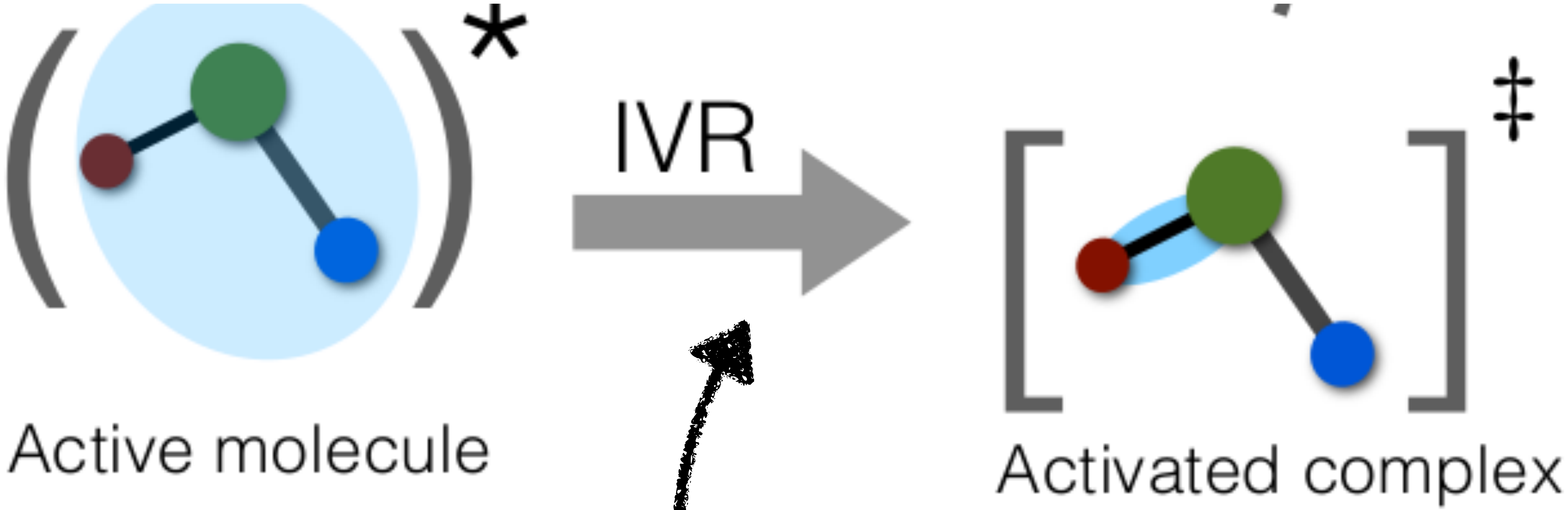
only for > 2 degrees of freedom!

Oxtoby and Rice, J. Chem. Phys. 65, 1676 (1976)

For two interacting oscillators (the case we have discussed so far), the zeroth order energy surface is one dimensional. This case is simple in that there is only one path from a given point to any other, so that narrow resonances do not overlap. For $n > 2$ oscillators, however, the energy hypersurface is of dimension $n - 1$, and centers of resonances are not points but $n - 2$ dimensional surfaces. For a given energy, one can study the positions and extent of overlap of the resonances on the energy hypersurface; the degree to which the energy hypersurface is covered by overlapping resonances determines the extent to which the system may be described stochastically. However, such a many-dimensional picture rapidly becomes very complicated even for quite small molecules, so the question arises of whether it can be replaced by an approximate one-dimensional picture.

Slower timescales…

Where are the bottlenecks?

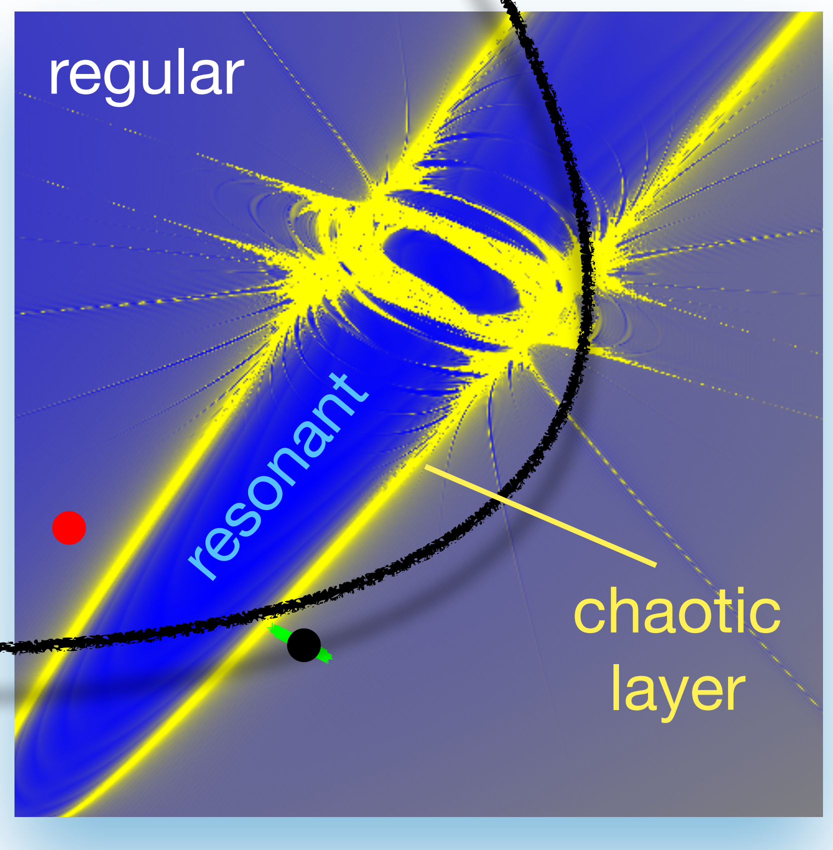


$\tau^{\ddagger}_{rxn} \cancel{\gg} \tau_{\mathrm{IVR}}$

Nonlinear resonances

$H(\mathbf{p}, \mathbf{q}) \longrightarrow H(\mathbf{J}, \theta)$

Arnold web?



Fast Lyapunov Indicator (FLI); *Froeschlé, Guzzo & Lega, Science 2000*

Transformations

Action-angle variables

$$H(\mathbf{p},\mathbf{q}) = \sum_{k=1}^{3}\left[\frac{1}{2}G_{kk}^{(0)}p_k^2 + V_k(q_k)\right] + \epsilon \sum_{k<l=1}^{3} G_{kl}^{(0)} p_k p_l$$

Action - - Angle transformation

$$H(\mathbf{J},\theta) = H_0(\mathbf{J}) + \boxed{\epsilon V(\mathbf{J},\theta)}$$

$$f_{lmn}(\mathbf{J})\cos(l\theta_1 + m\theta_2 + n\theta_3)$$

``frequencies lock"

Nonlinear resonances

$$l\dot{\theta}_1 + m\dot{\theta}_2 + n\dot{\theta}_3 \approx 0$$

IVR

H = E is 5-dimensional

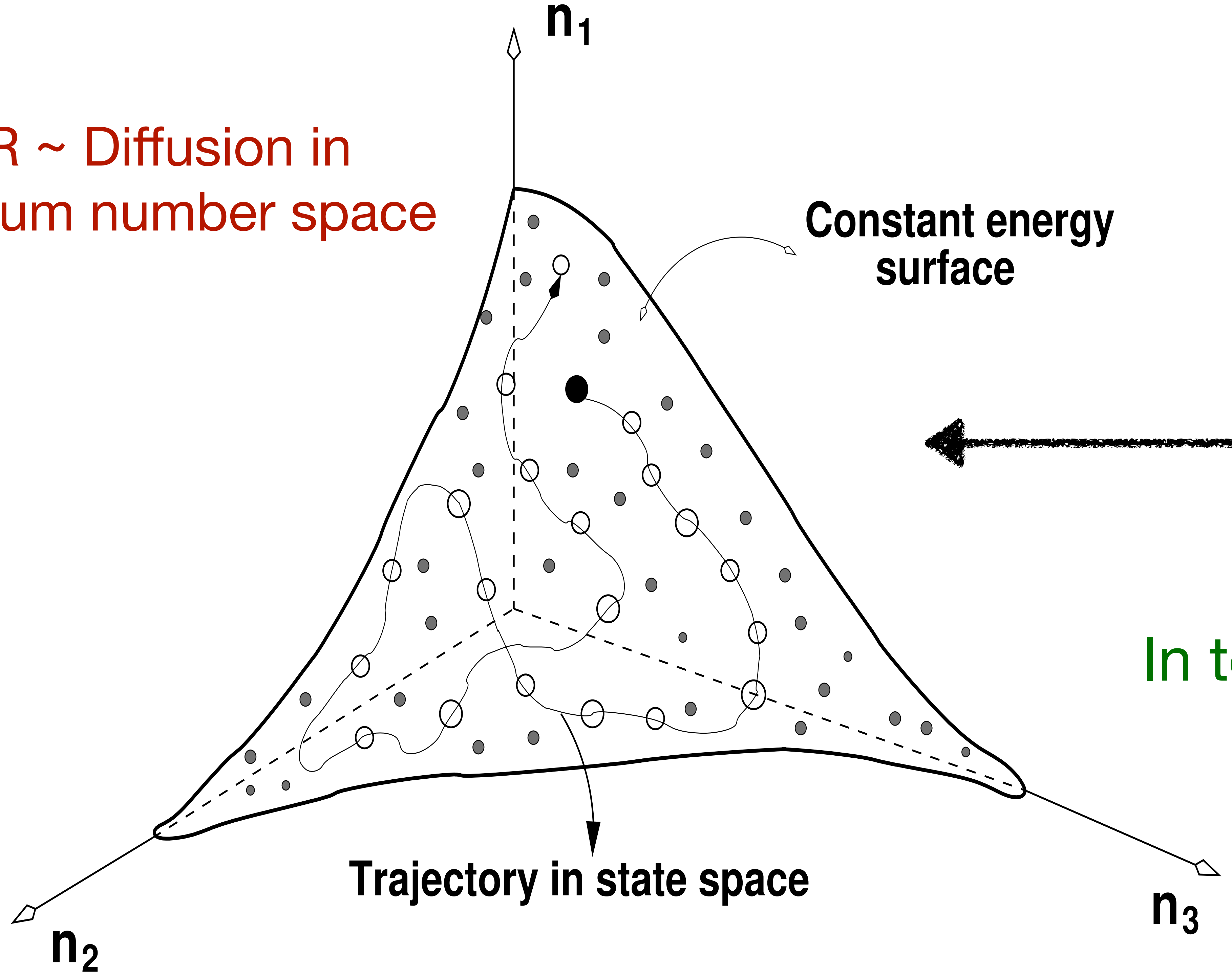
Pick a $(\theta_1, \theta_2, \theta_3)$ angle slice

Map the Arnold web in (J_1, J_2, J_3) action space

Advantage of using action space

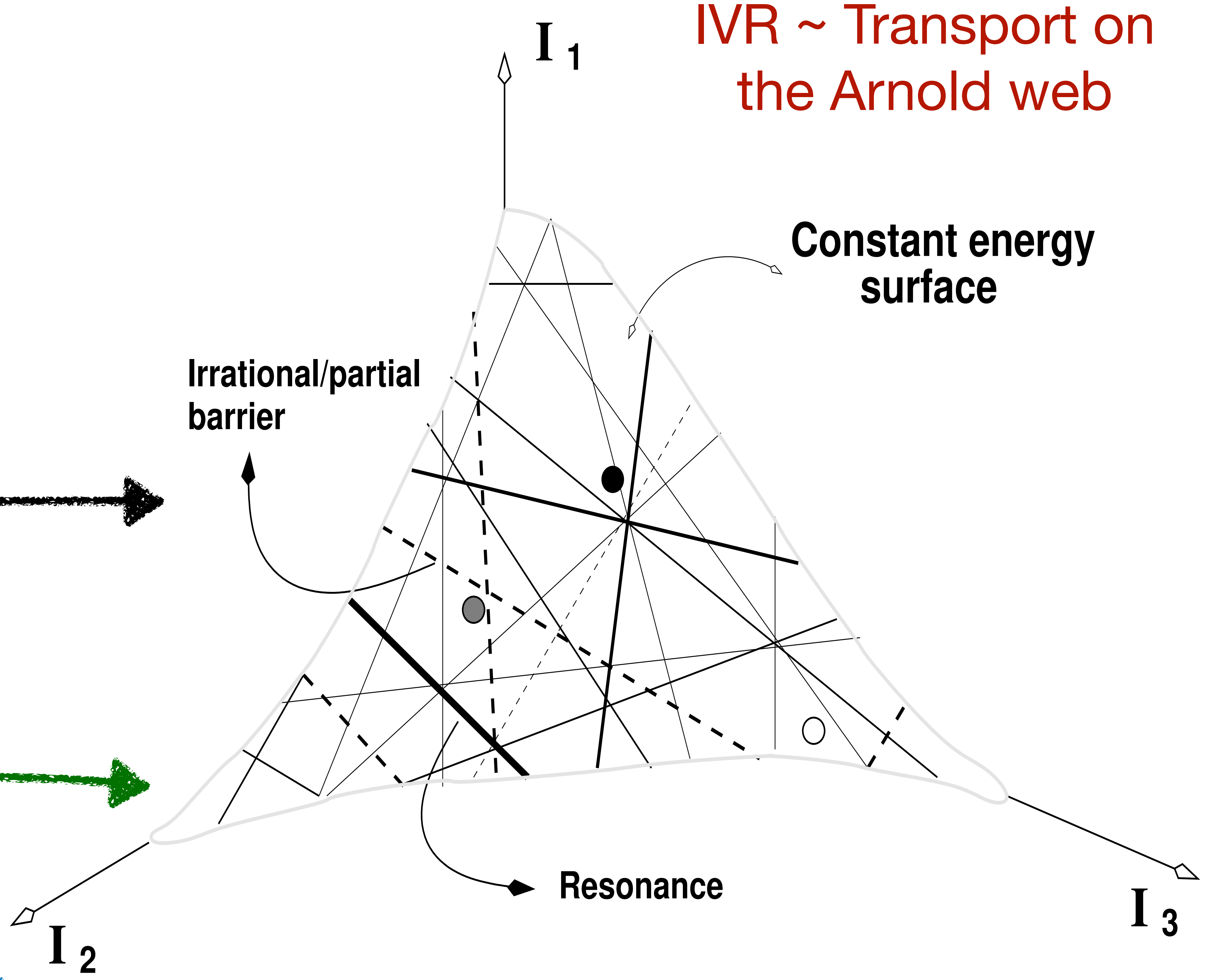
Classical-Quantum correspondence…

IVR ~ Diffusion in
Quantum number space



$$I_k \leftrightarrow \left(n_k + \frac{\mu_k}{2}\right)\hbar$$

IVR ~ Transport on
the Arnold web

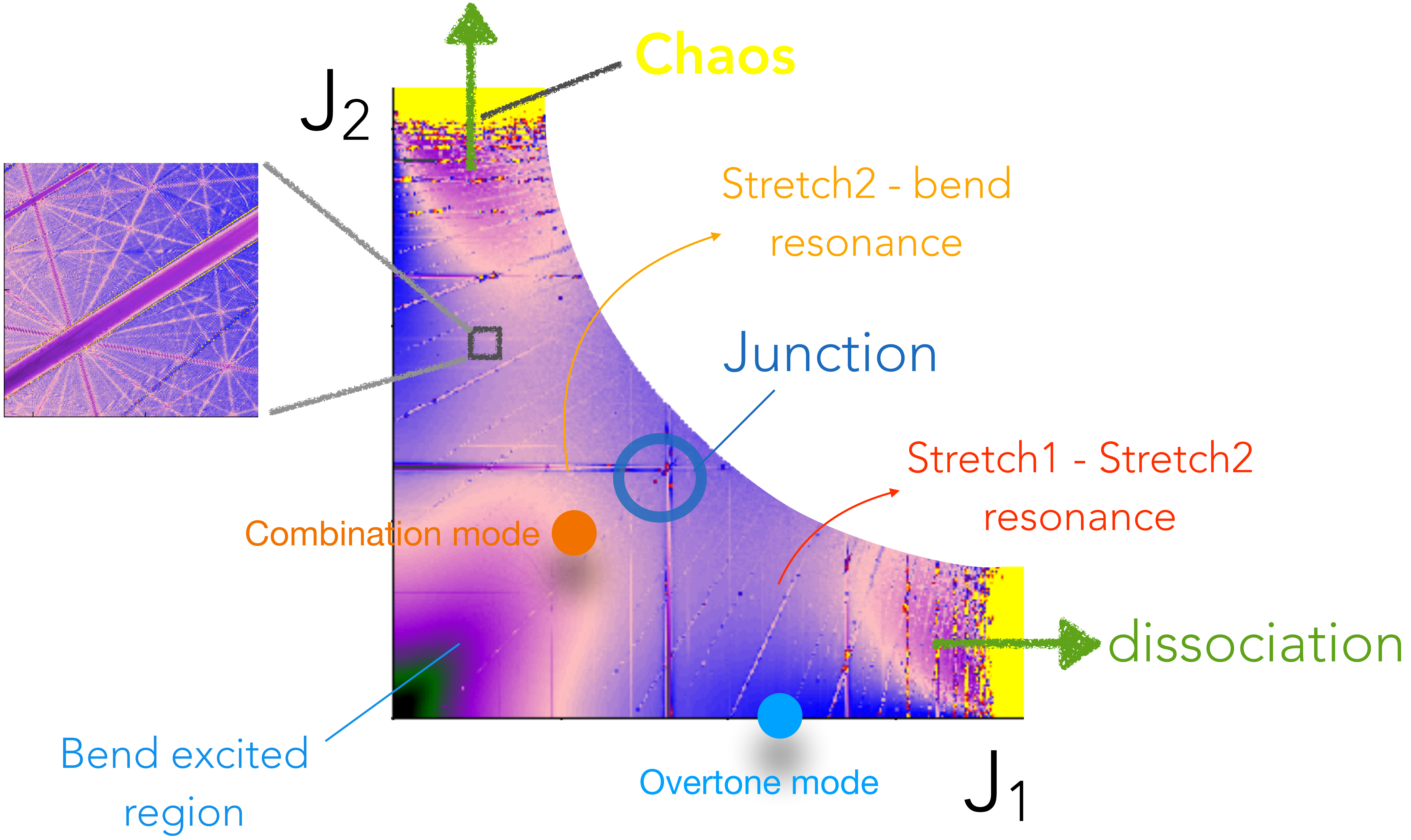


"deconstruct" T(E)
In terms of the Arnold web?

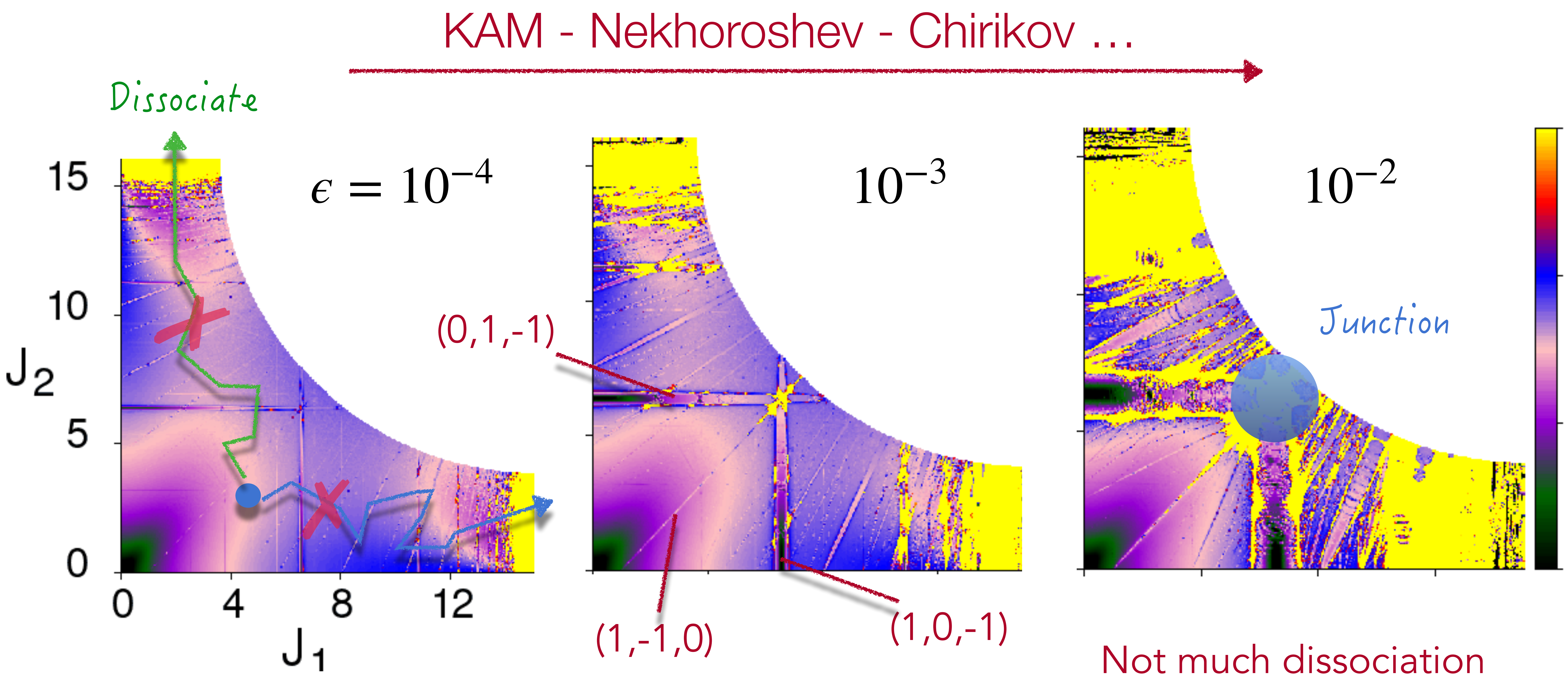
Identify truly
quantum effects!

$$T(E) \equiv \frac{2\pi}{3}\left[\sum_Q \langle|\psi_Q|\rangle \rho_Q\right]^2 \sim 1;$$ quantum ergodicity transition

WHAT TO EXPECT?

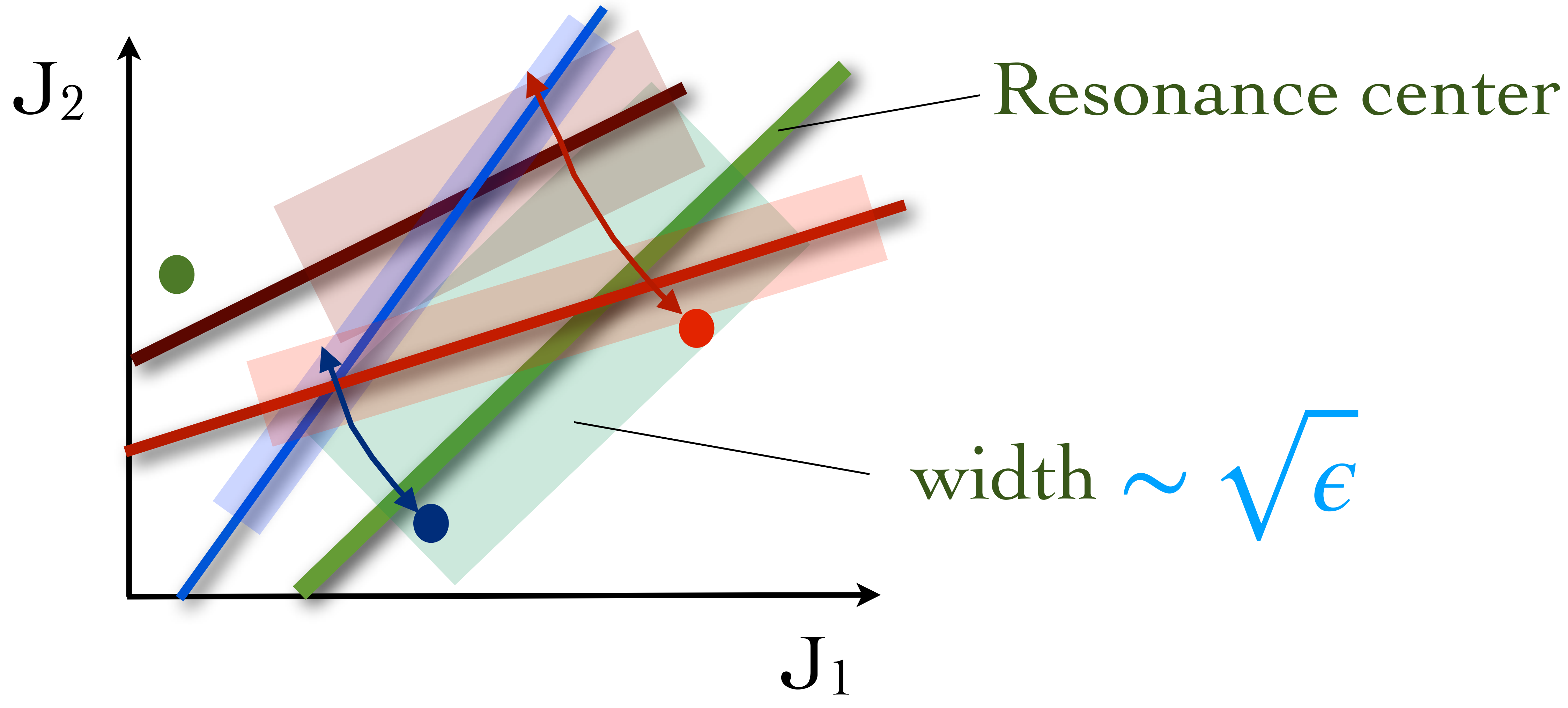


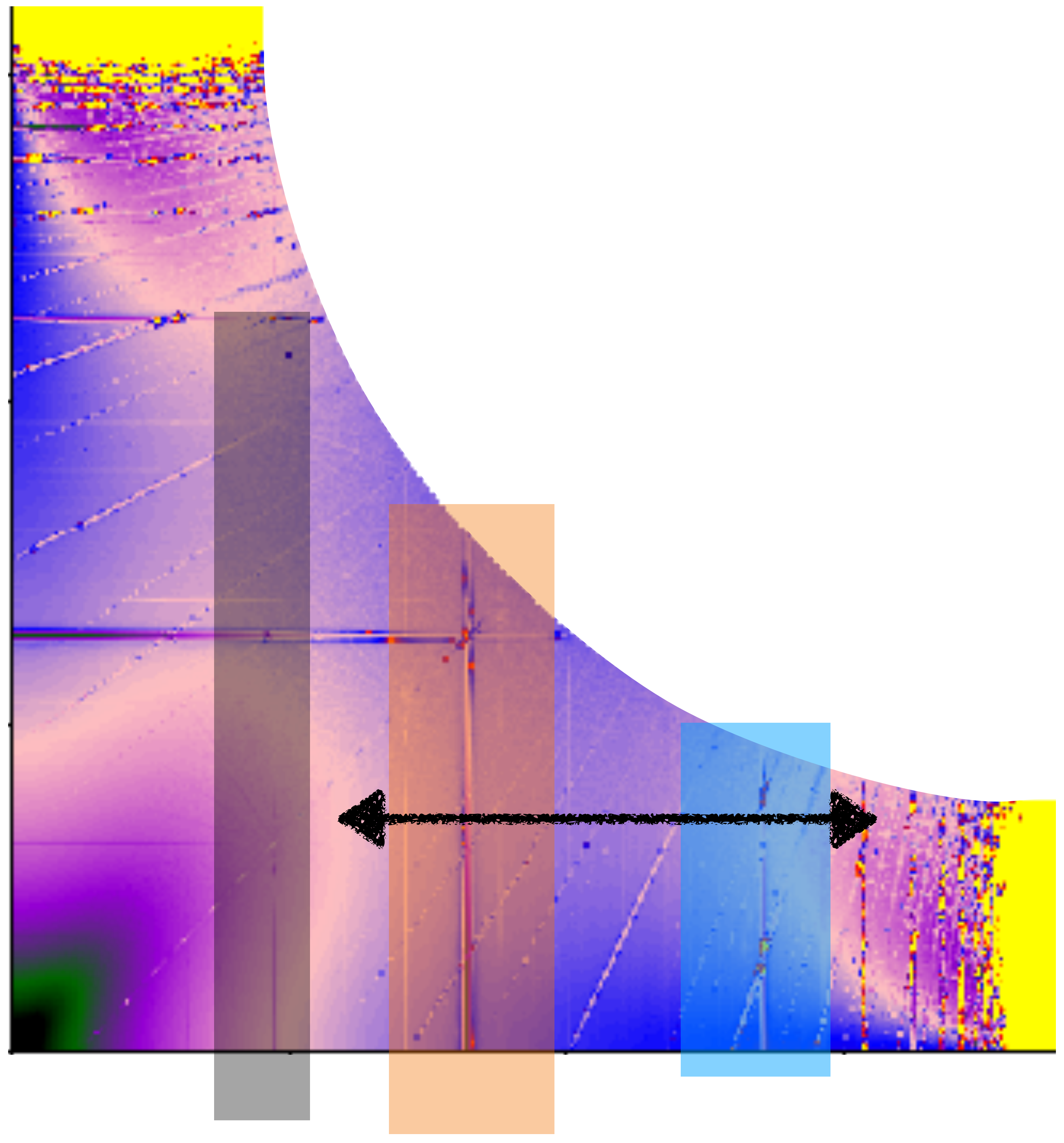
Low coupling strengths



Transition to statisticality?

Large scale resonance overlap…[`Chirikov” criterion]





2 degrees of freedom
Oxtoby and Rice, J. Chem. Phys. 65, 1676 (1976)

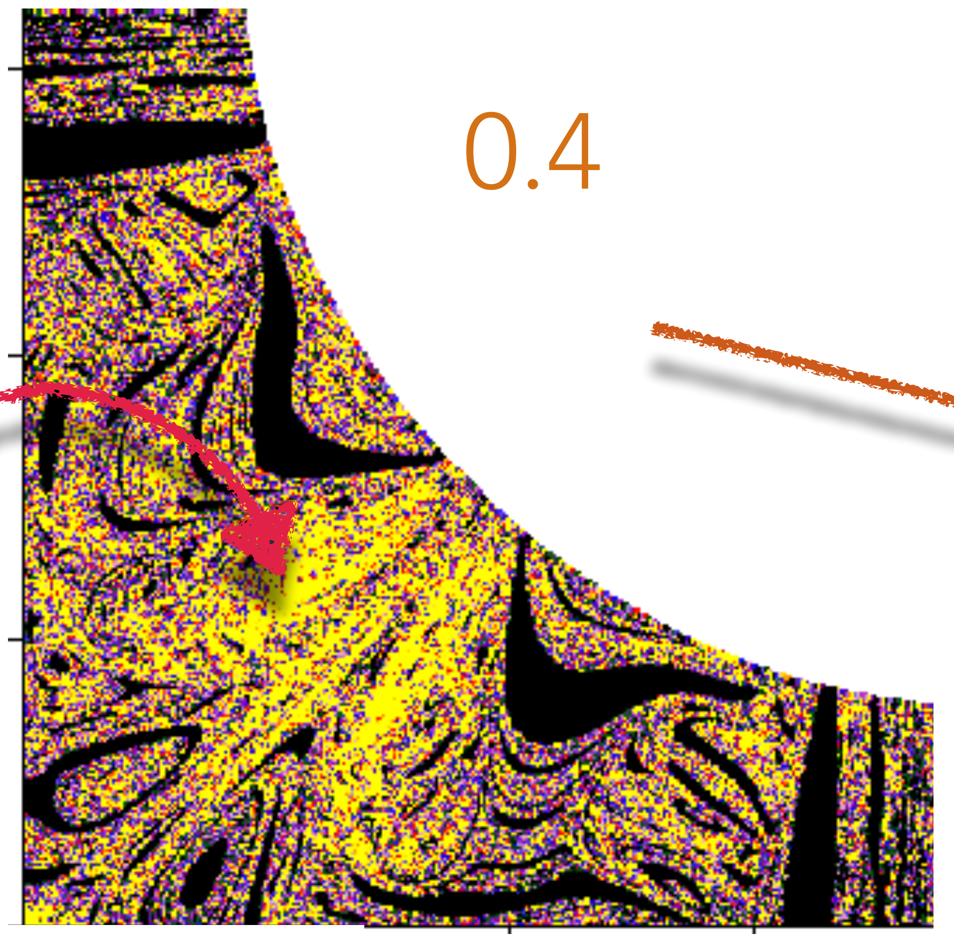
> 2 degrees of freedom?

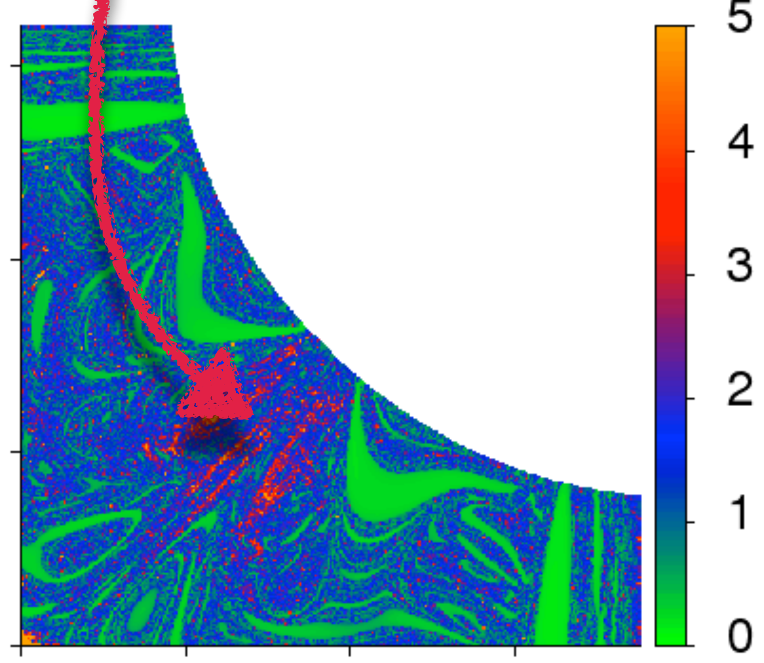
$\epsilon_c \sim 0.1 - 0.2$

However….

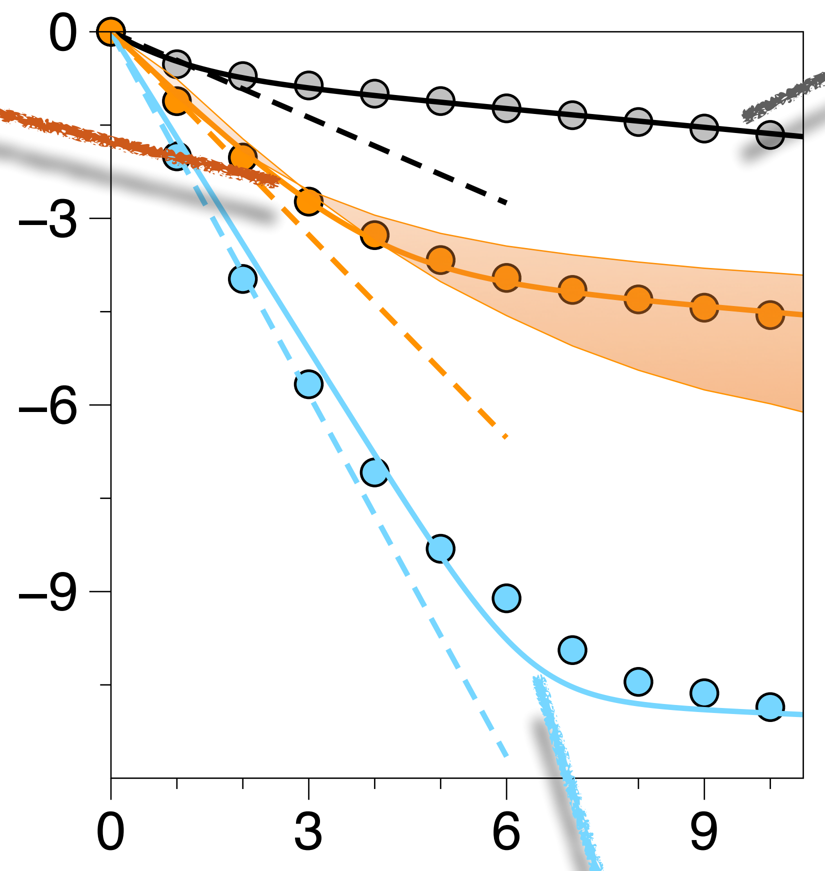
For ε ~ 0.4

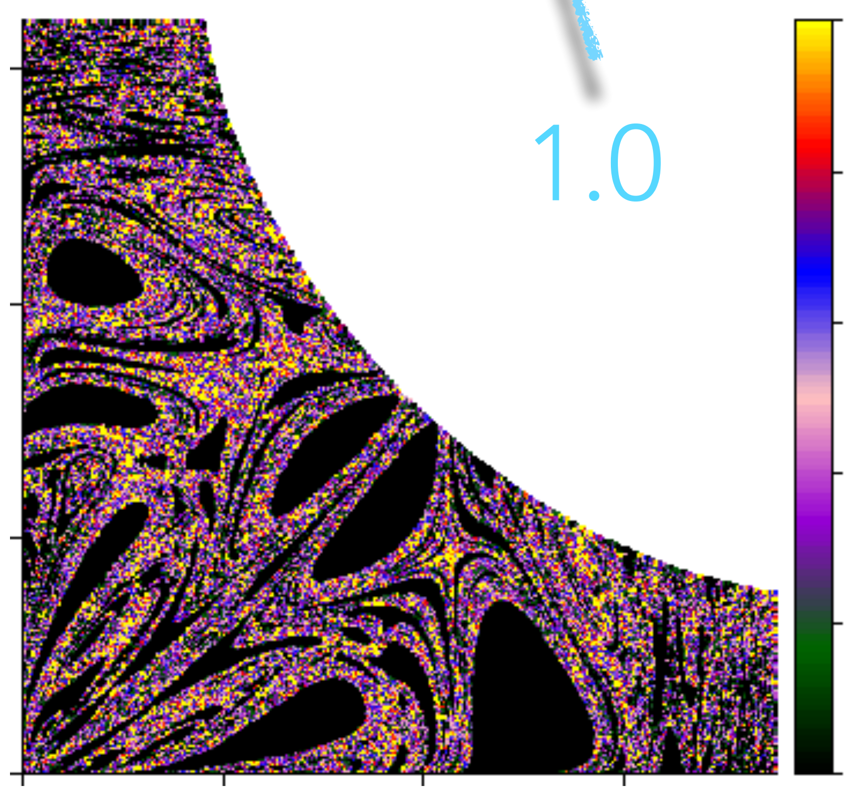
not much of a web!

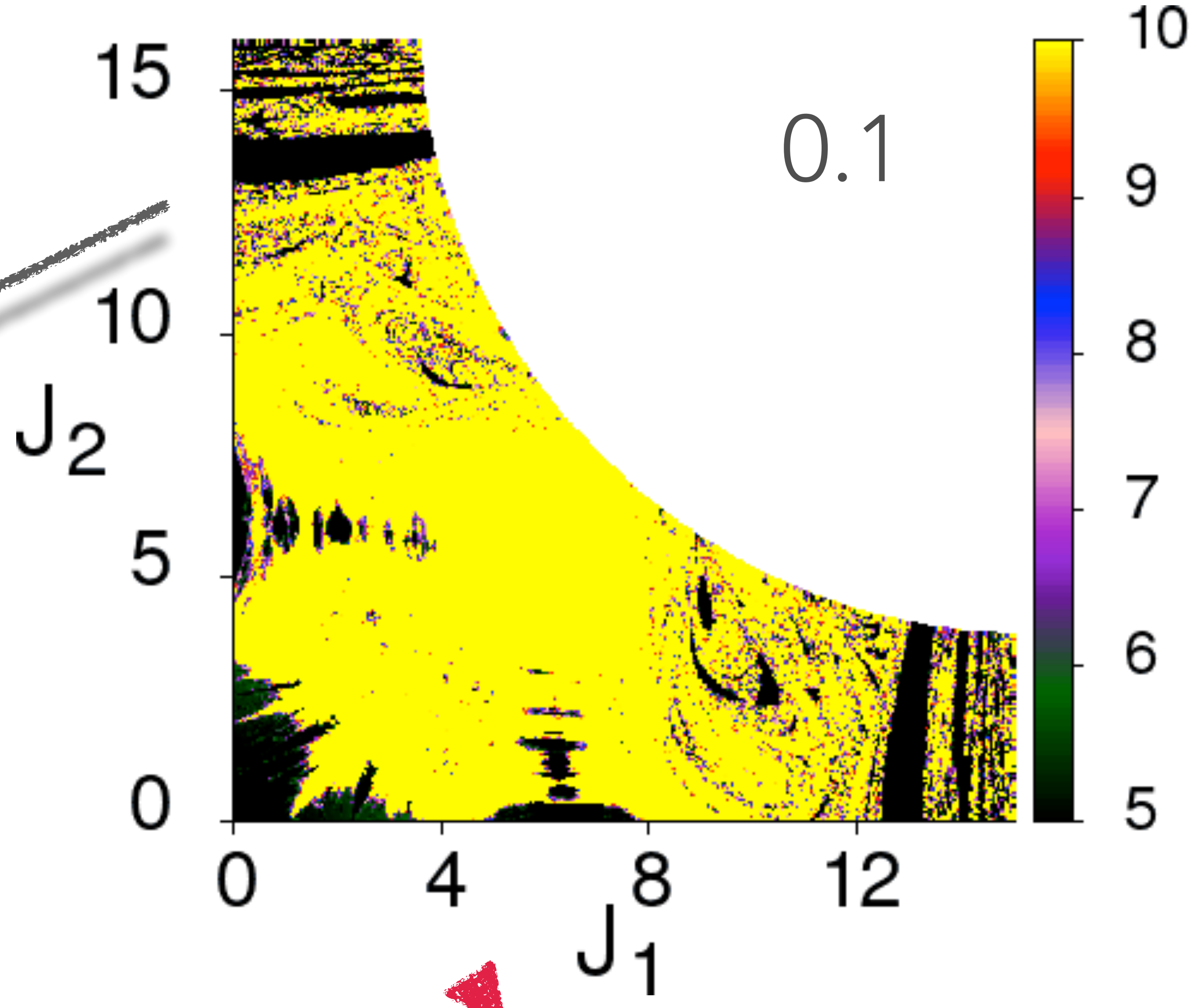


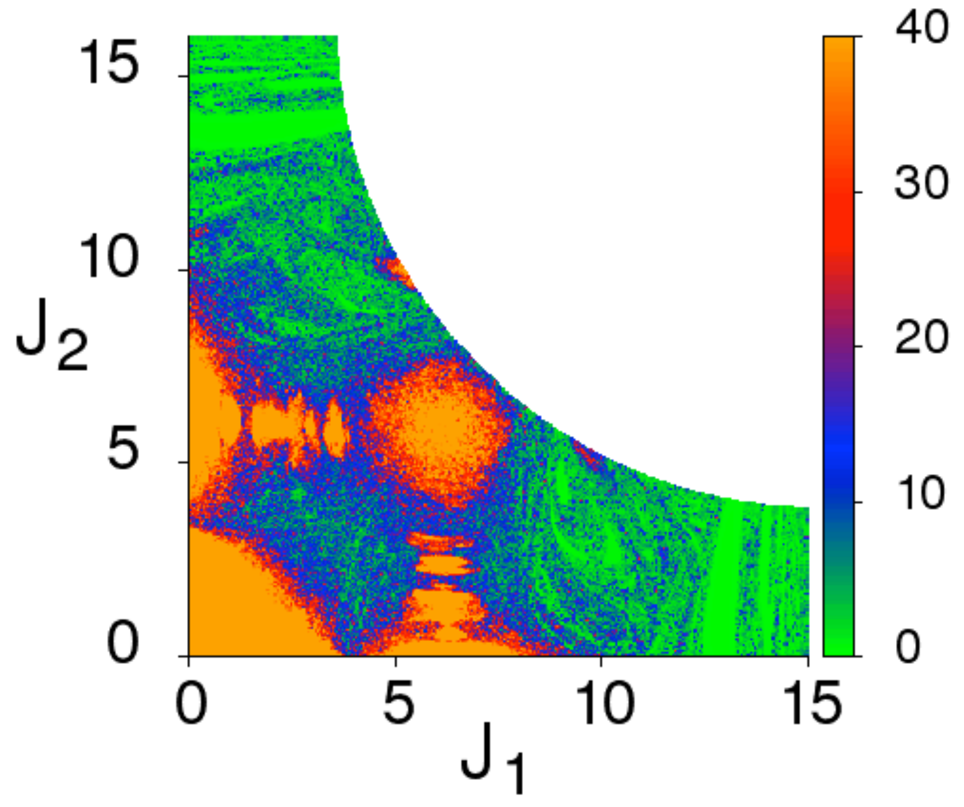


Lifetime (ps)







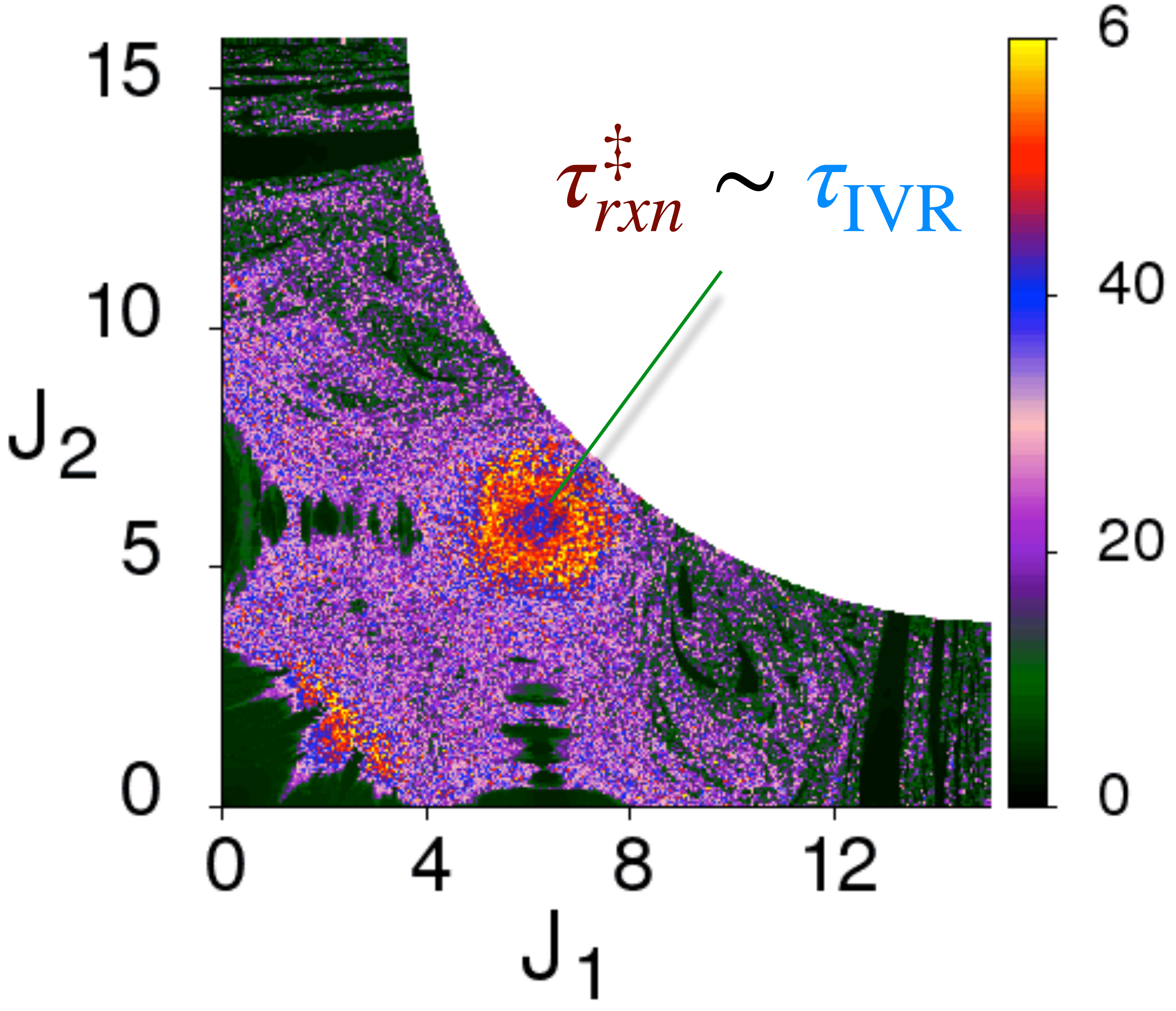


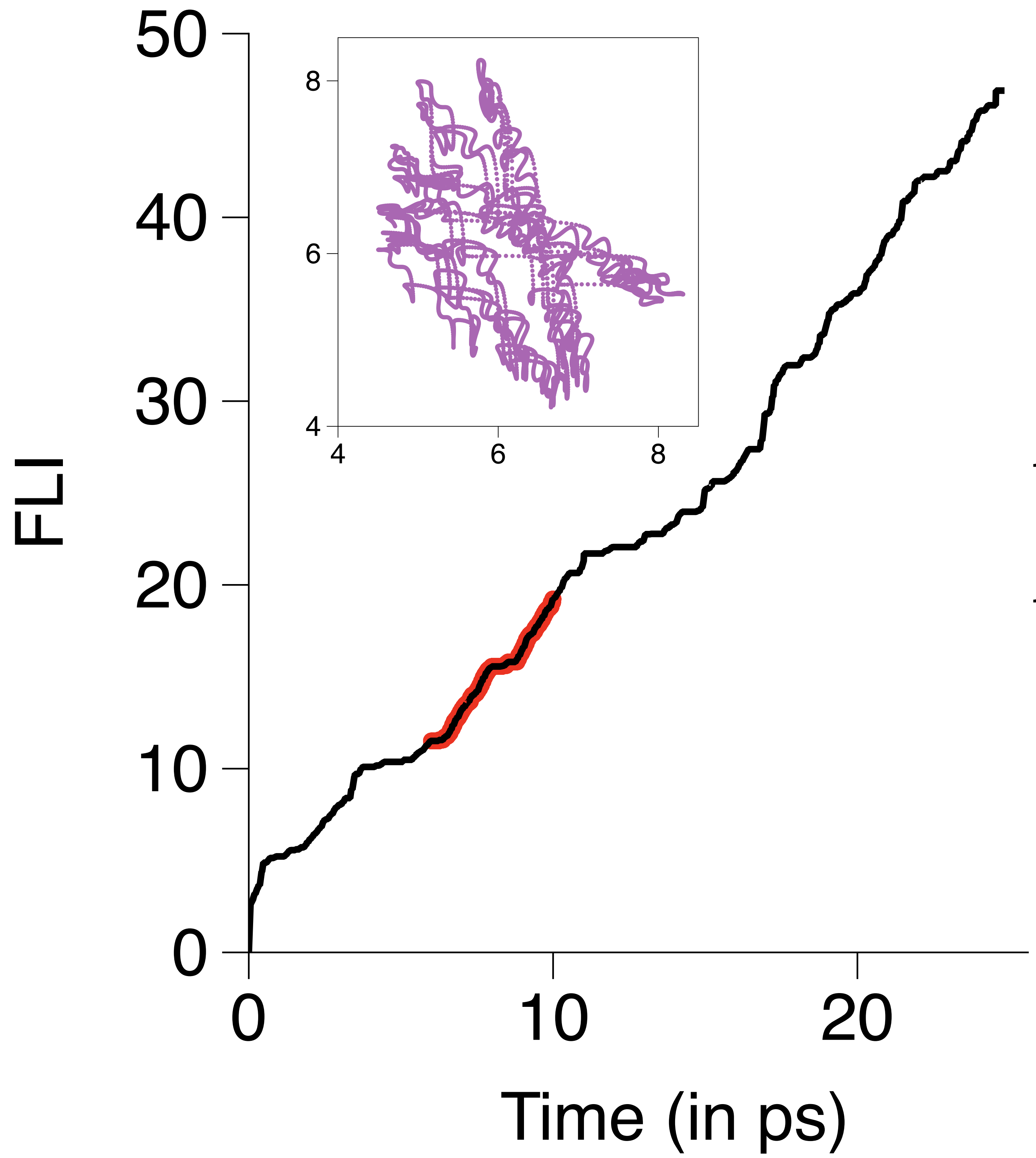
Lifetime (ps)

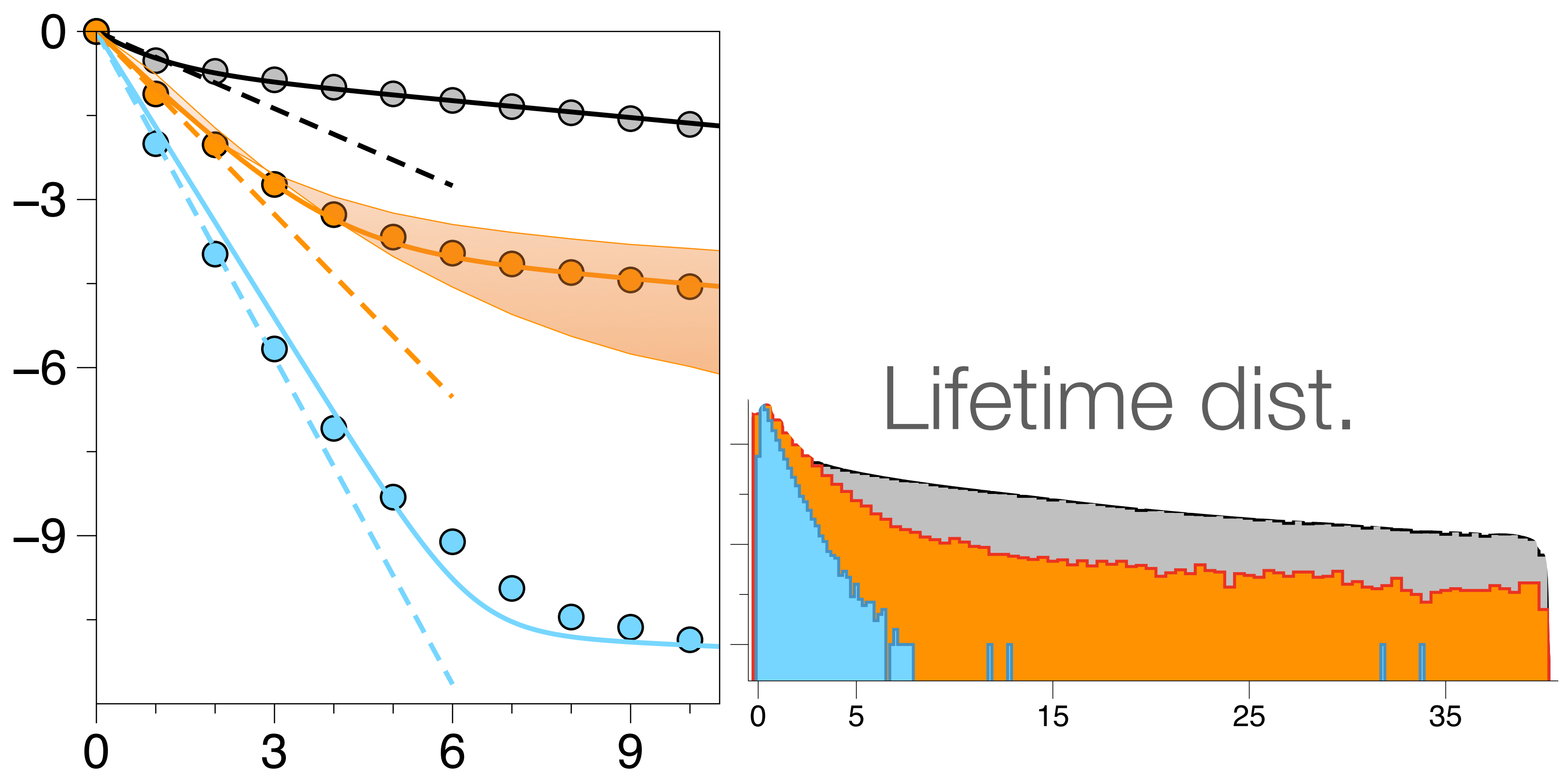
Junctions are key!

Local dynamical traps…stable chaos…

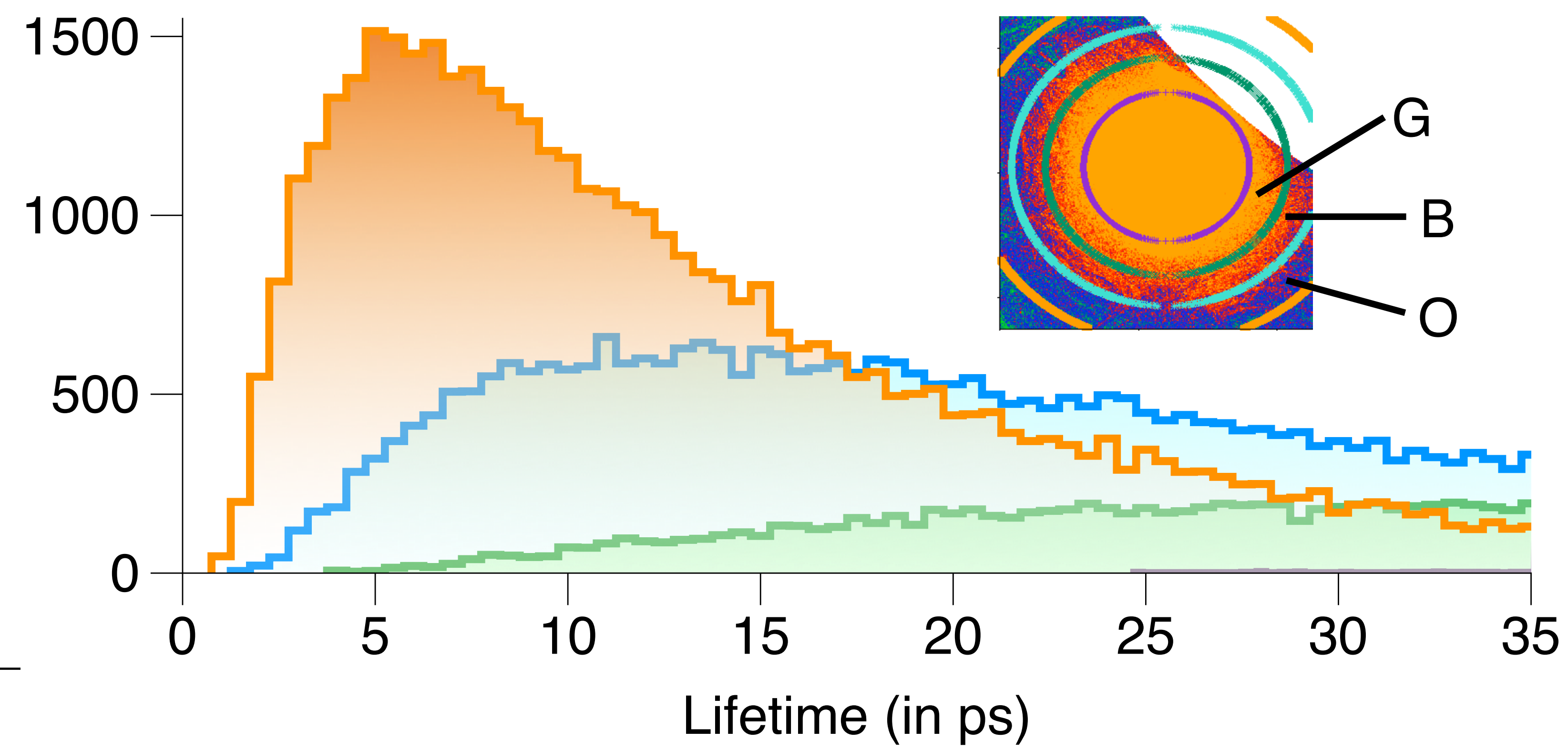
ε = 0.1





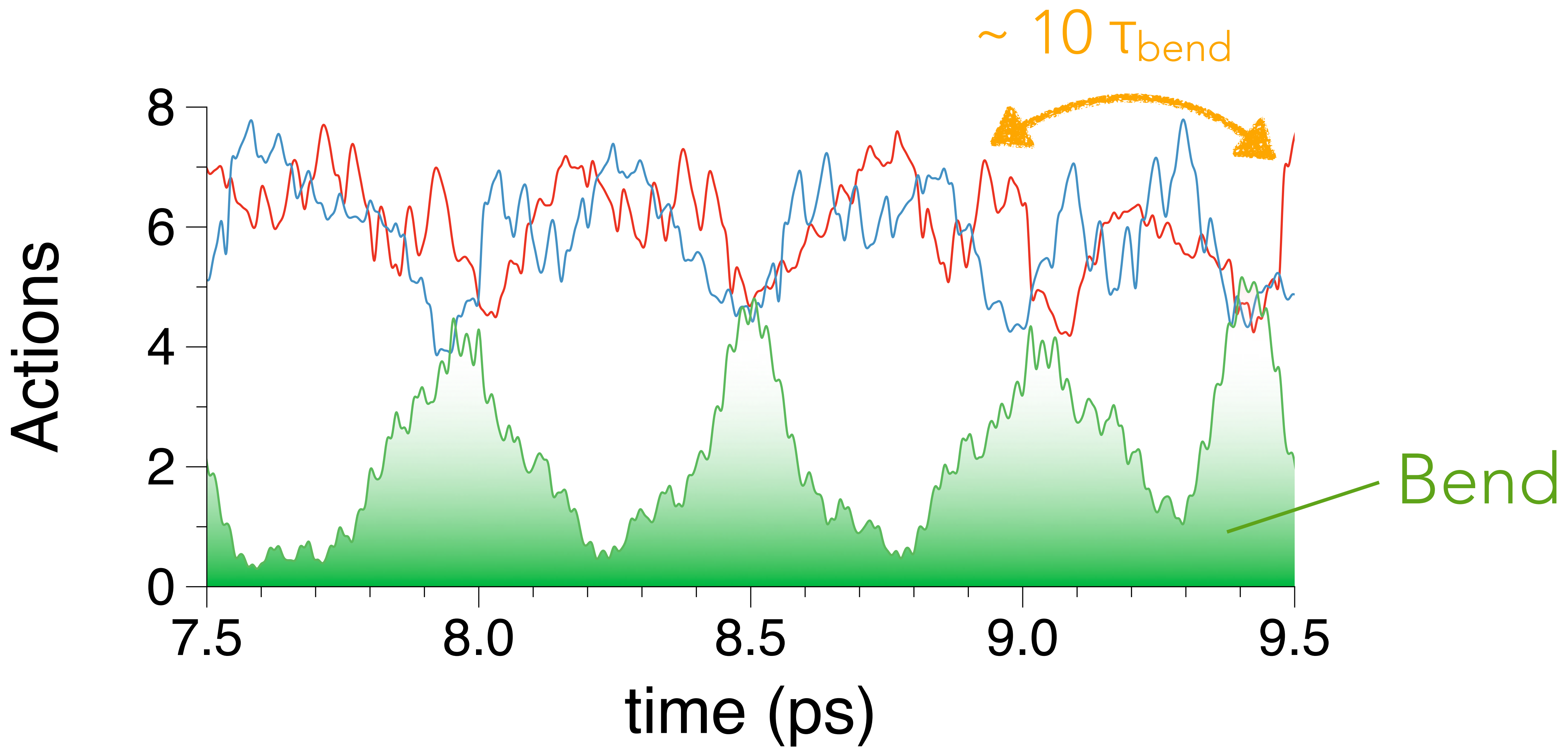


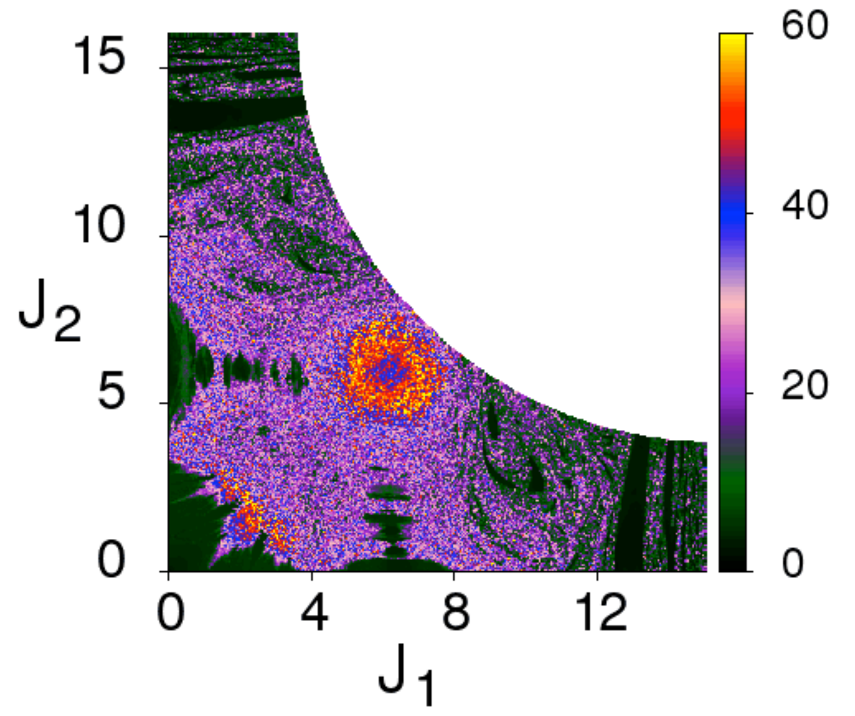
Long time tails….

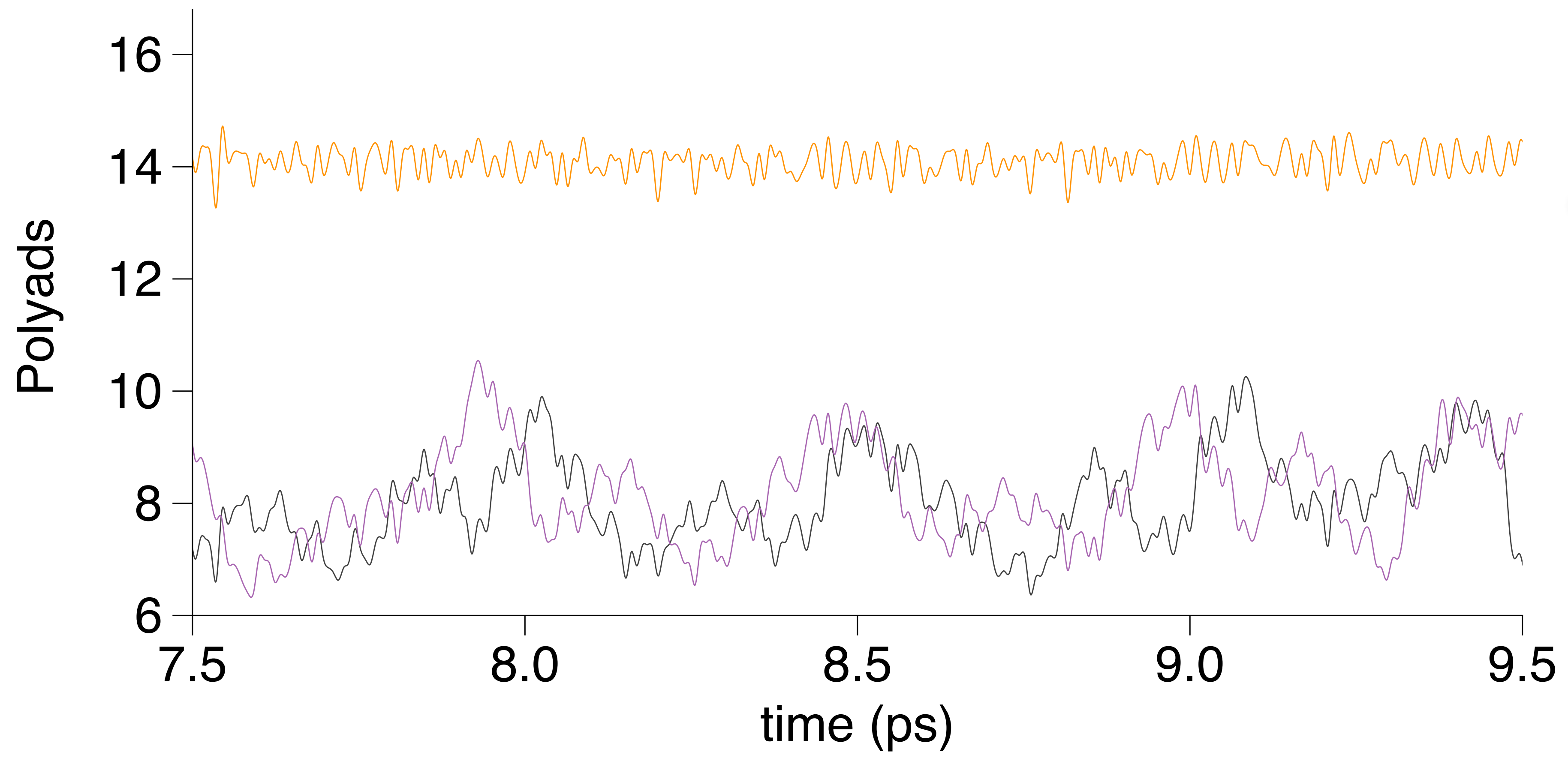


Expanded FLI scale…

Correlated dynamics…







$$P \equiv J_1 + J_2 + J_3 \;\;;\;\; [H, P] \approx 0$$

Local integrals of motion

OCS molecule

Martens, Davis, Ezra, Chem. Phys. Lett. (1987)

Paškauskas, Chandre, Uzer, J. Chem. Phys (2009)

Vela-Arevalo, Wiggins (2002)

C_2H_2

Holme, Levine, Chem. Phys. (1989)

Atkins & Logan, J. Chem. Phys. (1992)

Reinhardt, Hutchinson, Sibert, Hynes,…

Connections …. only a glimpse

Lange, Bäcker & Ketzmerick
EPL 116, 30002 (2016)

Multi-exponential
[Marcus, Hase, Swamy 1984]

Paskauskas, Chandre, Uzer
JCP 130, 164105 (2009)

$$\frac{N(t)}{N(0)} \neq e^{-k(E)t}$$

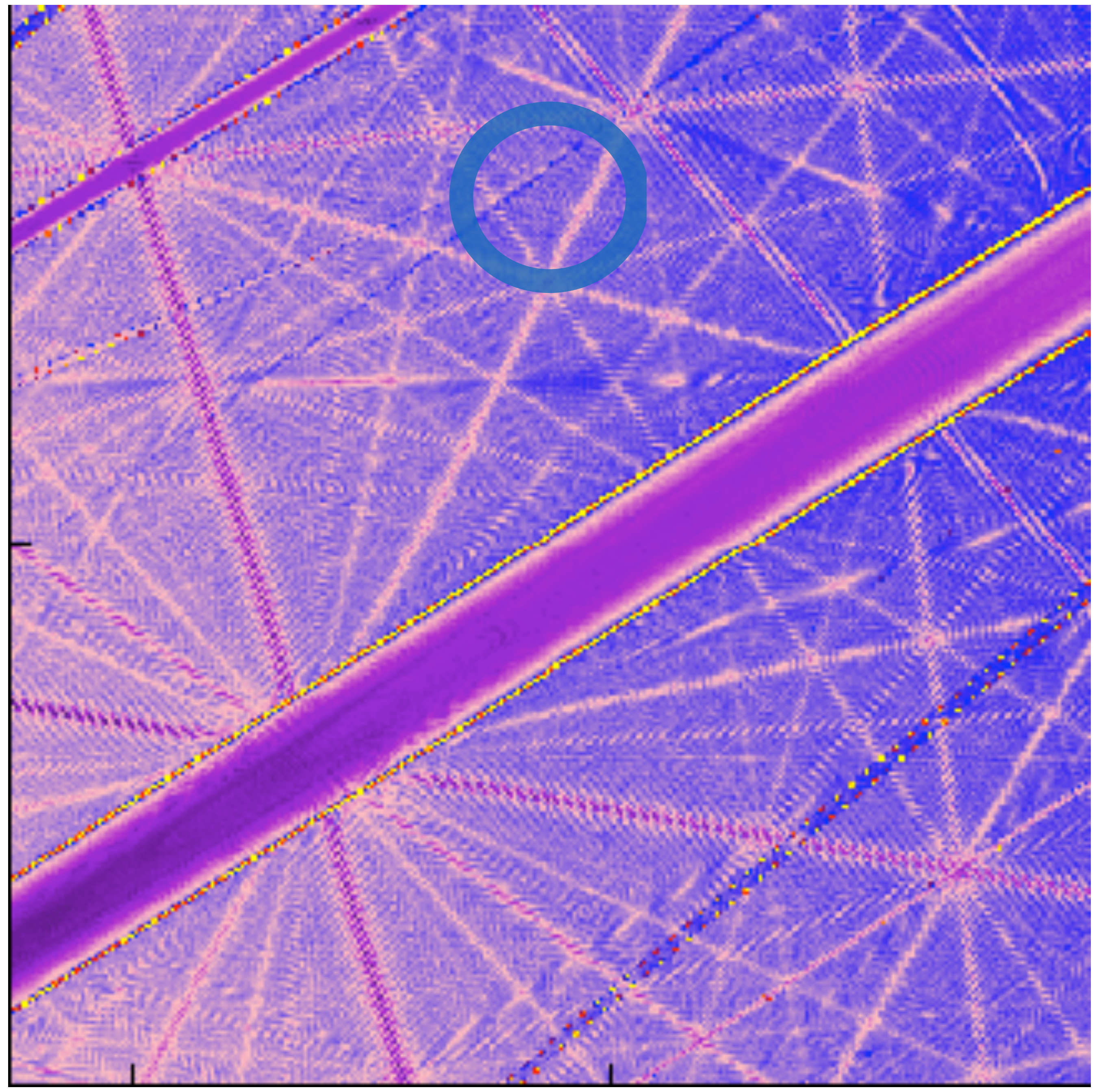
Stretched exponential/power law
[Ezra, Waalkens, Wiggins 2009]

Shirts & Reinhardt
JCP 77, 5204 (1982)

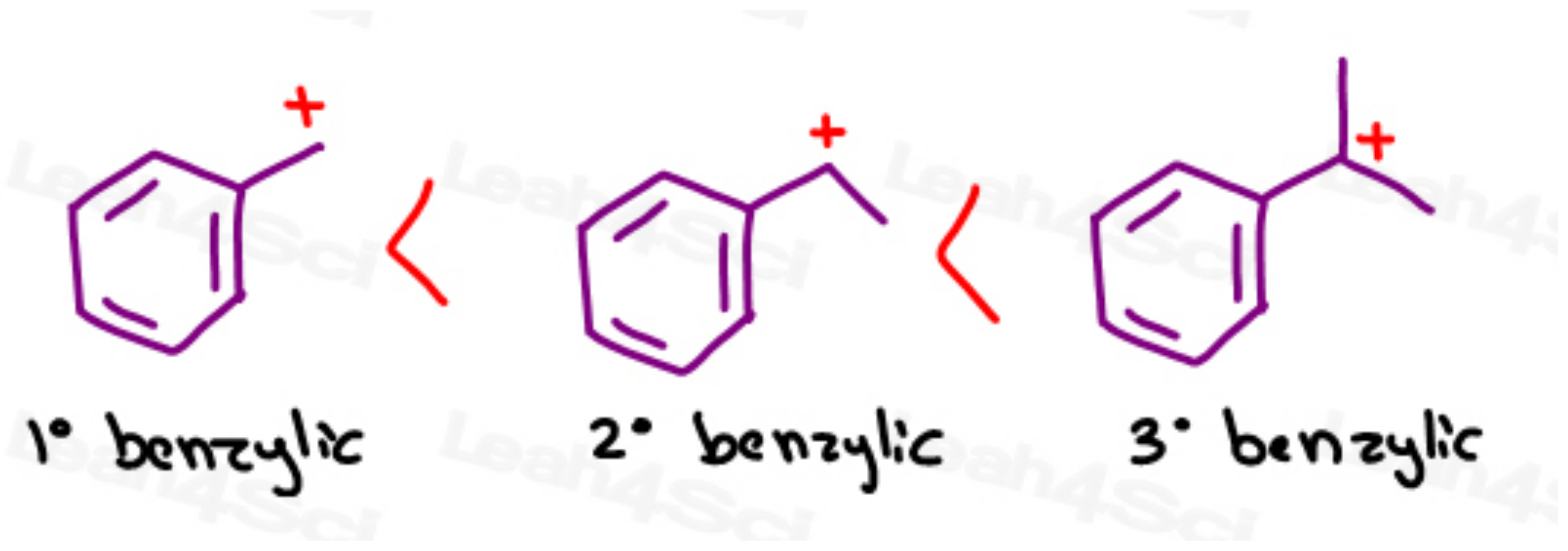
Exponential/power law
[Shojiguchi, Li, Komatsuzaki, Toda 2008]

Leitner & Wolynes
JCP 105, 11226 (1996)

An analogy of sorts …



At a junction, independent resonances delocalise energy
``Dynamical stability"



More resonant structures delocalise charge
``Energetic stability"

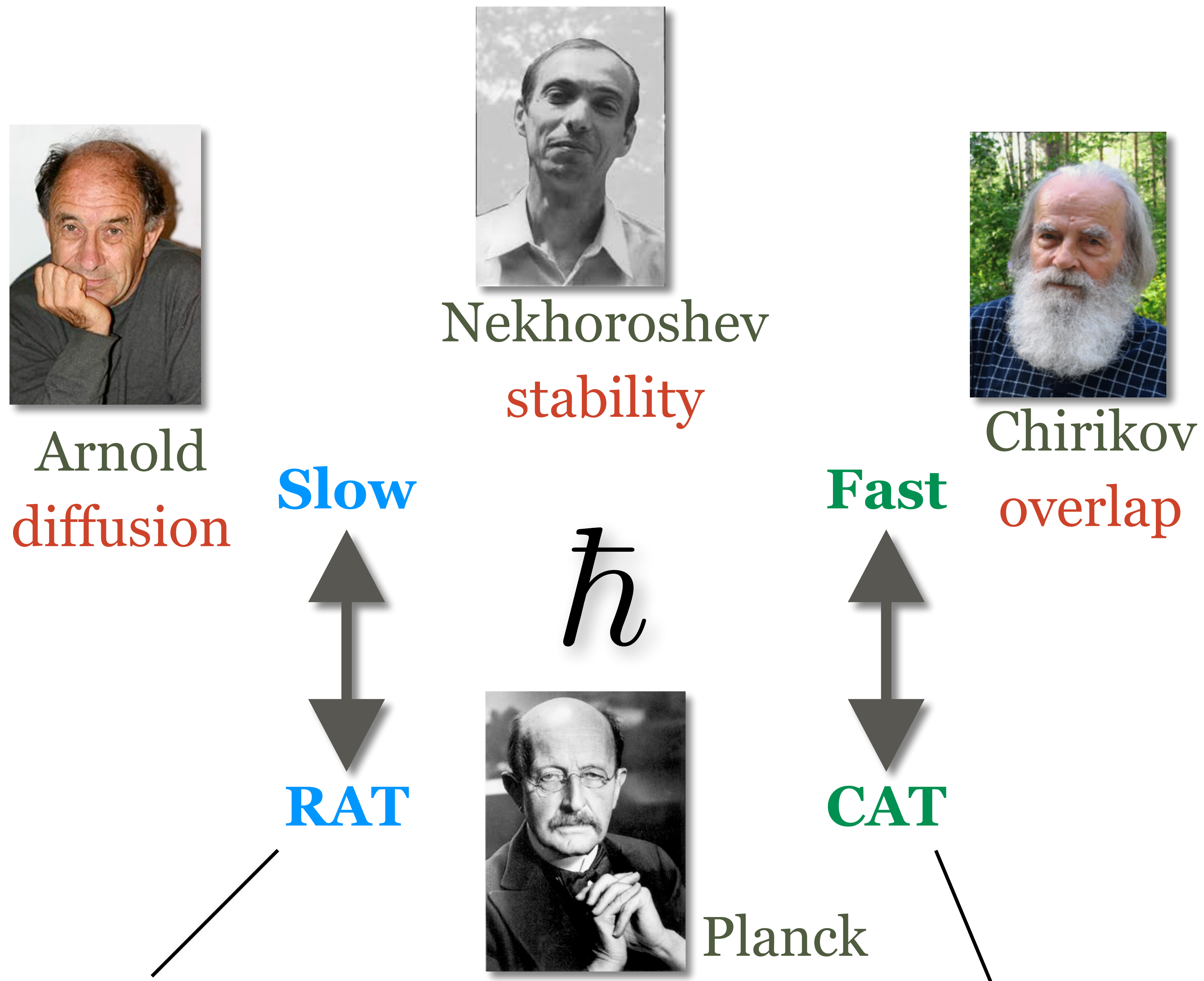
1. Is quantum sensitive to the junction?

~ Yes, modulo dynamical tunnelling

Quantum ergodicity transition:

$$T(E) \equiv \frac{2\pi}{3}\left[\sum_{Q} \langle |\psi_Q| \rangle \rho_Q \right]^2 \sim 1$$

Conjecture: Influence of junctions minimal?



Resonance-assisted tunnelling

Chaos-assisted tunnelling

$SCCl_2$ IVR dynamics: Manikandan and Keshavamurthy, PNAS (2014)

Martens' model & connections to LRMT: Karmakar and Keshavamurthy, PCCP (2020)

2. Stable chaos

Nekhoroshev's theorem

An example of stable chaos in the Solar System

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Observatoire de Paris, Meudon, Groupe EUROPA-DAEC, 5 place Jules Janssen, F-92195 Meudon, France

MANY planets have been shown to have chaotic instabilities in their orbital motions, but the long-term significance of this is not fully understood[1]. The eccentricity of Mercury, for example, changes by about 25% of its value over 40 times the Lyapunov time[2,3] (the e-folding time for divergence of nearby orbits), but the orbit of Pluto, in an integration lasting 50 Lyapunov times[4], shows no significant change. Here we show that the orbit of the near-Jupiter asteroid 522 Helga is chaotic, with an unusually short Lyapunov time of 6,900 yr. We integrate its motion, including perturbations from the outer giant planets, over a period 1,000 times longer than this, and find no significant instability. Chaos in the orbit of 522 Helga is caused by a 7:12 resonance with the orbit of Jupiter, but the size of the chaotic region in phase space is small; stability is ensured because the eccentricity and precession of the orbit are such that it avoids close encounters with Jupiter. Asteroid orbits with larger proper eccentricity would, we suggest, be genuinely unstable, consistent with the sparse asteroid population near Helga. Although Helga is the first clear-cut example of a stable chaotic orbit, we argue that 'stable chaos' may be a rather common feature of Solar System dynamics.

Given the set up as above, the celebrated Nekhoroshev's theorem provides results regarding the stability of various types of initial conditions on the Arnold web. Roughly speaking§, for $\varepsilon < 1$, an initial condition $(\mathbf{J}(0), \boldsymbol{\theta}(0))$ satisfies

$$||\mathbf{J}(t) - \mathbf{J}(0)|| \leq \varepsilon^{1/2(f-m)} \tag{25}$$

for times

$$|t| \leq \exp\left(c\varepsilon^{-1/2(f-m)}\right) \tag{26}$$

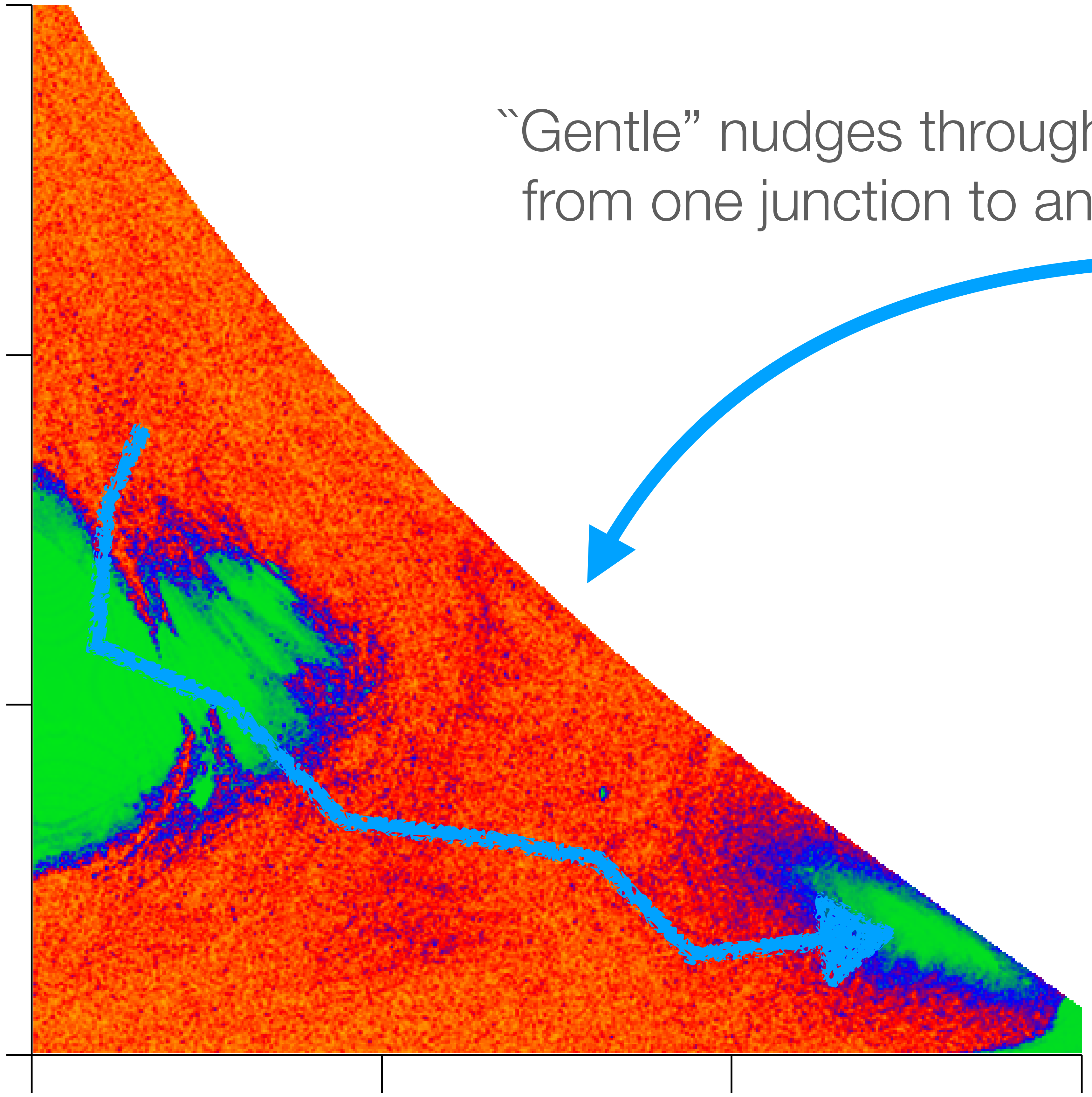
f: degrees of freedom ~ 3N-6, m: multiplicity of the junction
(How many independent resonances intersect?)

For large molecules junctions of various multiplicities....non-RRKM?

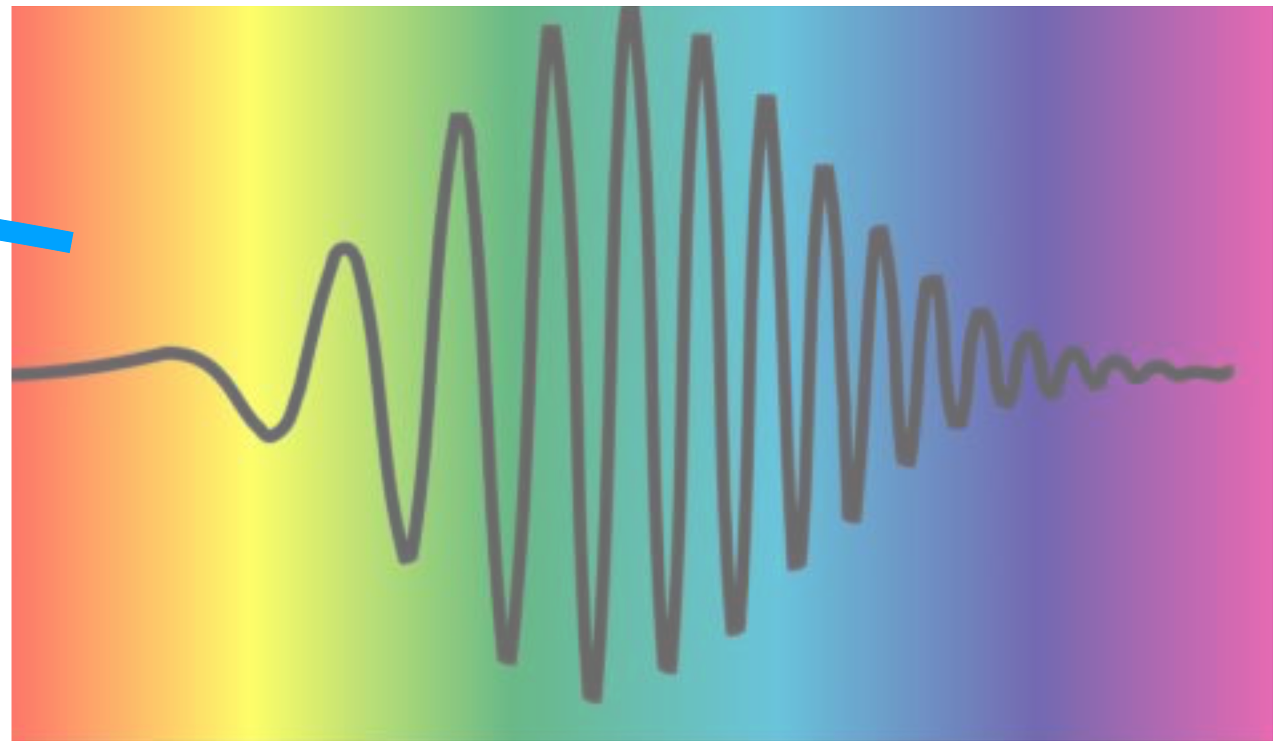
Will quantum effects ``de-trap''?

3. Use the junctions to control?

"Field chirping" for polyatomic molecules…



"Gentle" nudges through chaos from one junction to another?



HCN dissociation

Yadav, Karmakar, Keshavamurthy (unpublished)

Quo vadis?

Pankaj Yadav Sourav Karmakar

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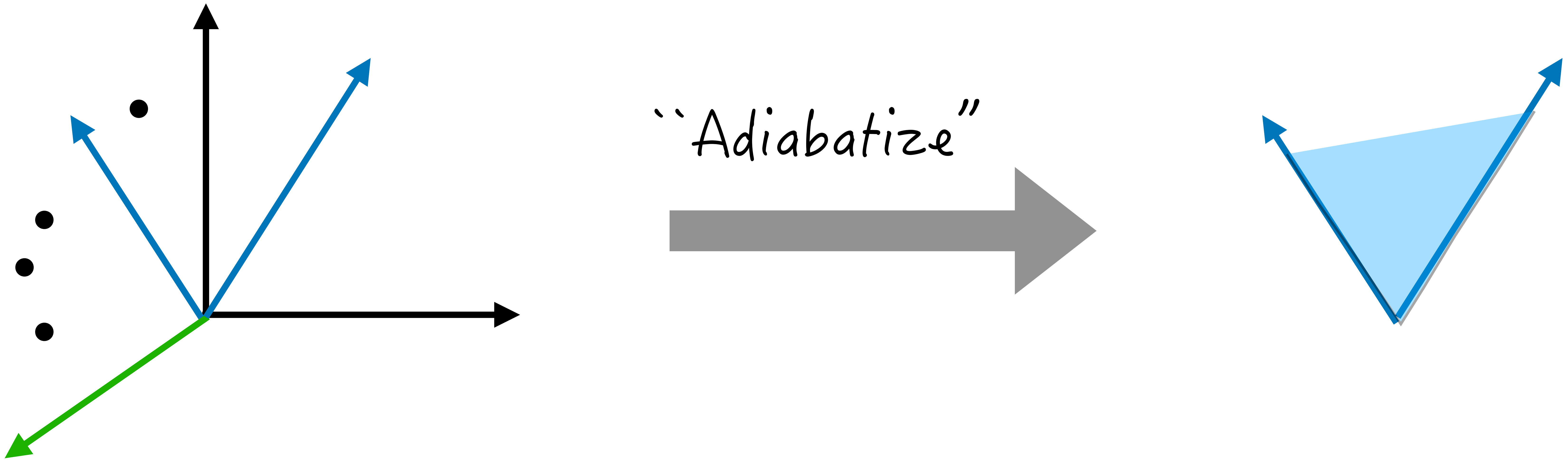
High Performance computing centre, IIT Kanpur

- Which junctions important? Quantum, Classical….
- Mapping the web for large systems?
- Junctions unimportant in the presence of a ``bath”?
- Nonadiabatic dynamics….



``BO” slow web