NEW PERSPECTIVES INTO THE CHAOTIC DYNAMICS IN MOLECULES

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Grupo de Sistemas Complejos

Universidad Politécnica de Madrid (Spain)

Dynamics Days Central Asia VI

5 June 2020

NOLINEAL 20

12th International Conference on Nonlinear Mathematics and Physics

Madrid (Spain)

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NOLINEAL 20-21

12th International Conference on Nonlinear Mathematics and Physics

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OUTLINE

Introduction

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Methodology

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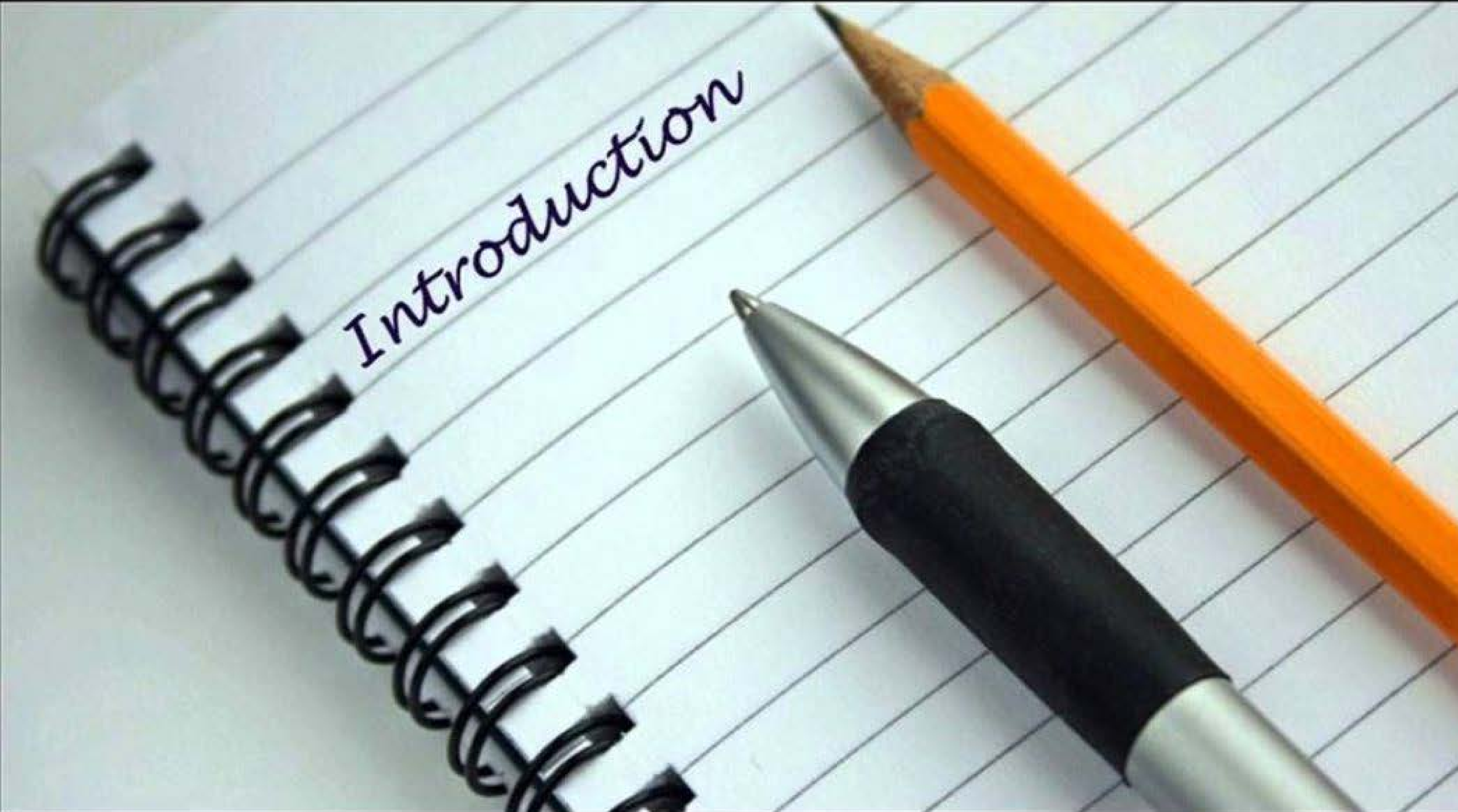
Conclusions


Introduction

PHYSICAL REVIEW E **99**, 032221 (2019)

Unveiling the chaotic structure in phase space of molecular systems using Lagrangian descriptors

F. Revuelta,[1,2,*] R. M. Benito,[1,†] and F. Borondo[2,3,‡]

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[2] *Instituto de Ciencias Matemáticas (ICMAT), Cantoblanco, 28049 Madrid, Spain*

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CHAOS INDICATORS

PSOS - Poincaré Surface of section

Lyapunov exponent

Frequency Analisys - Laskar

SALI and **GALI** (Small and Generalized ALignment Index - Skokos.

FLI (Fast Lyapunov Indicator) - Lega, Guzzo, Froeschlé.

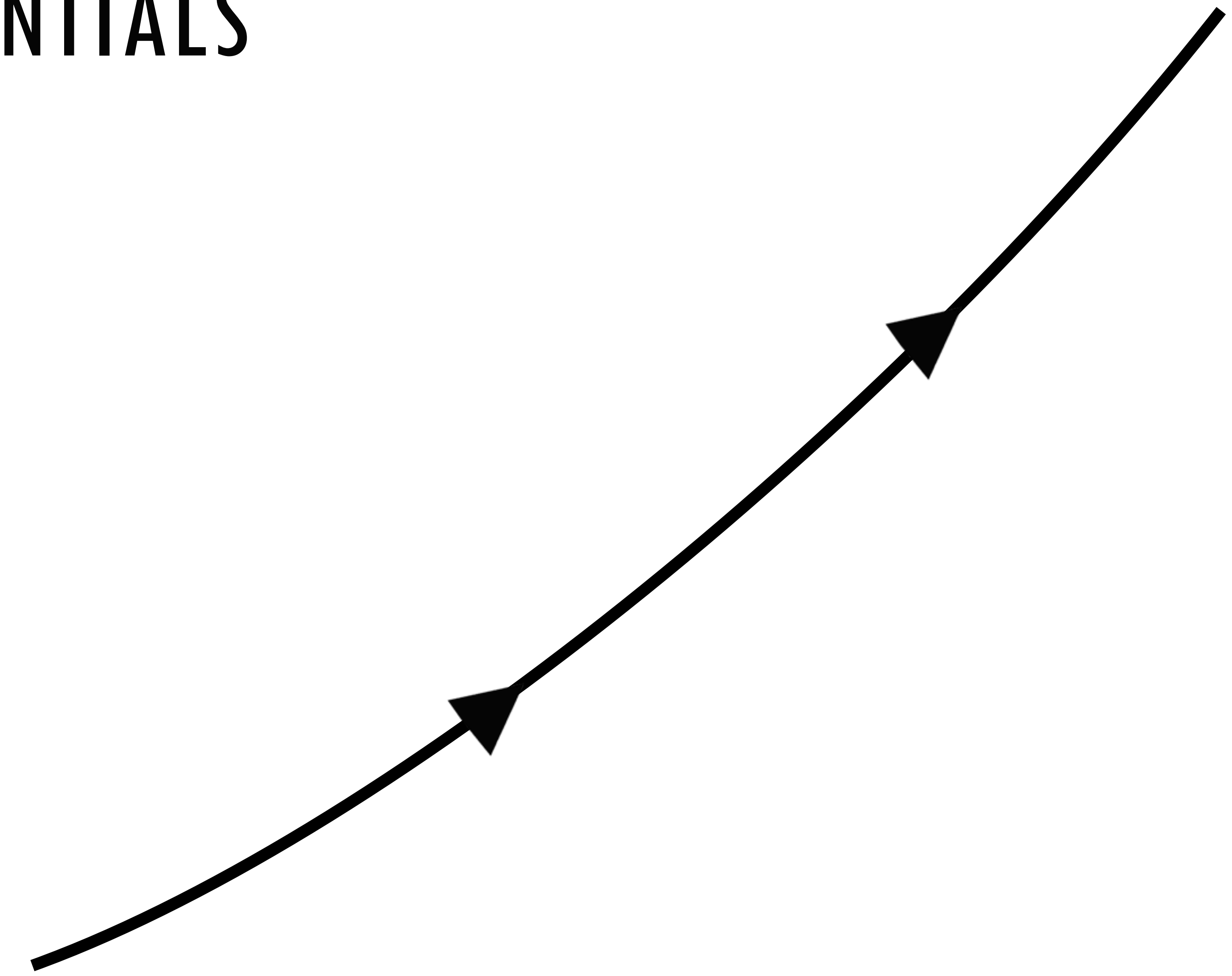
OFLI (Orthogonal Fast Lyapunov Indicator) - Barrio.

MEGNO (Mean Exponential Growth Factor of Nearby Orbits) - Cincotta, Simó

…

ESSENTIALS

ESSENTIALS



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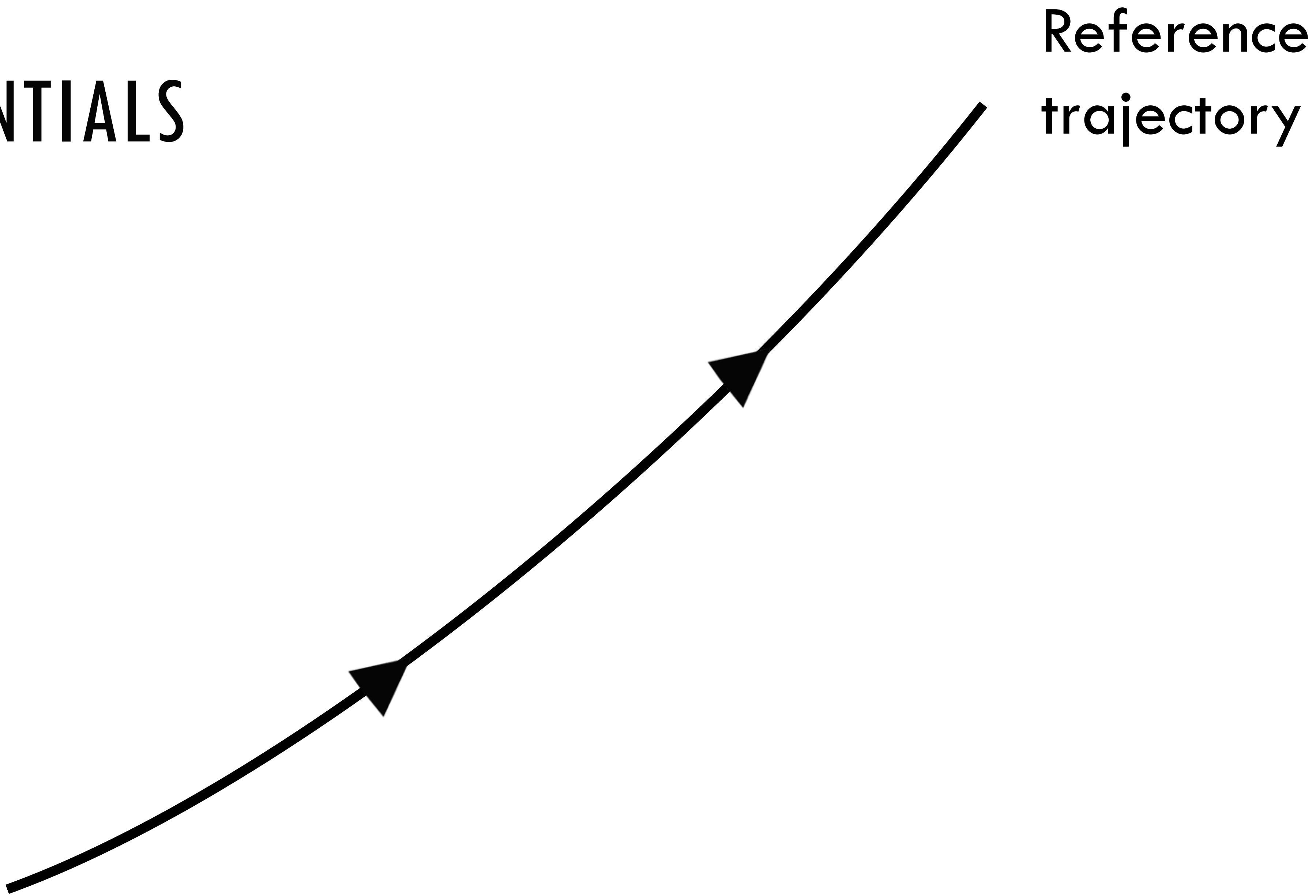

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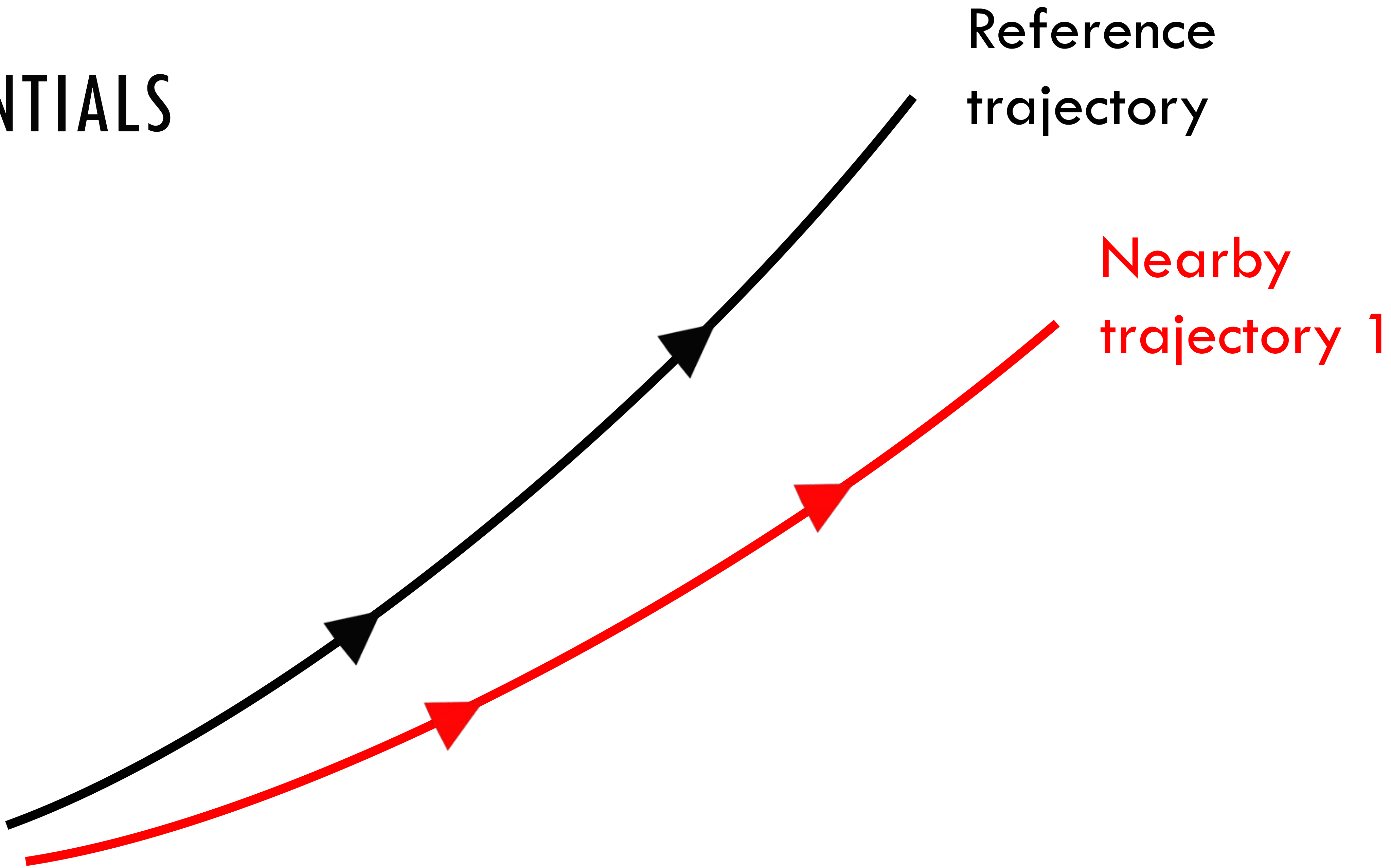

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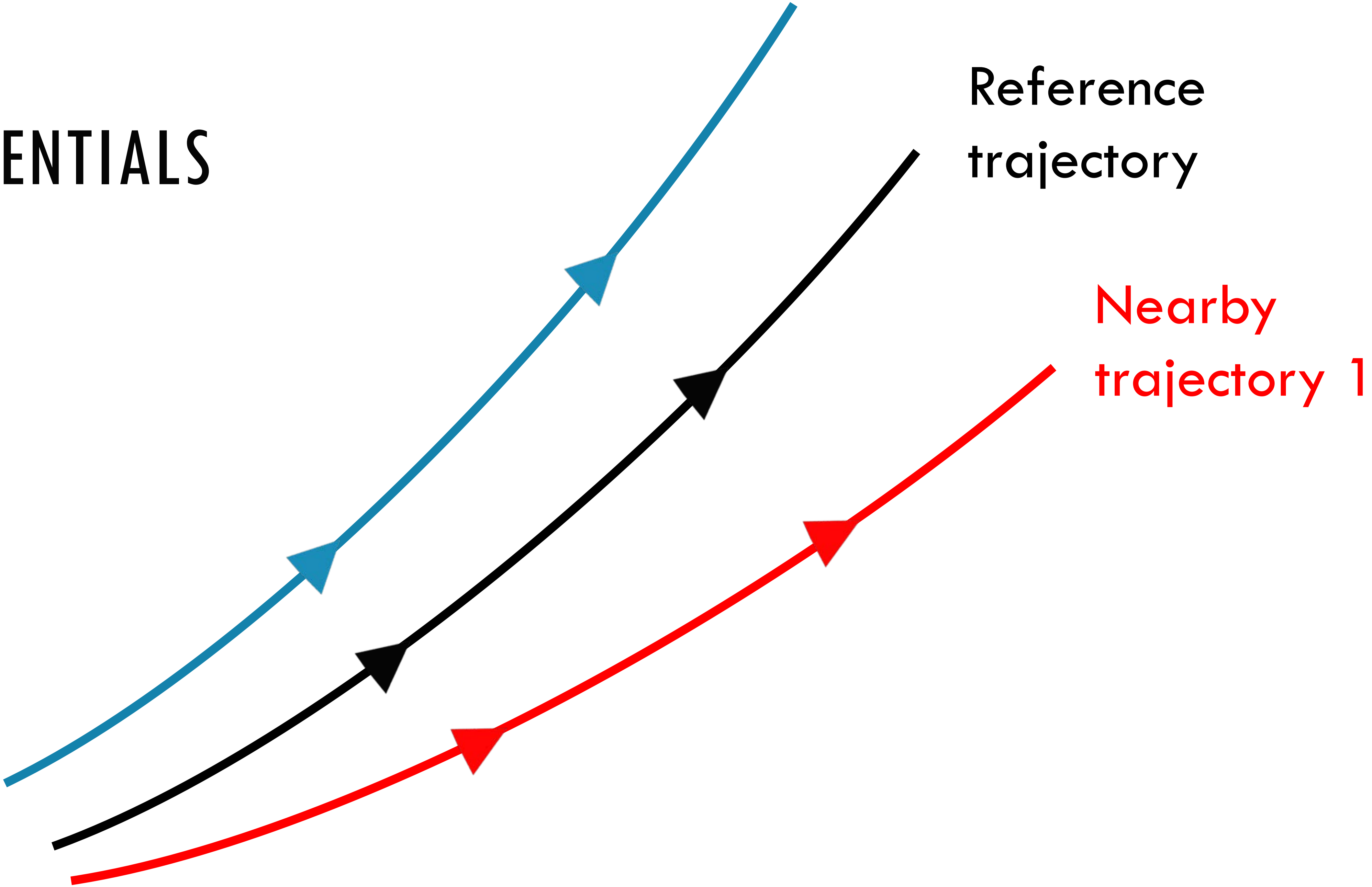

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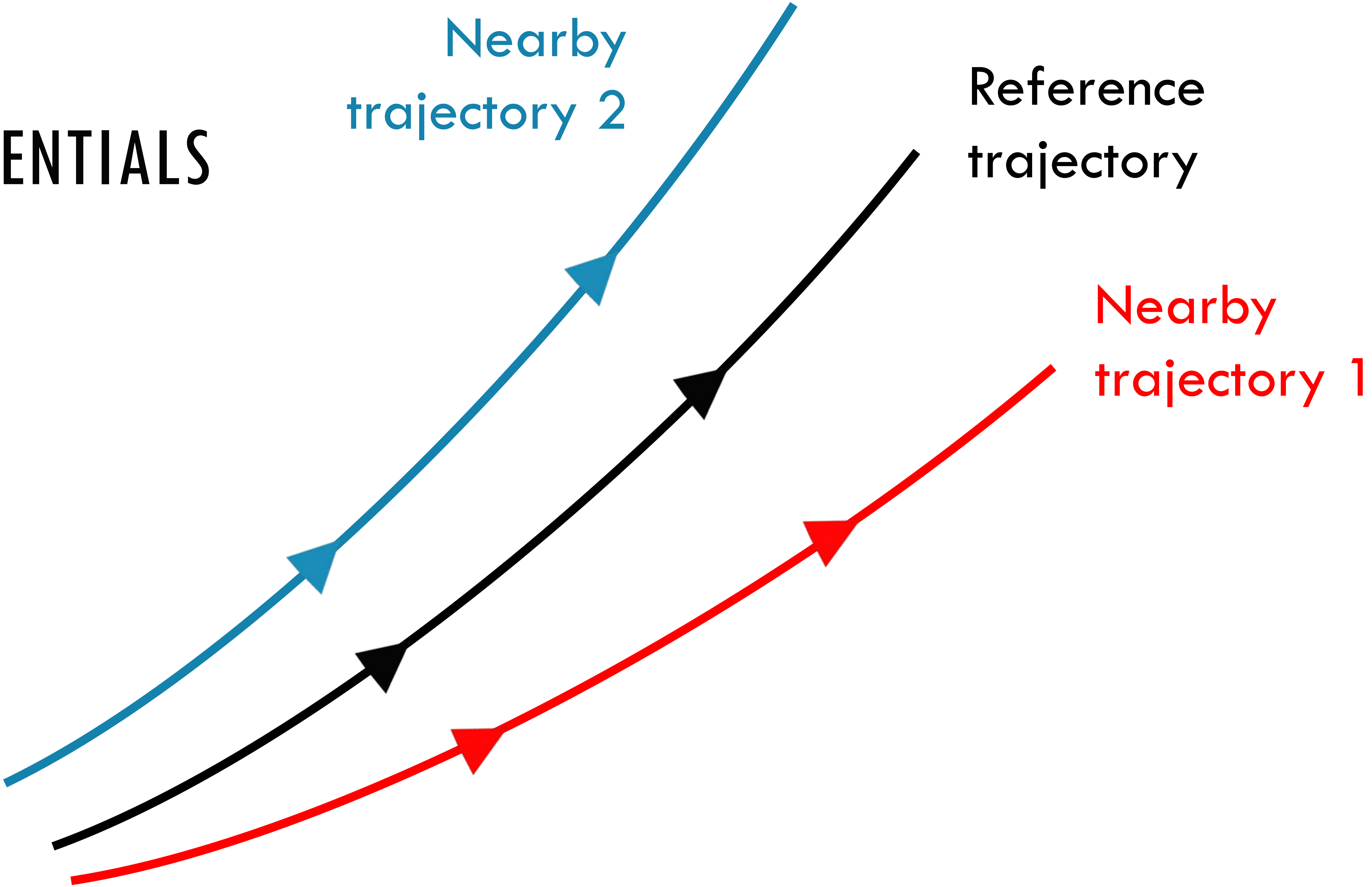
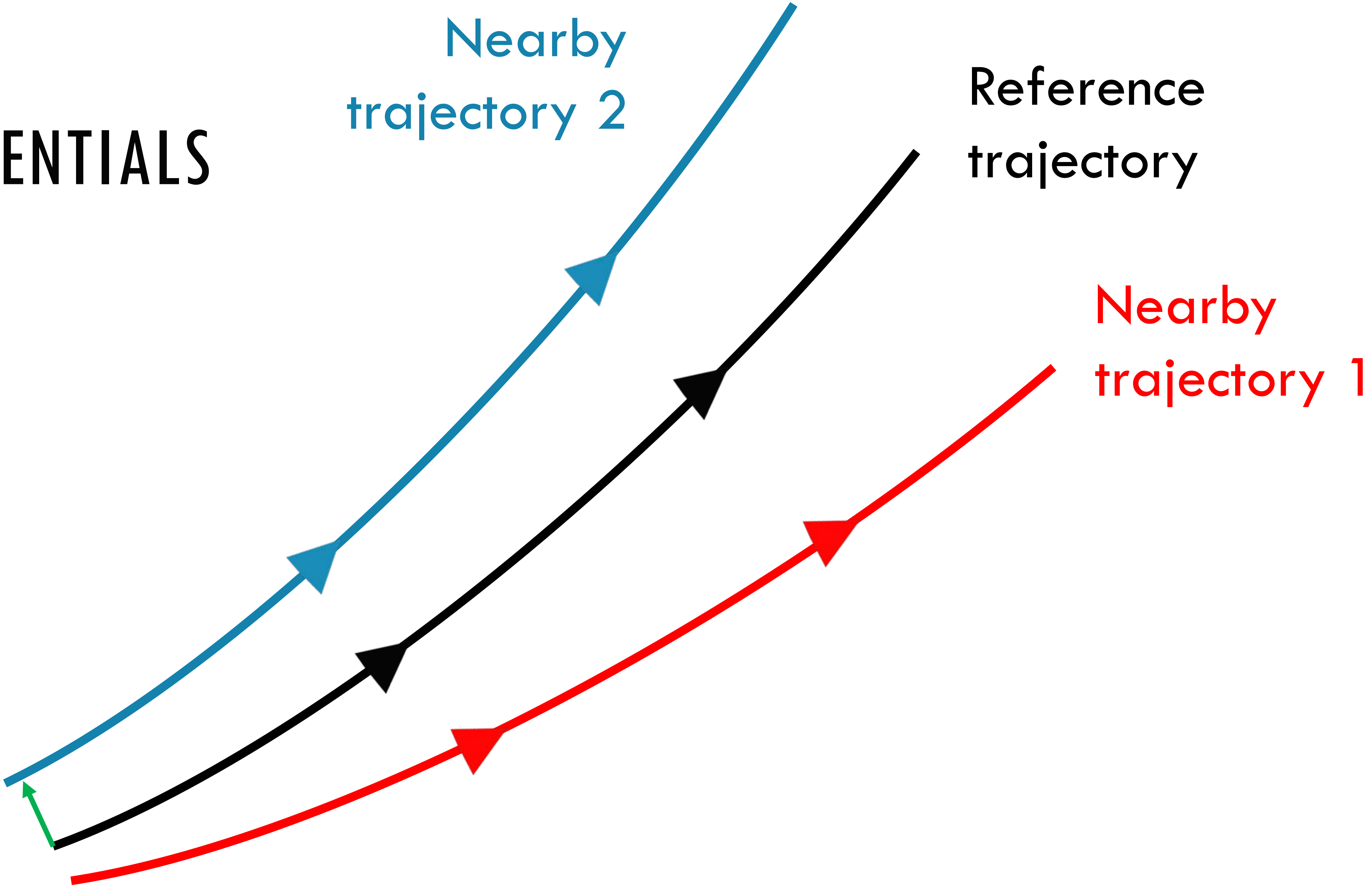
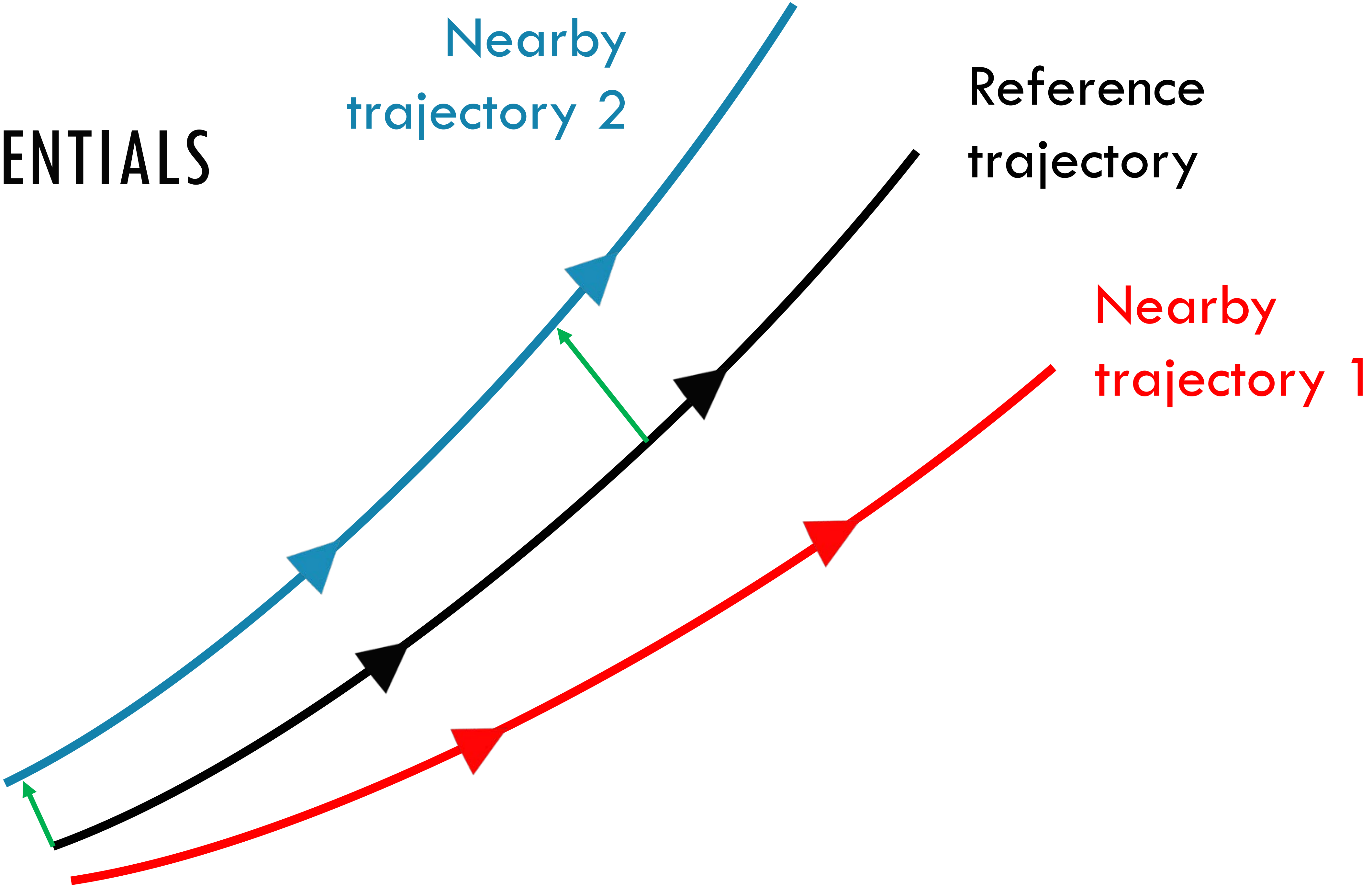

Nearby
trajectory 2
Reference
trajectory
Nearby
trajectory 1

ESSENTIALS


Nearby trajectory 2
Reference trajectory
Nearby trajectory 1

ESSENTIALS


Nearby
trajectory 2
Reference
trajectory
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trajectory 1

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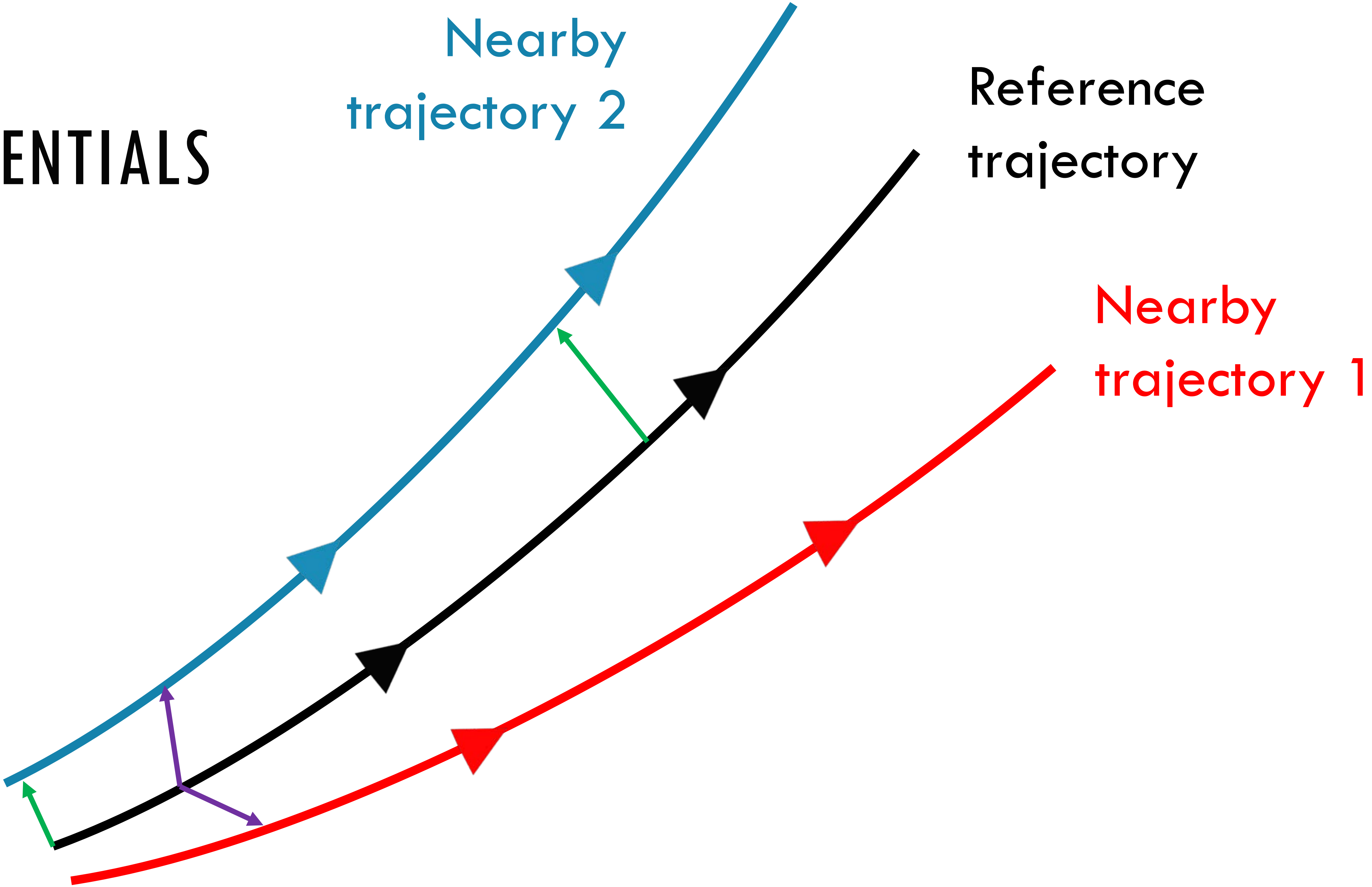
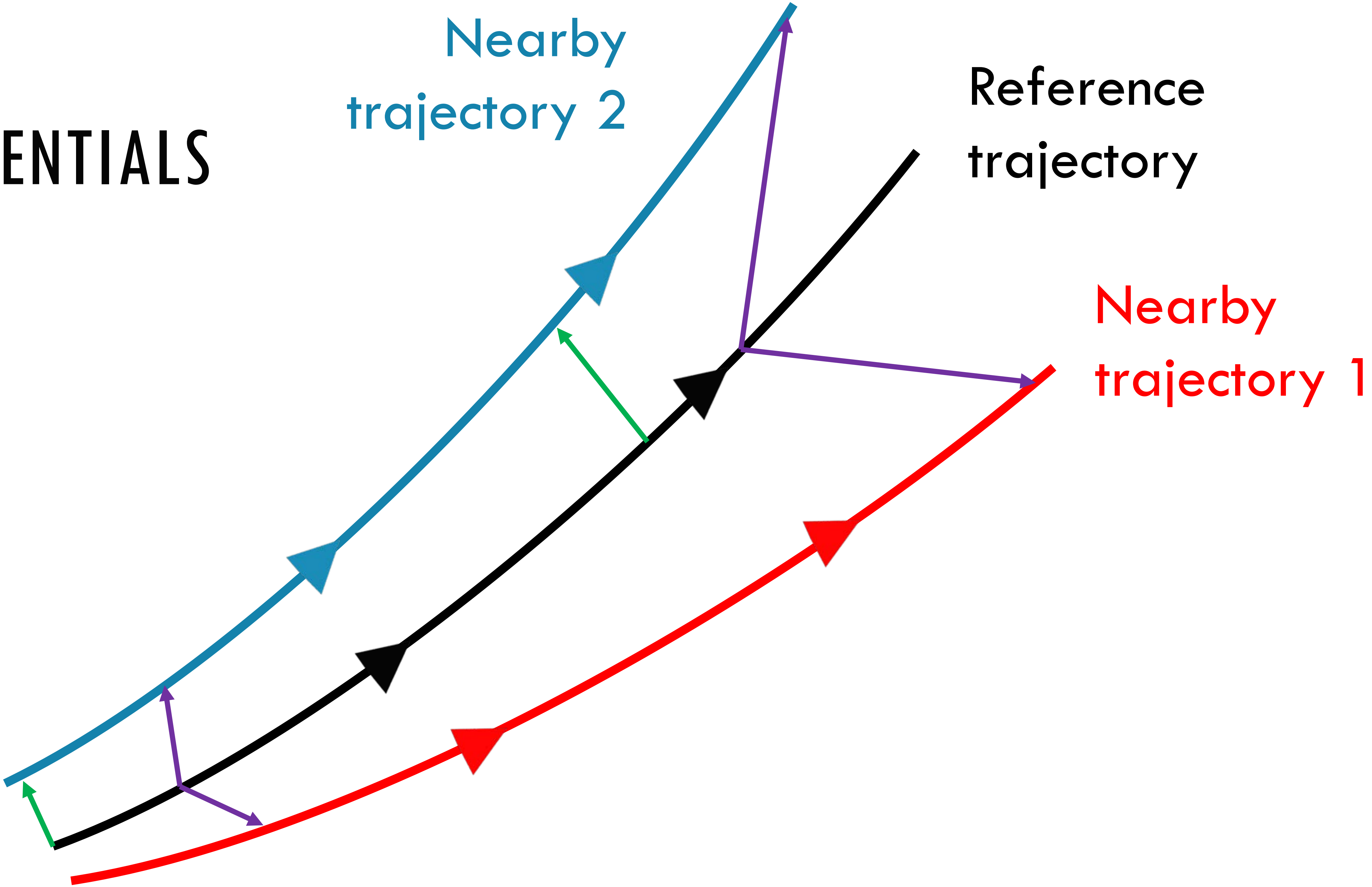


Nearby trajectory 2
Reference trajectory
Nearby trajectory 1

ESSENTIALS


Nearby
trajectory 2
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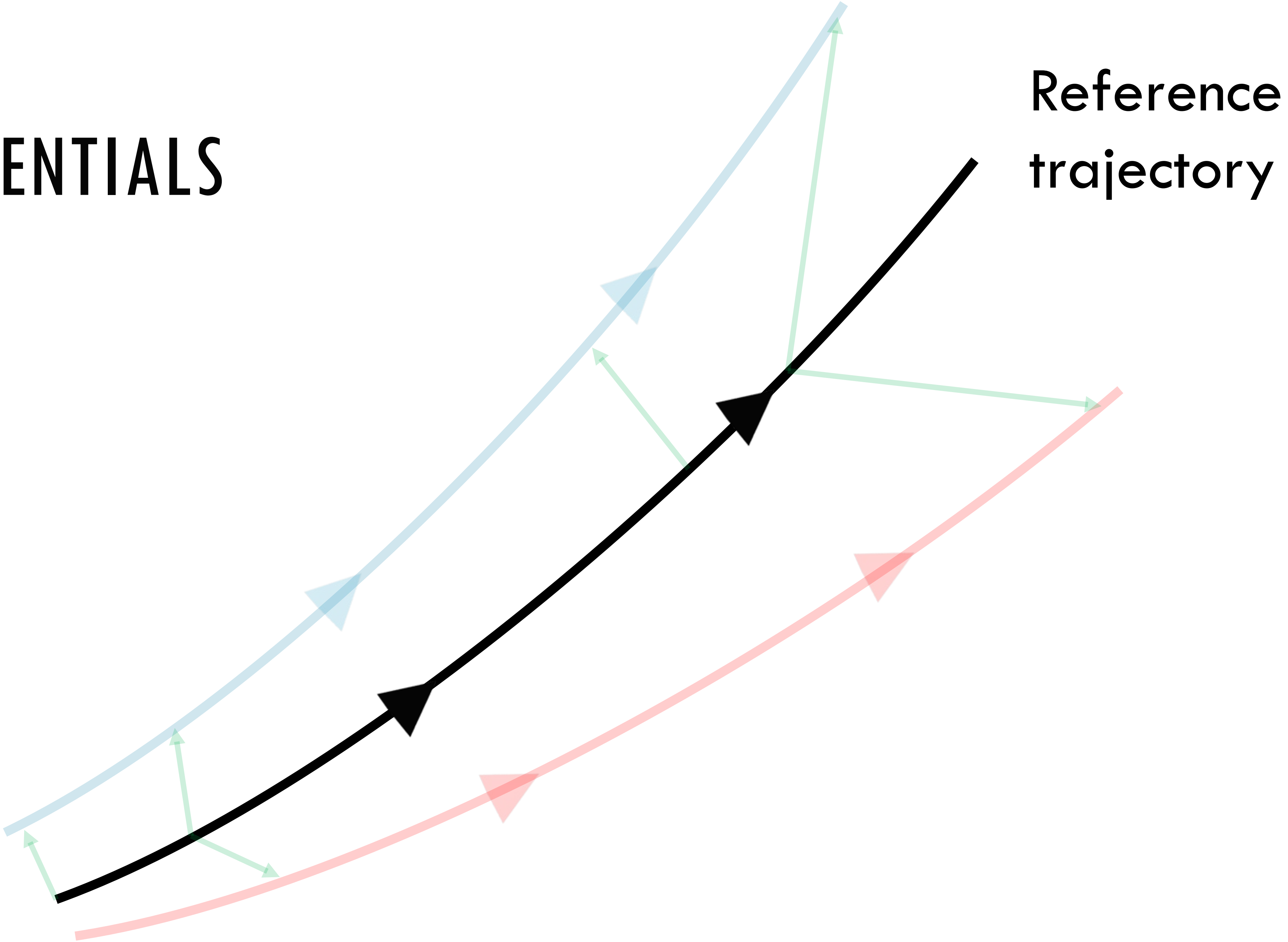

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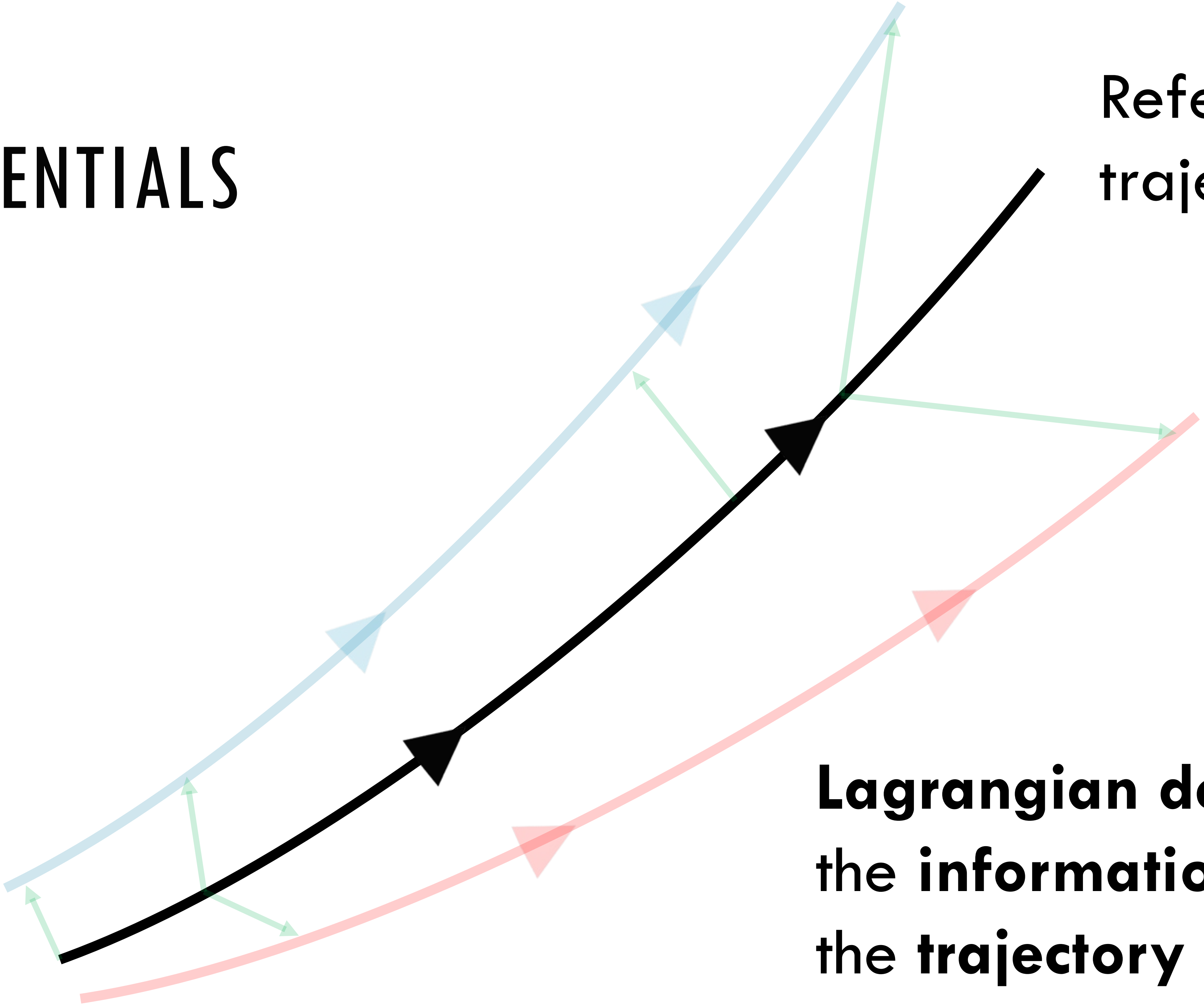

Reference trajectory

Lagrangian descriptors: all the **information** encoded in the **trajectory** itself!

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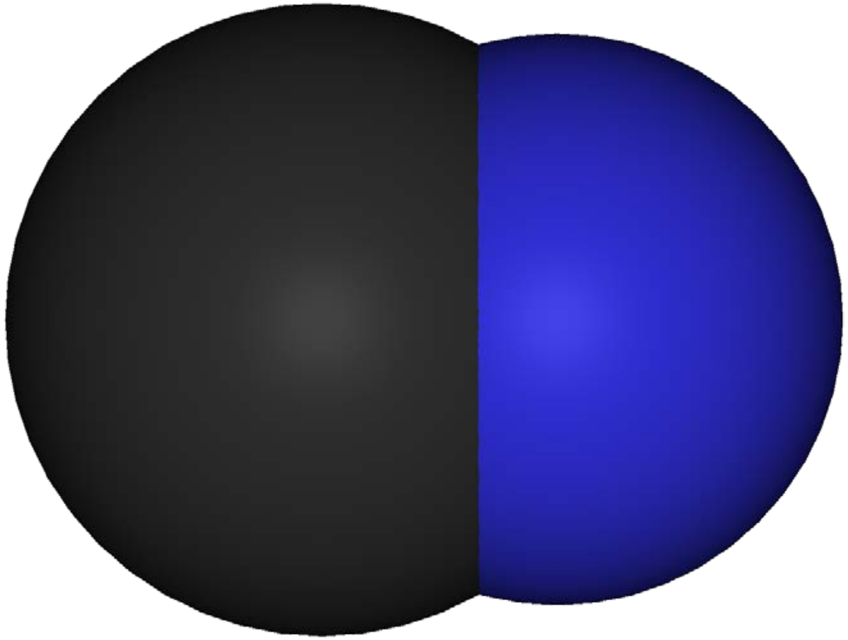
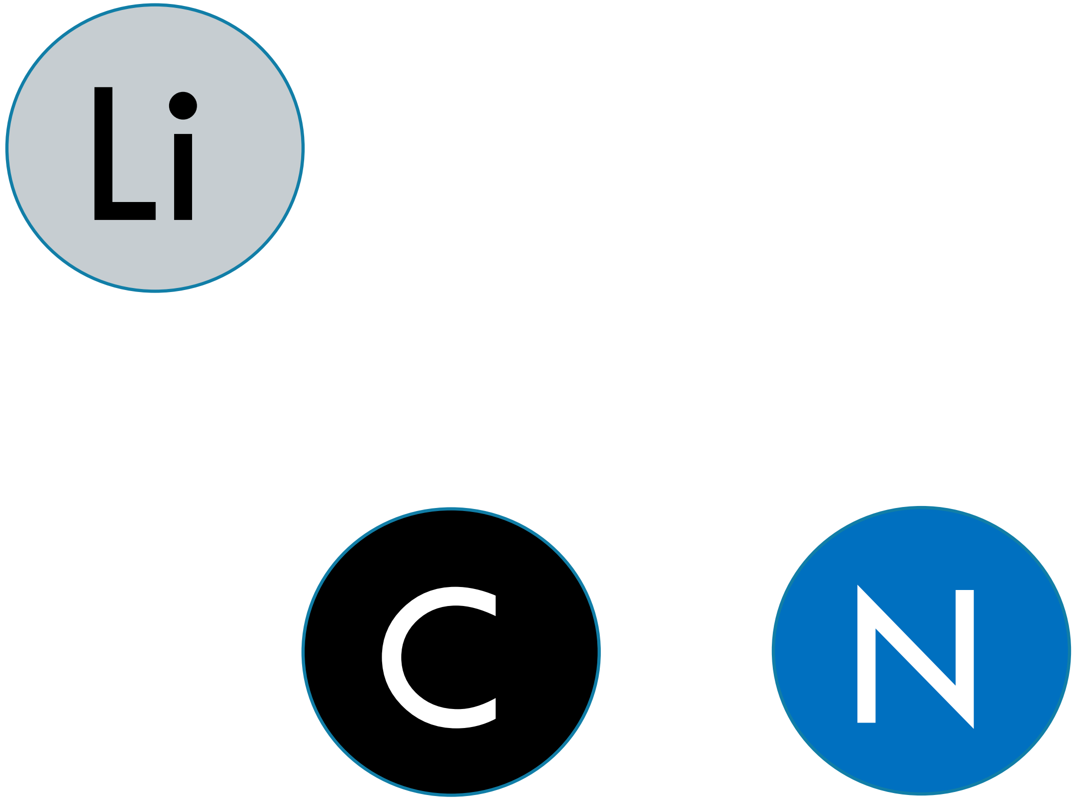
SYSTEM



WHY MOLECULES???

1. Atomic and molecular systems: excellent platforms for application of **dynamical systems theory**
2. ⇑⇑⇑ **anharmonic**
3. “Simple” (**2 dof**)

SYSTEM



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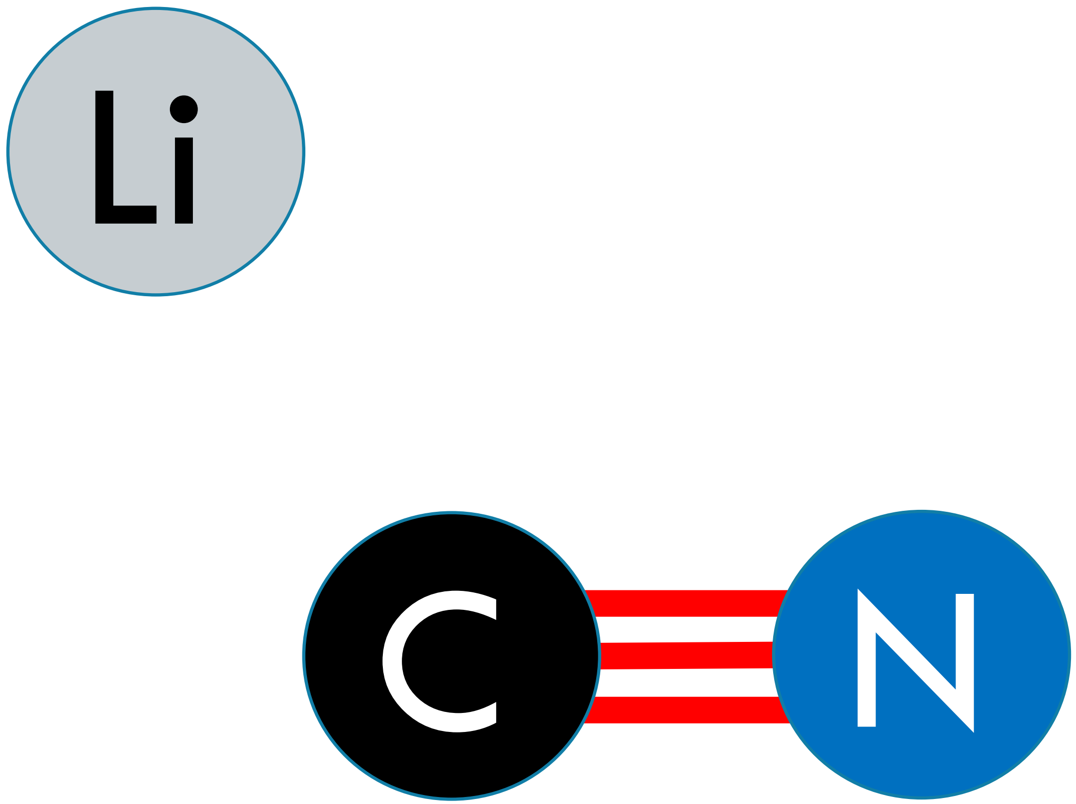

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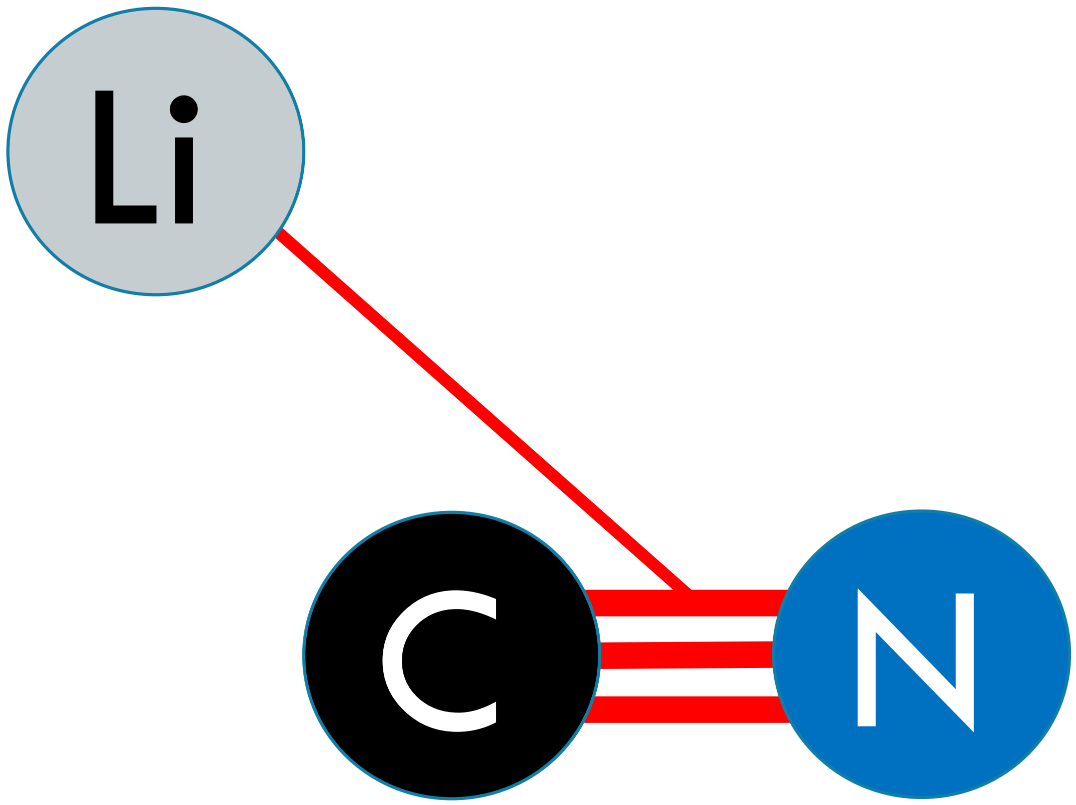

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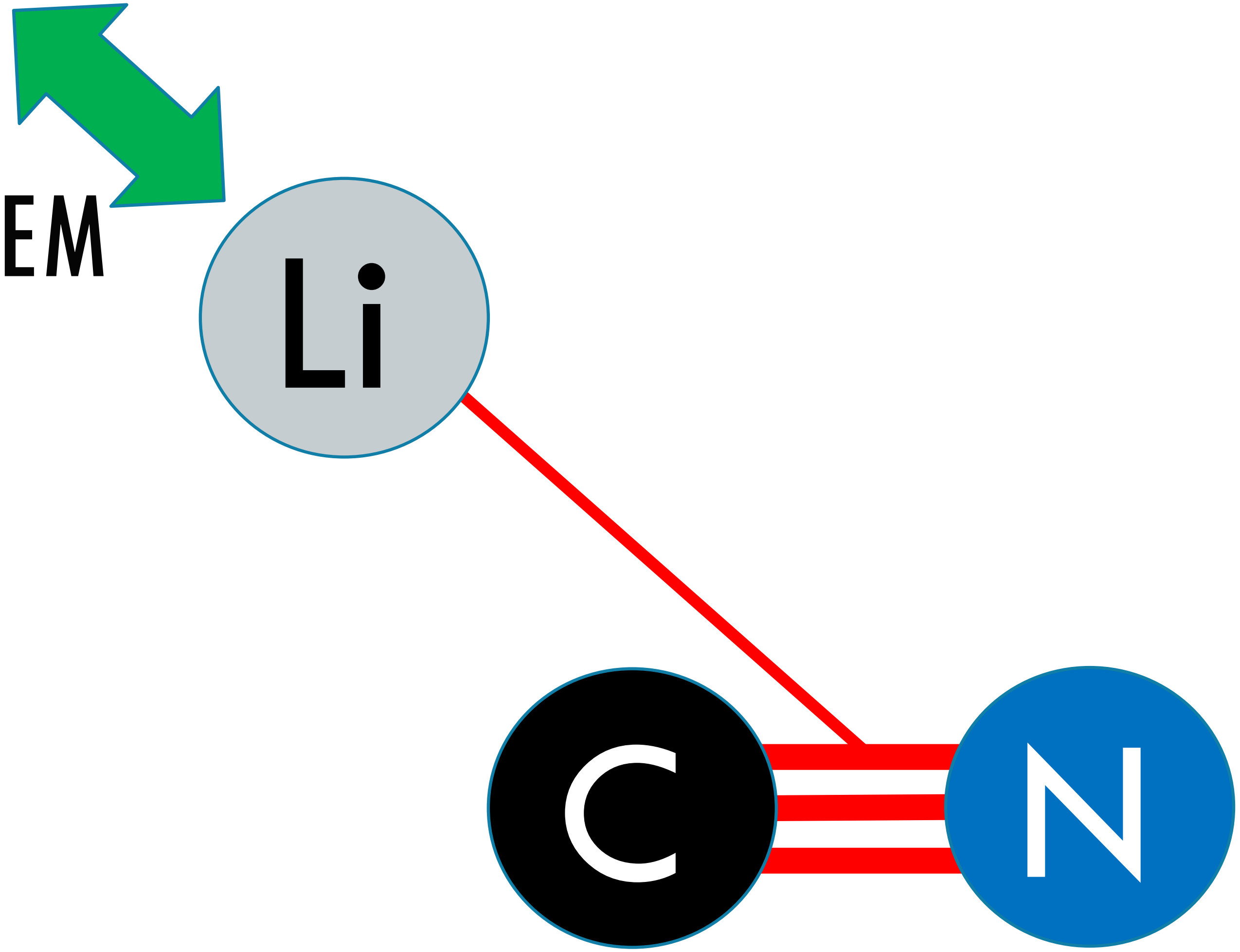

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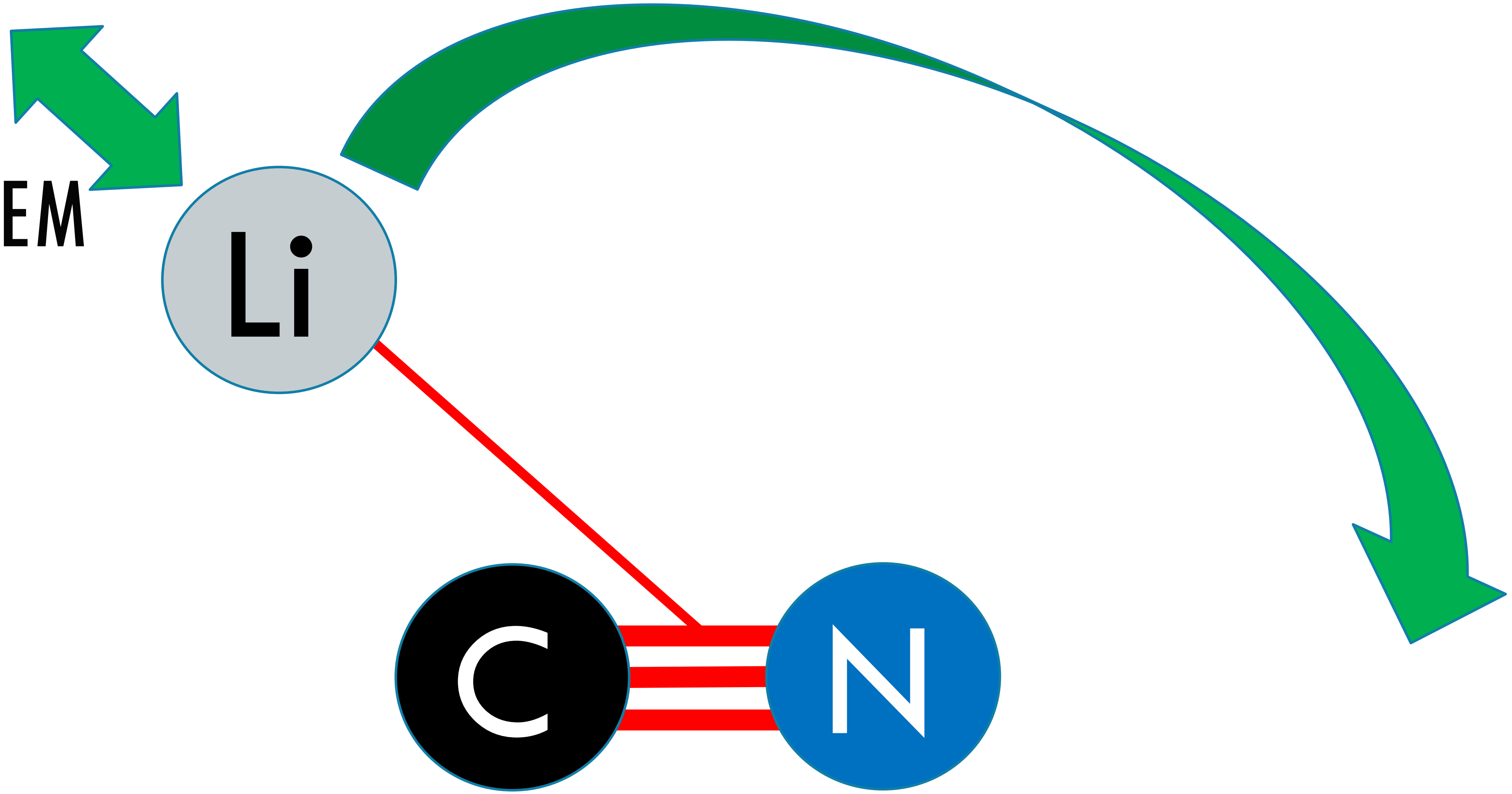

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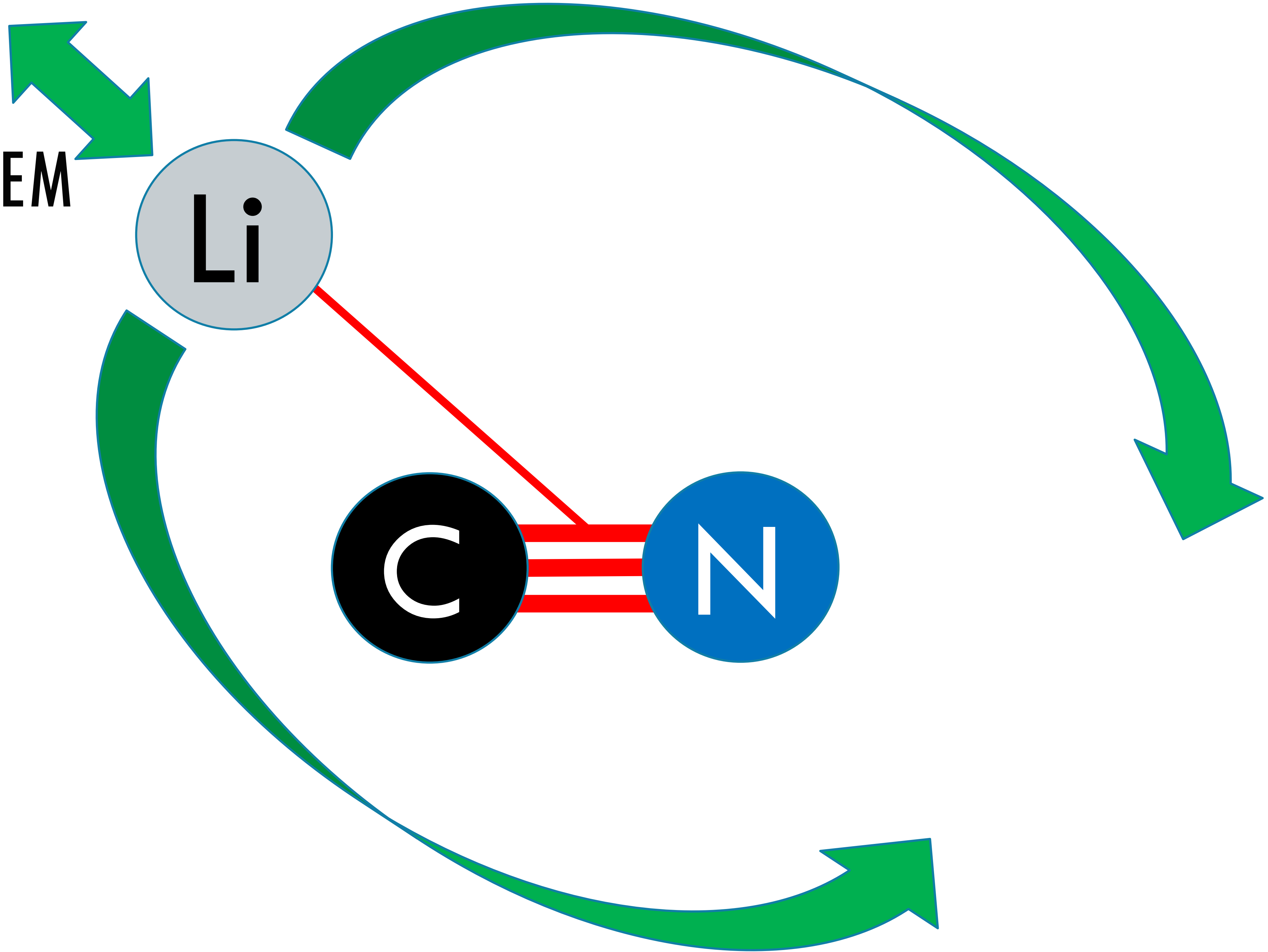
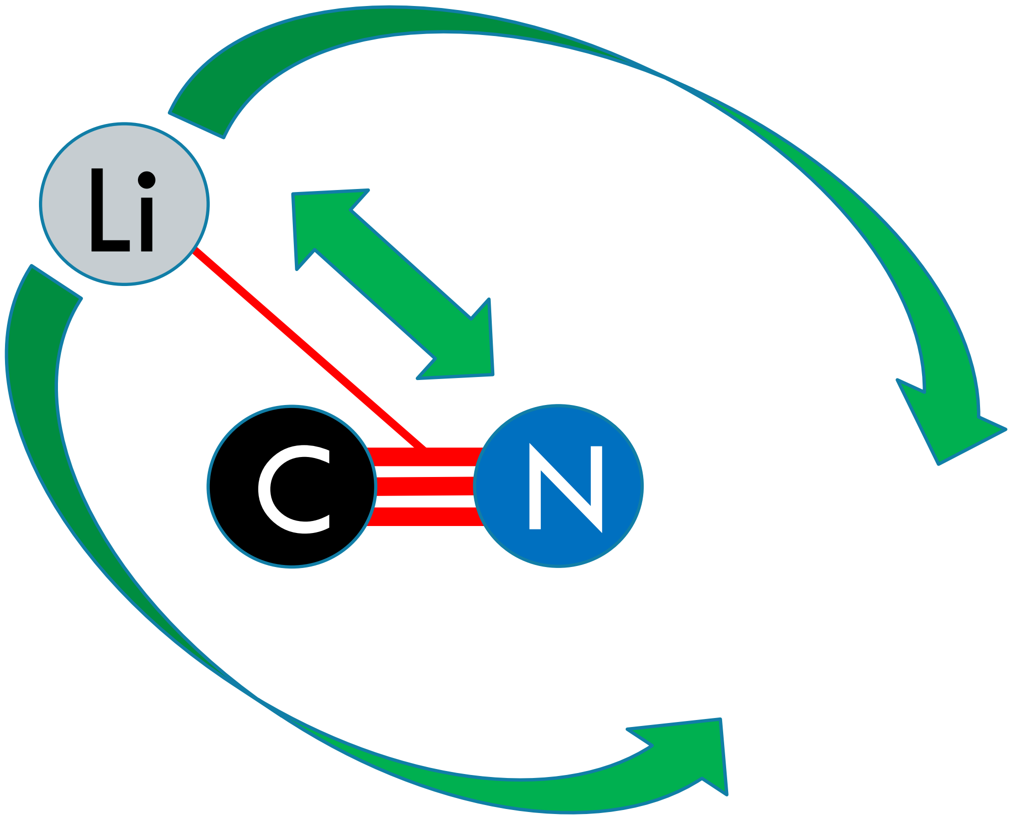
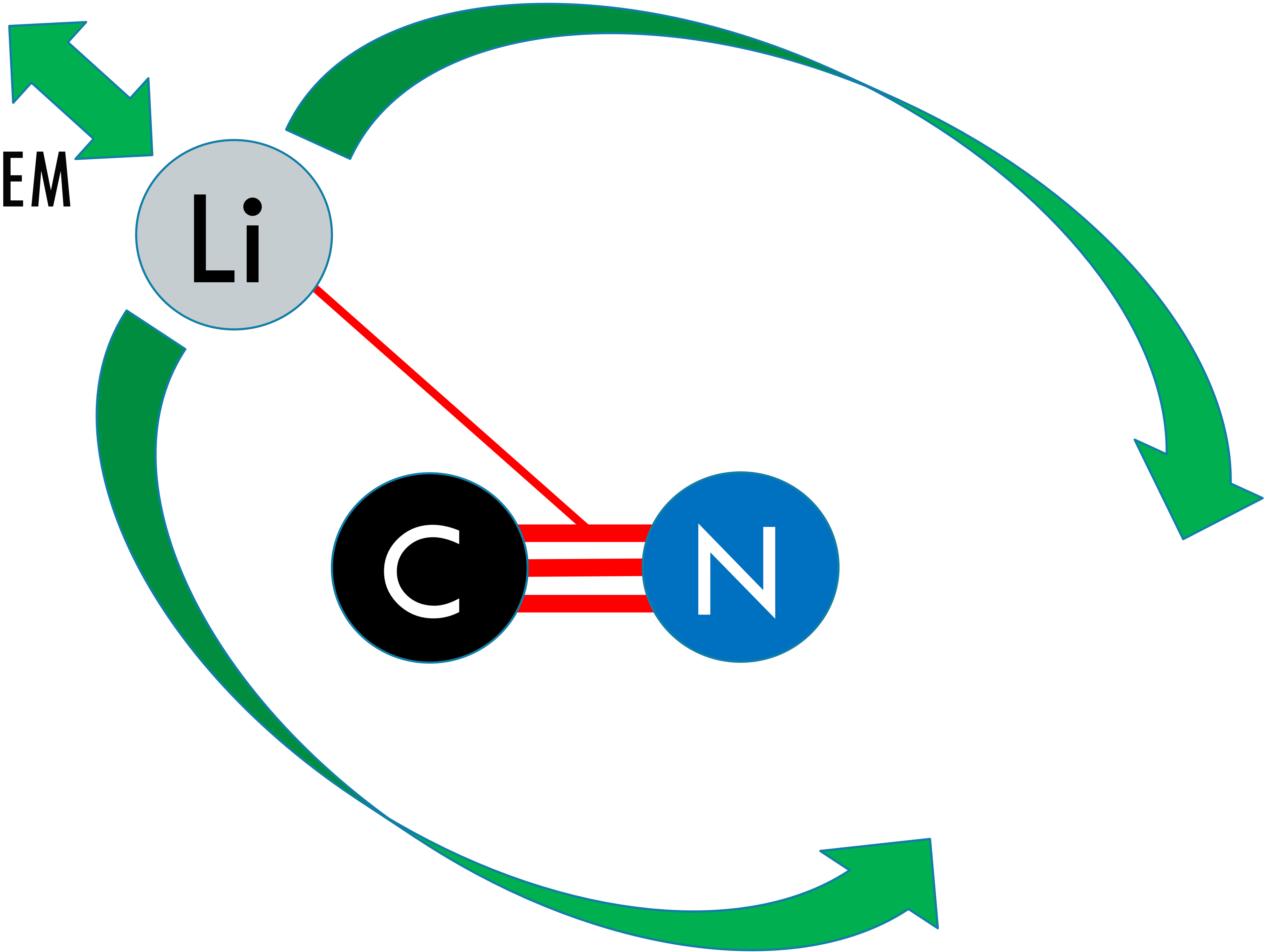


SYSTEM

1. 3 atoms: 9 dof
2. No rotation: - 6 dof
3. Coordinates: **R**, **θ**, **r**



SYSTEM



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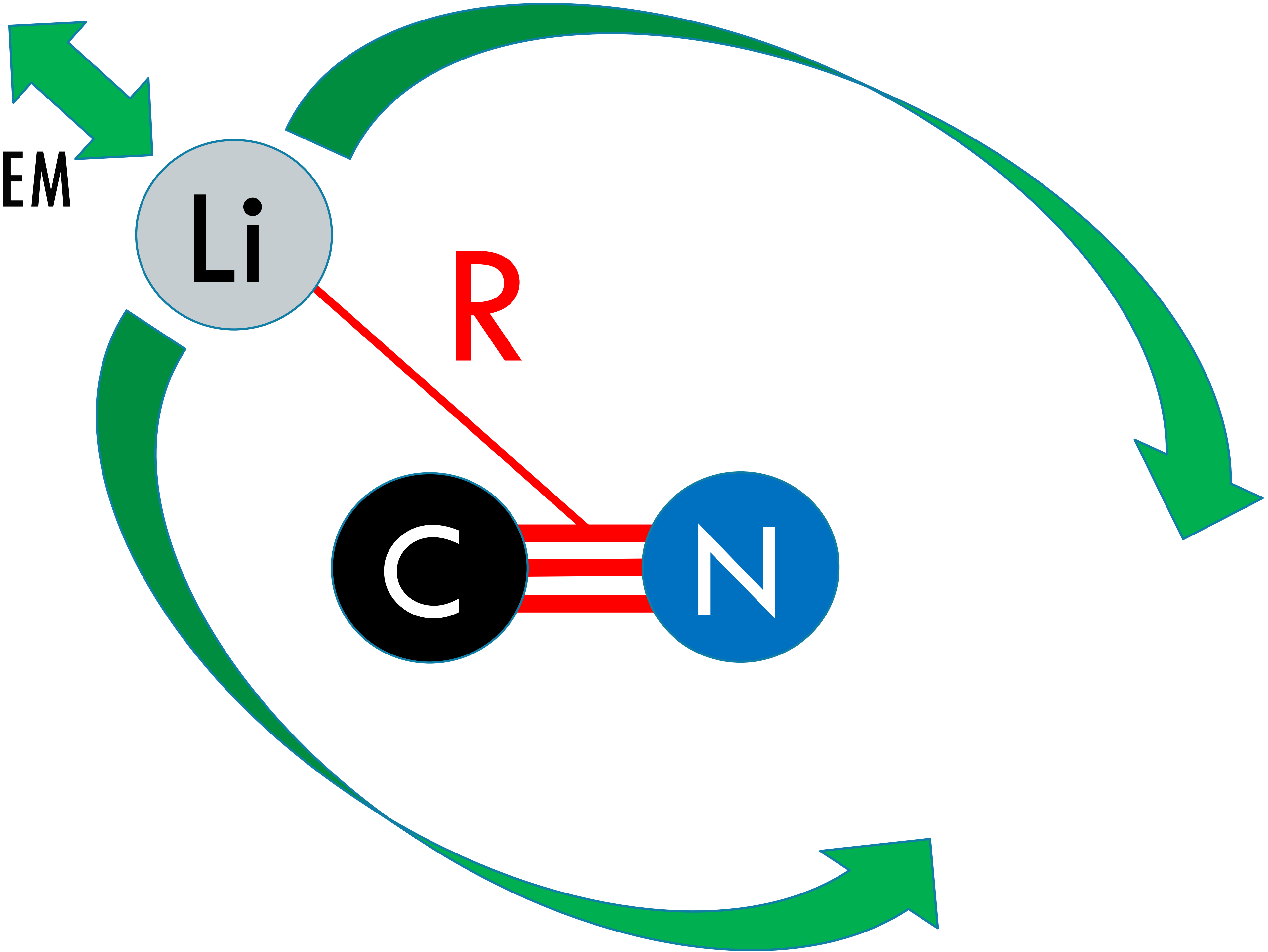

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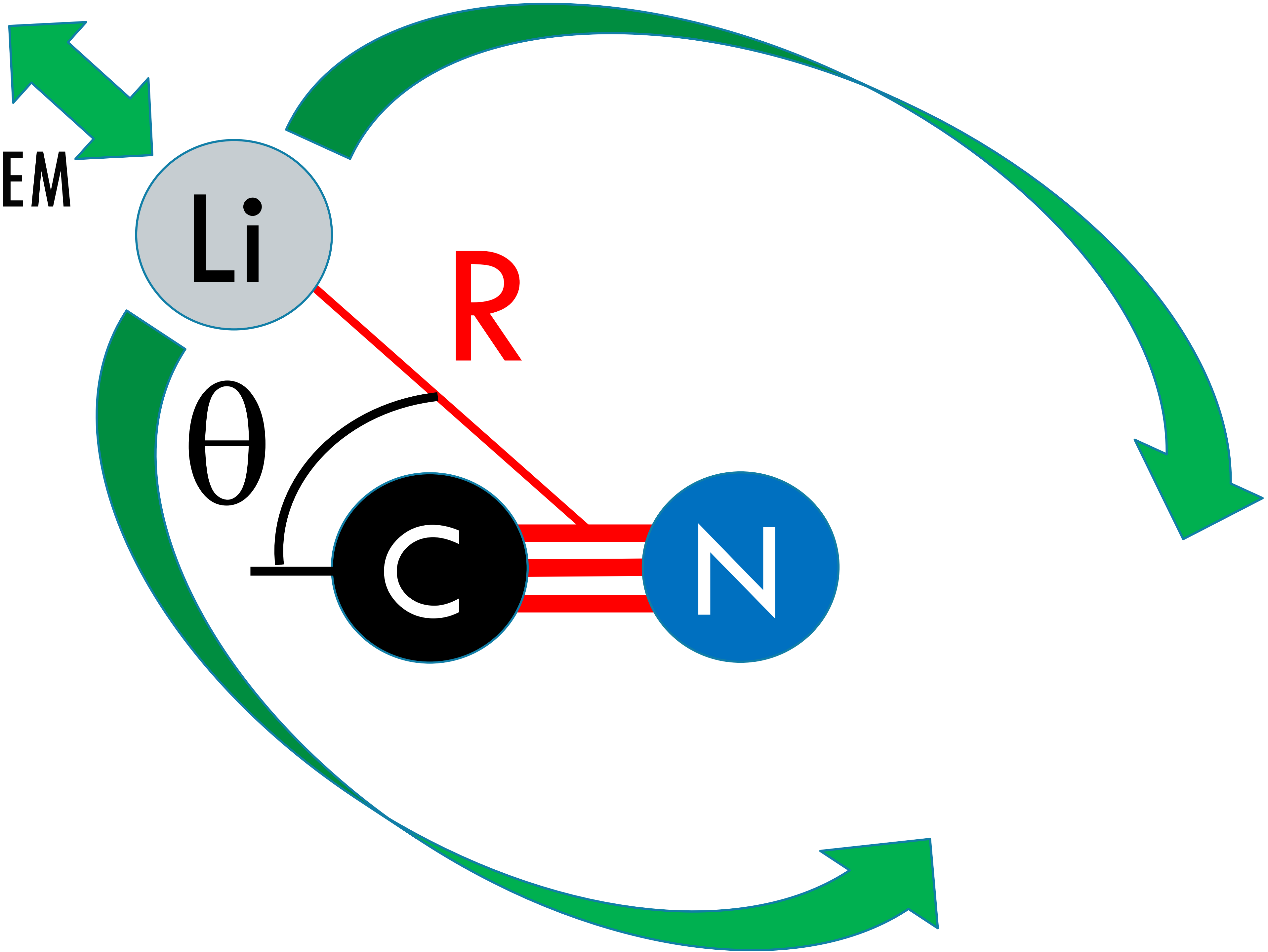

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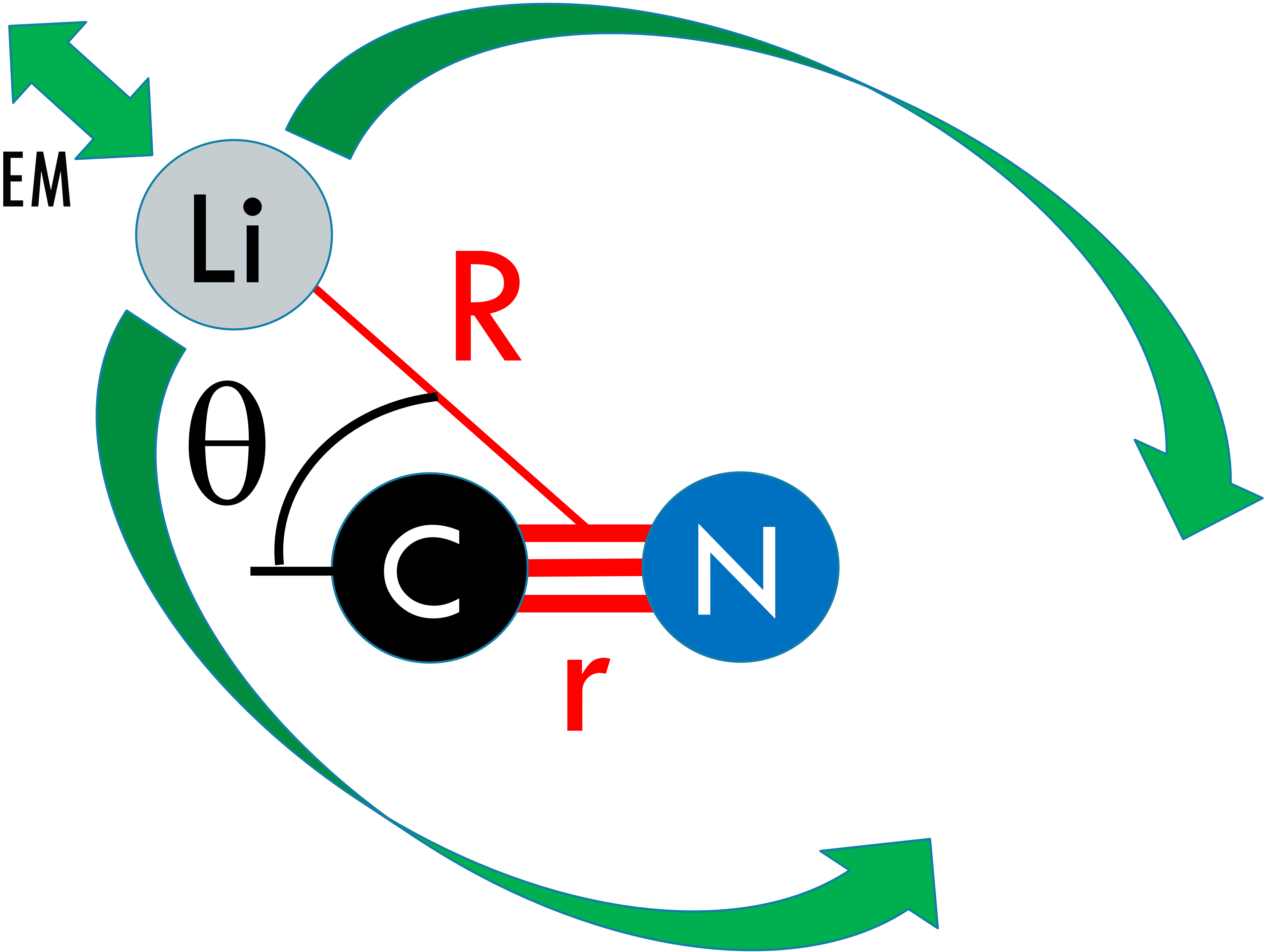
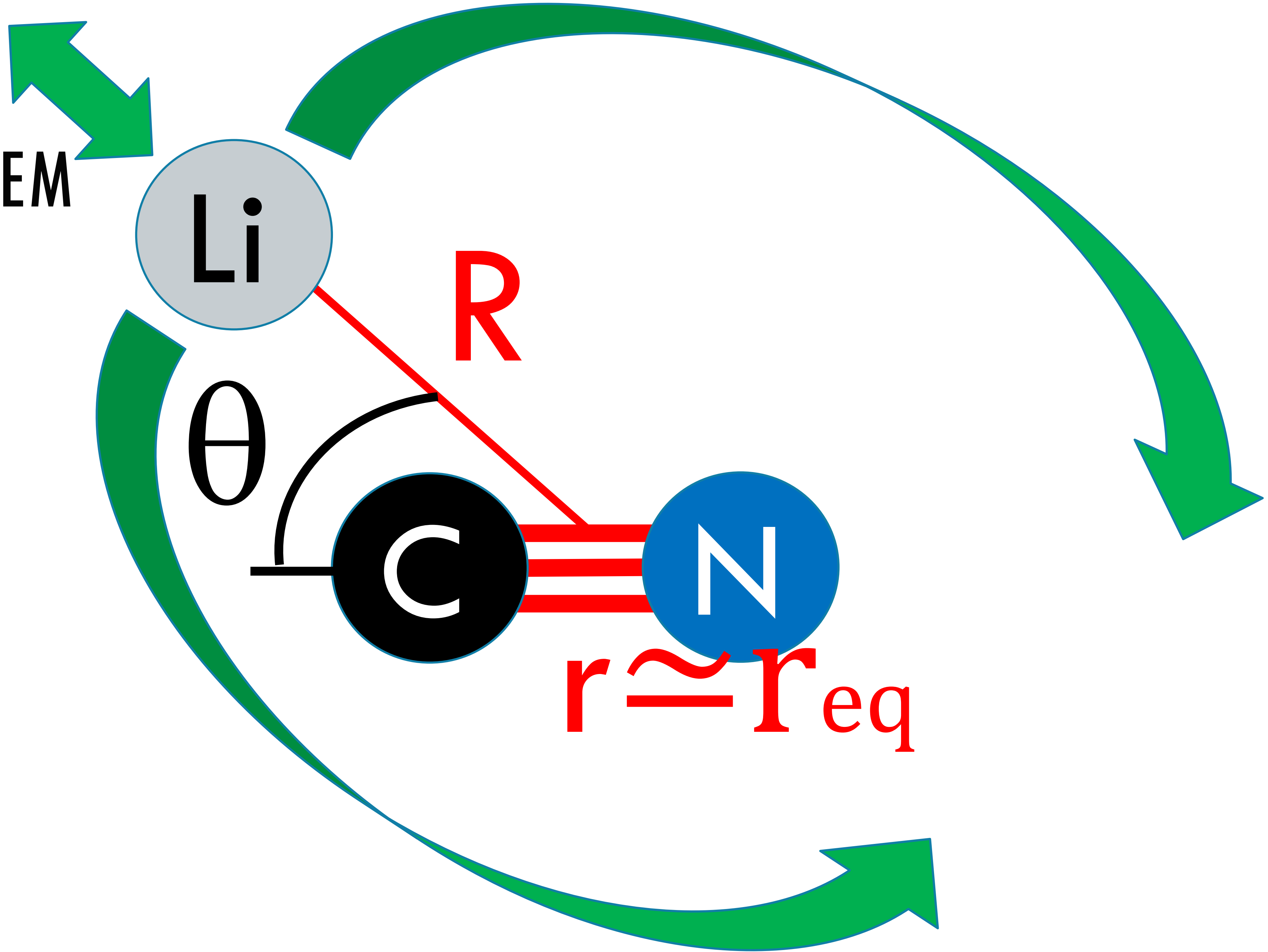
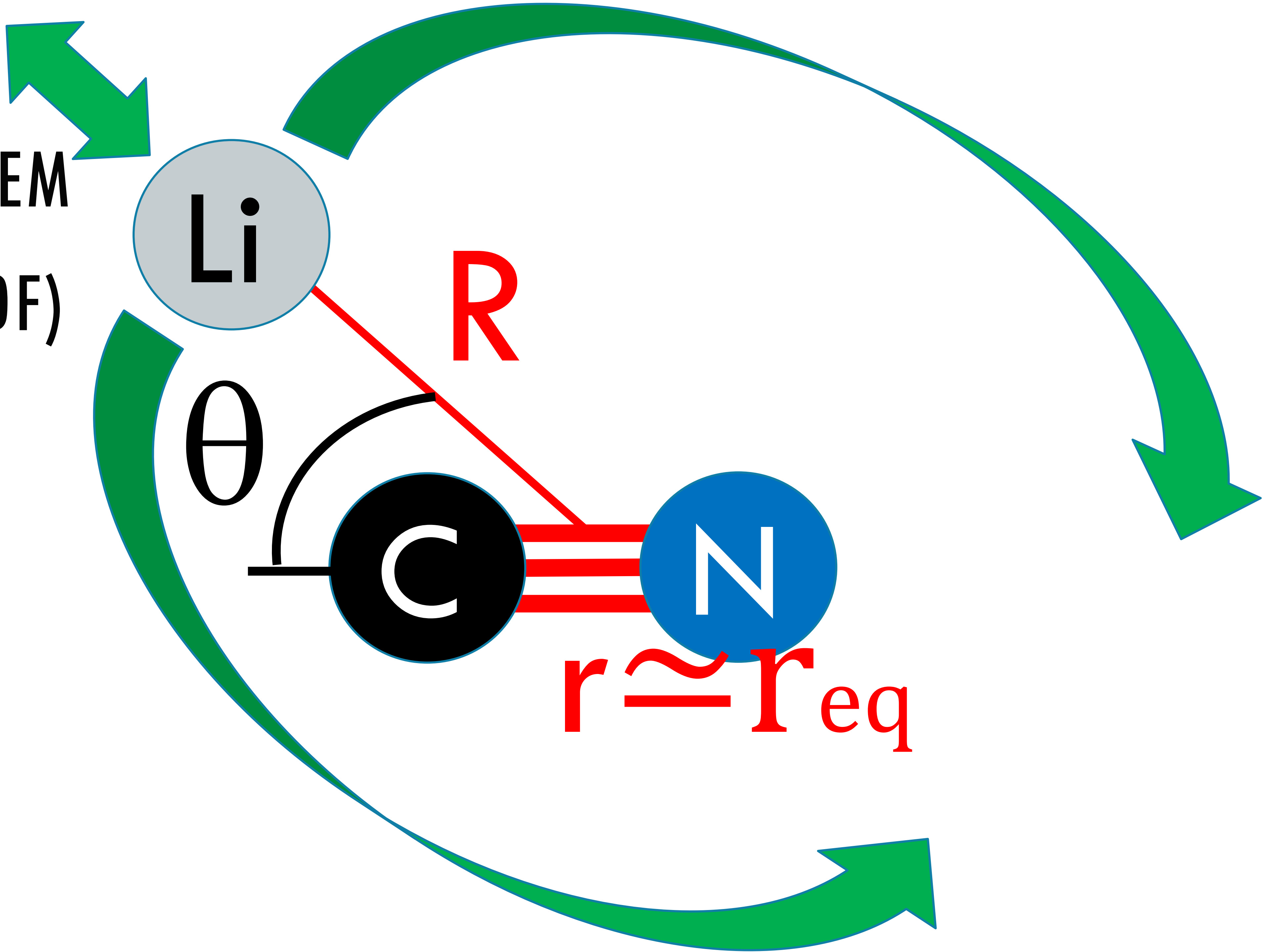


SYSTEM



SYSTEM (2 DOF)



HAMILTONIAN

HAMILTONIAN

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

HAMILTONIAN

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

$$\mu_1 = m_{\mathrm{K}}(m_{\mathrm{C}}+m_{\mathrm{N}})/(m_{\mathrm{K}}+m_{\mathrm{C}}+m_{\mathrm{N}})$$

HAMILTONIAN

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

$$\mu_1 = m_{\mathrm{K}}(m_{\mathrm{C}}+m_{\mathrm{N}})/(m_{\mathrm{K}}+m_{\mathrm{C}}+m_{\mathrm{N}})$$

$$\mu_2 = m_{\mathrm{C}}m_{\mathrm{N}}/(m_{\mathrm{C}}+m_{\mathrm{N}})$$

HAMILTONIAN

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

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HAMILTONIAN

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

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$$\mu_2 = m_{\mathrm{C}}m_{\mathrm{N}}/(m_{\mathrm{C}}+m_{\mathrm{N}})$$

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HAMILTONIAN

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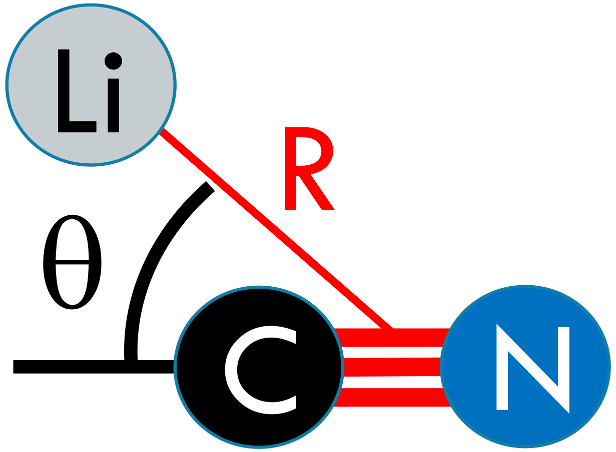
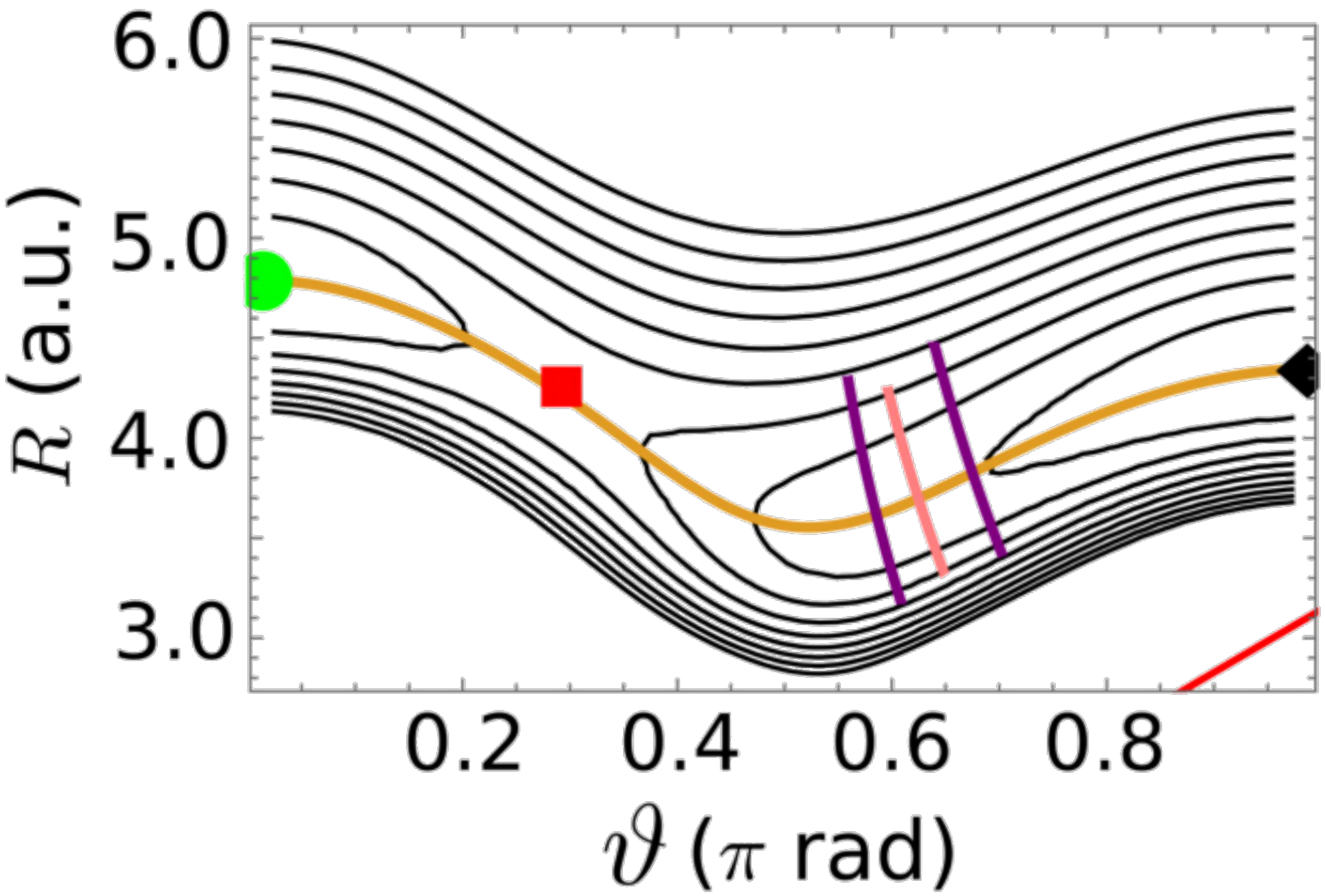
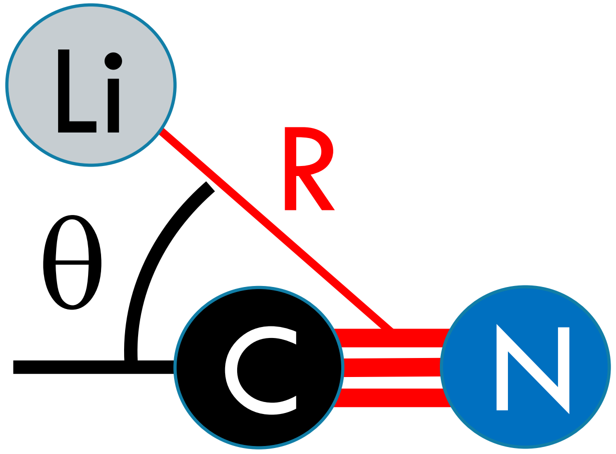
$$H = \frac{P_R^2}{2\mu_1} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r_{\text{eq}}^2}\right)\frac{P_\theta^2}{2} + V(R, r_{\text{eq}}, \theta)$$

POTENTIAL ENERGY SURFACE



POTENTIAL ENERGY SURFACE





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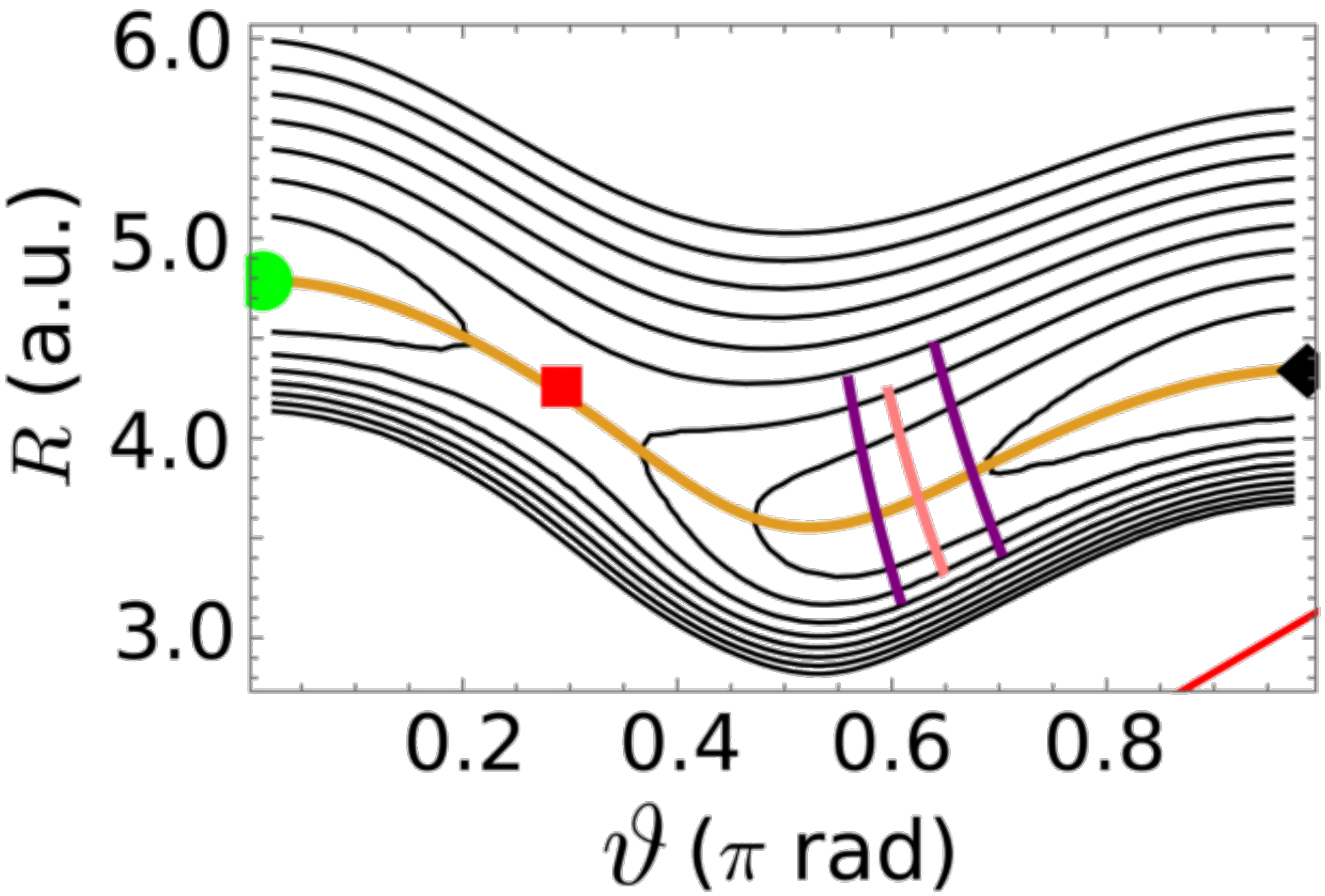
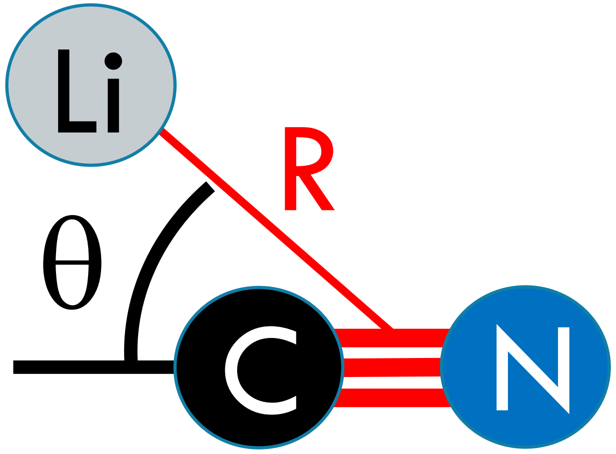
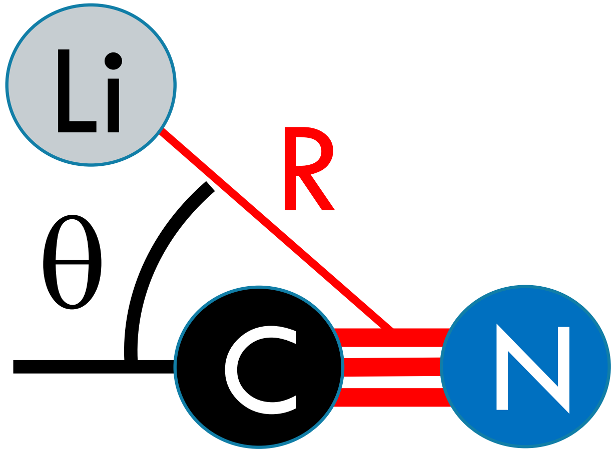
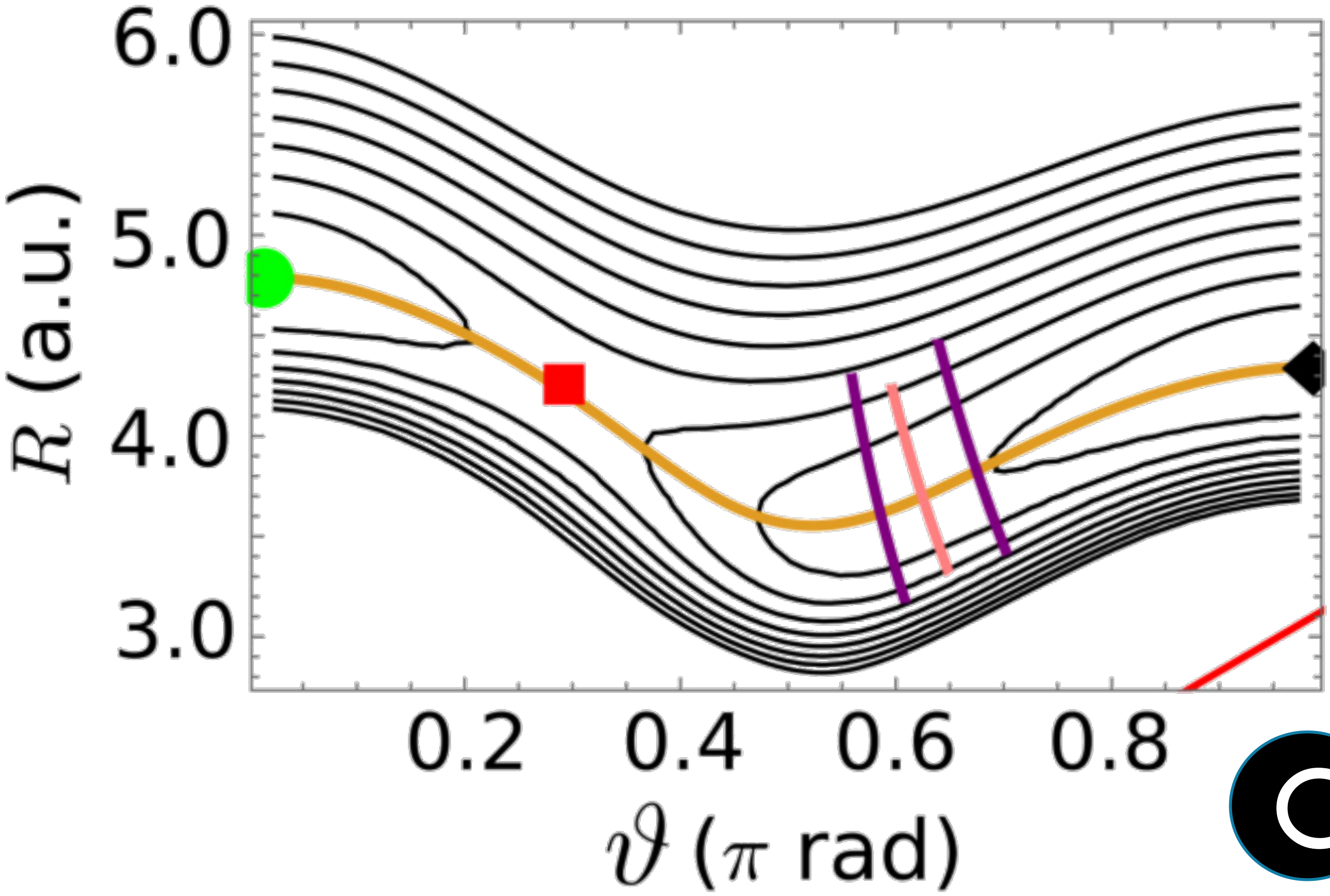




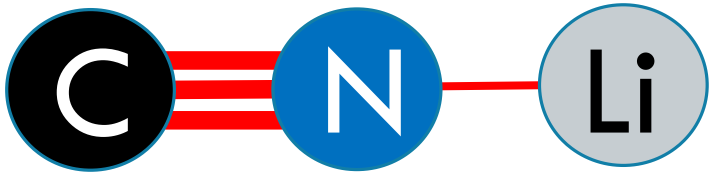
Absolute minimum

POTENTIAL ENERGY SURFACE



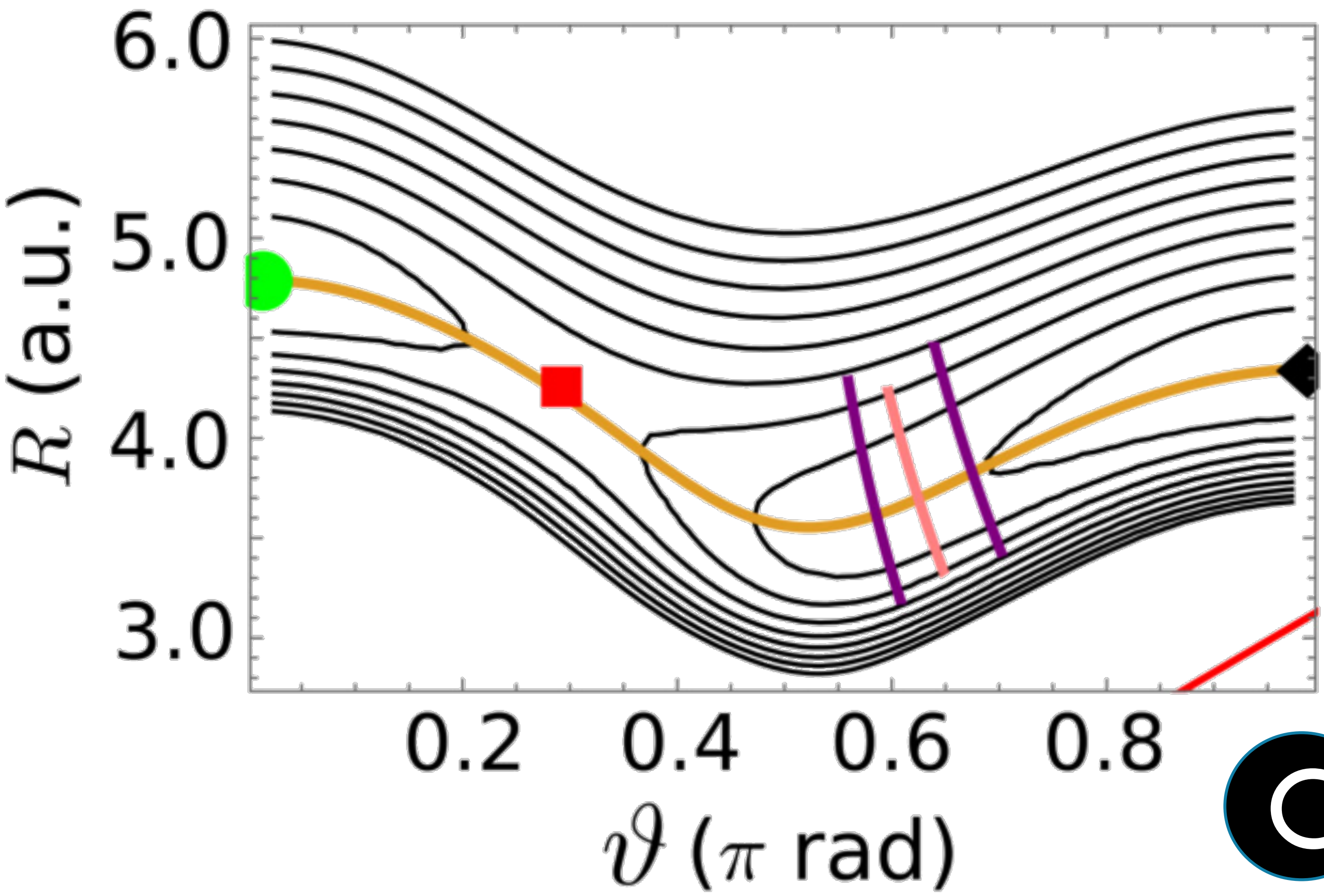


Absolute minimum

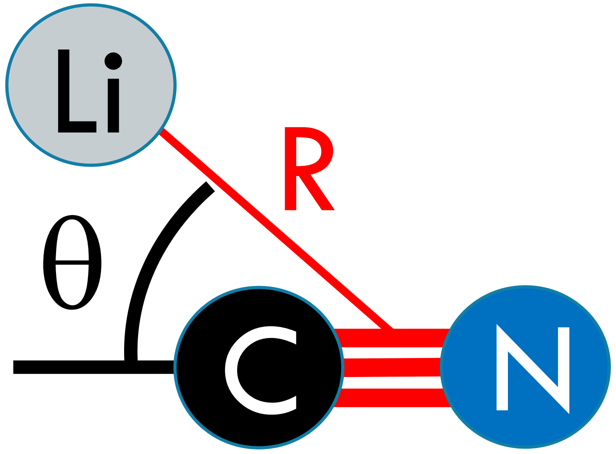


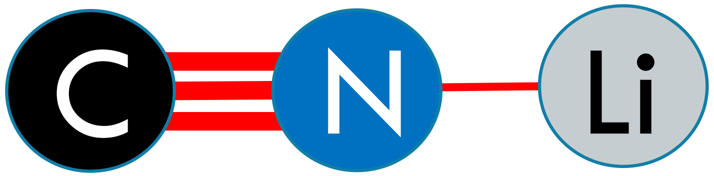
POTENTIAL ENERGY SURFACE

Relative minimum



Absolute minimum





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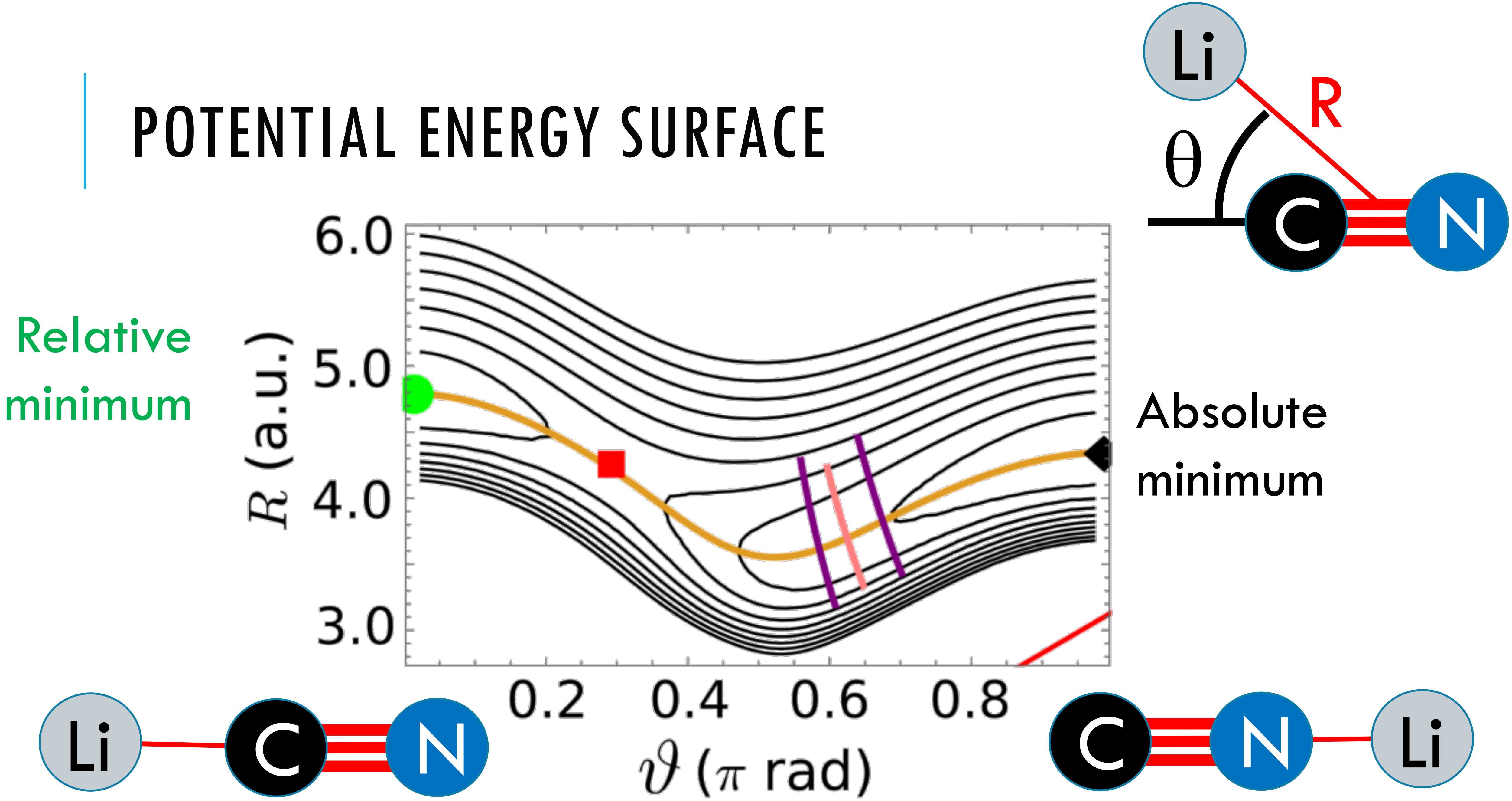

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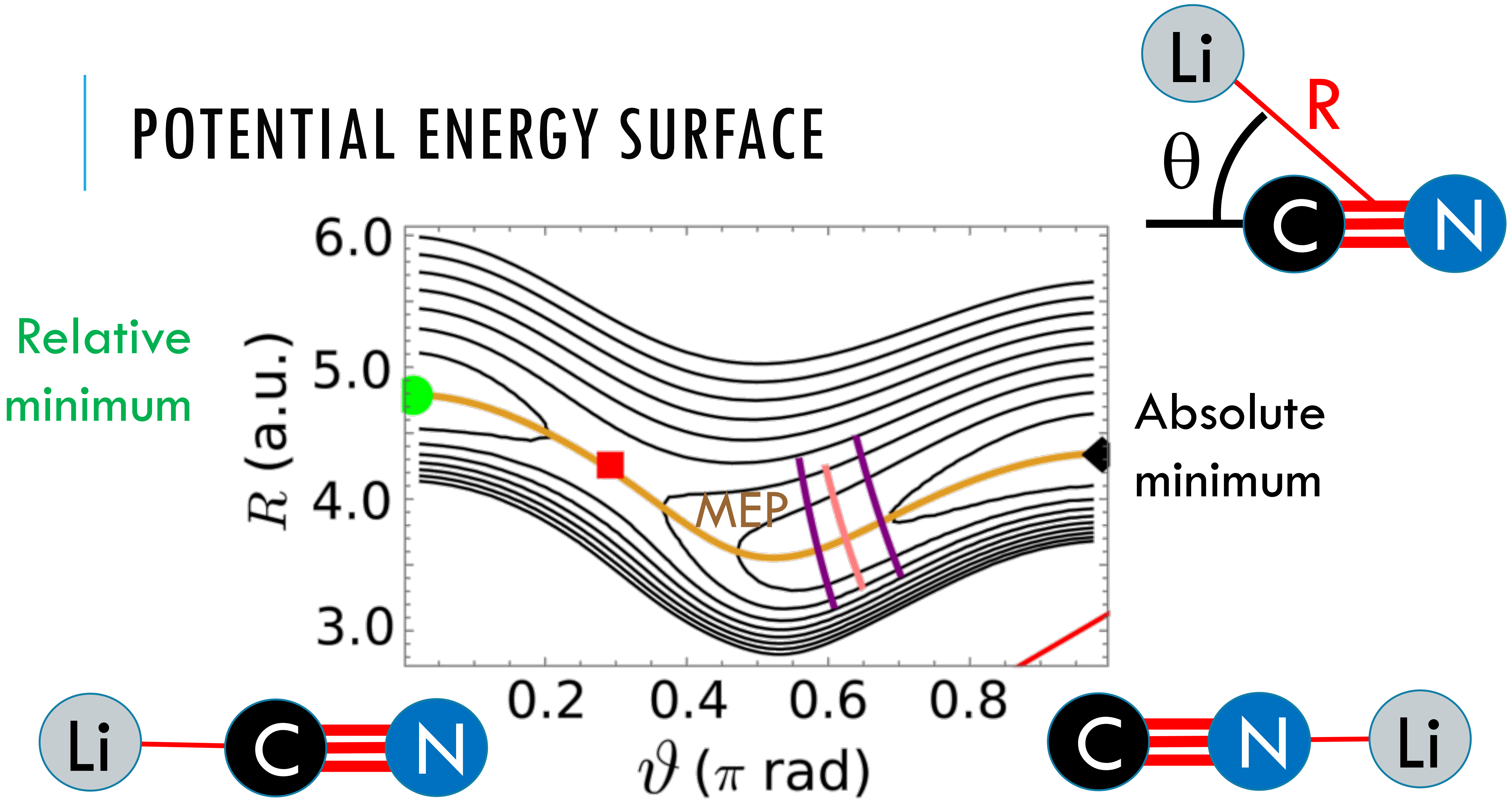

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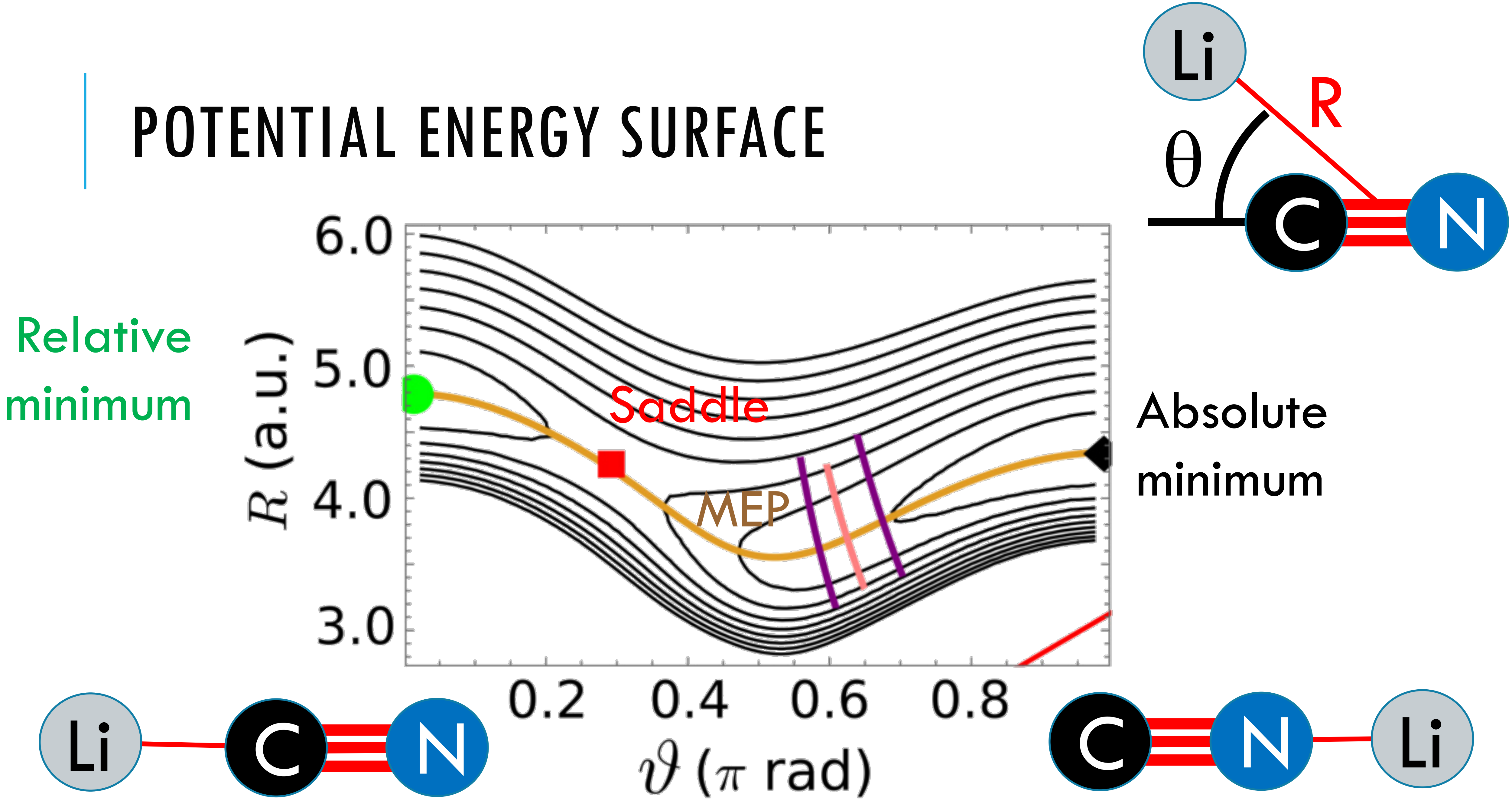

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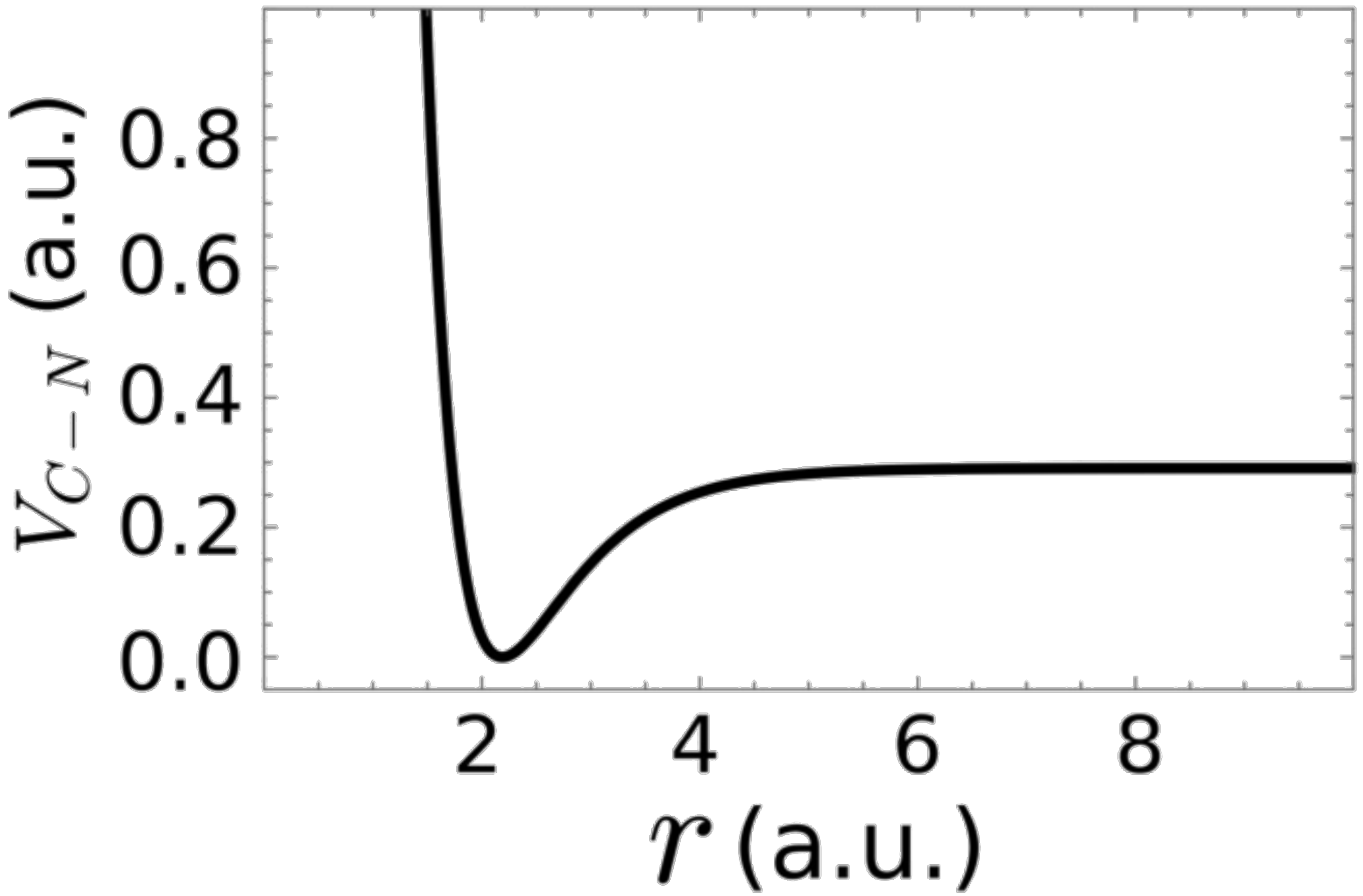
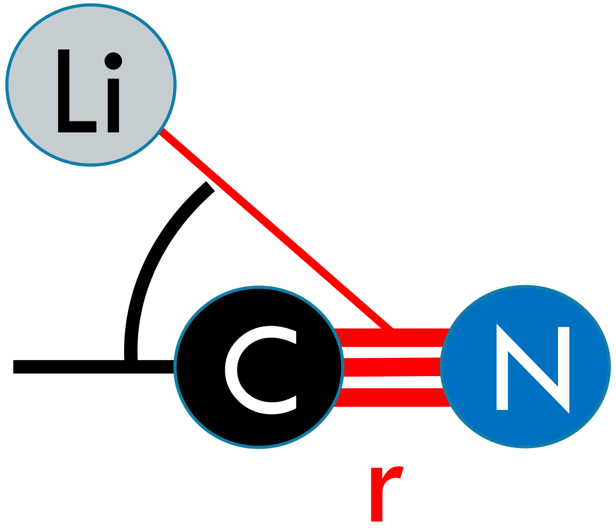
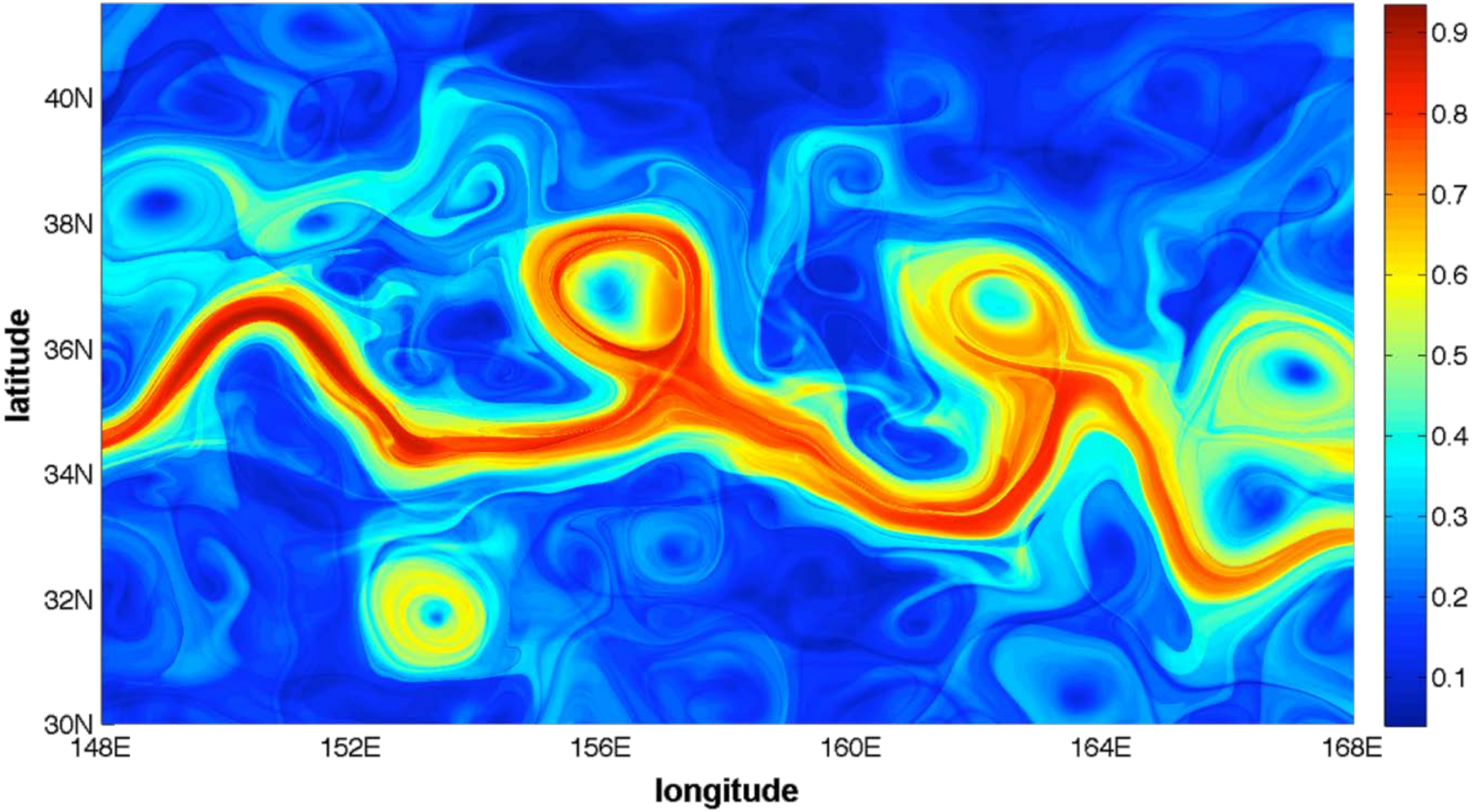




Methodology

LAGRANGIAN DESCRIPTORS



Oceanic flows

Figure:
C. Mendoza, A. M. Mancho, Nonlin. Processes Geophys. **19**, 449, 2012

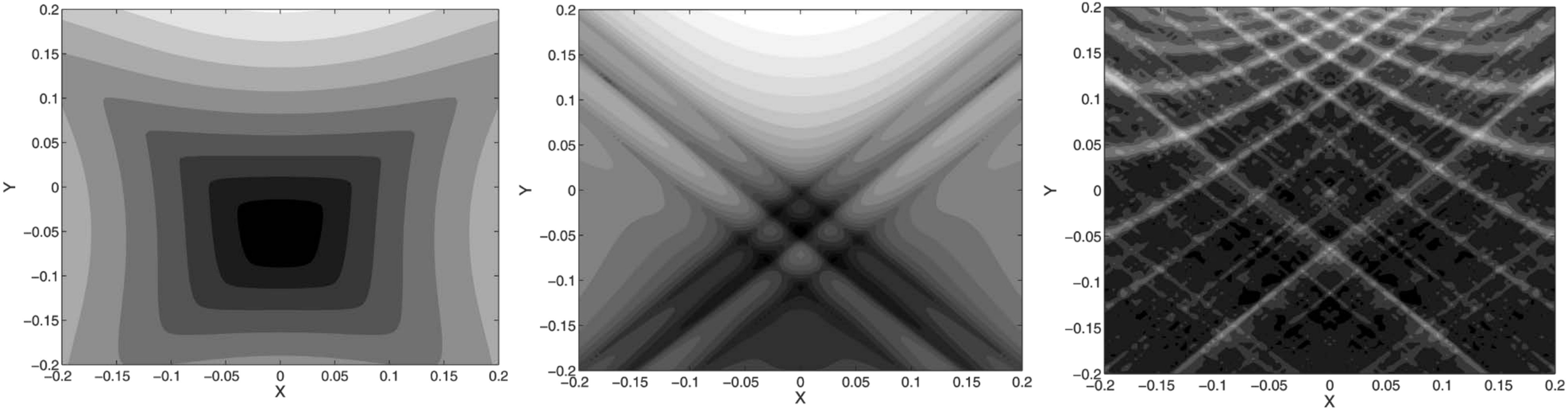
LAGRANGIAN DESCRIPTORS

$$\dot{\mathbf{z}} = f(\mathbf{z}_0, t)$$

$$M(\mathbf{z}_0, \tau) = \int_{-\tau}^{\tau} \sqrt{\sum_{i=1}^{N} |\dot{z}_i(t)|^2 dt}$$

EXAMPLE: INVARIANT MANIFOLDS IN DUFFING EQ.

$$\dot{x} = y, \qquad \dot{y} = x - x^3 + \varepsilon \sin(t)$$



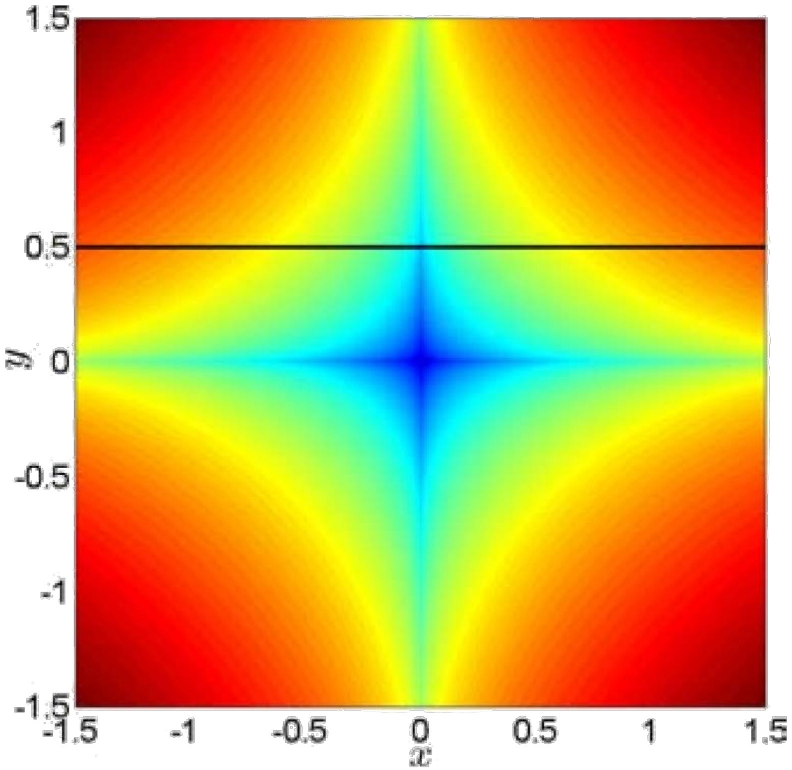
J. A. Jiménez Madrid, A. M. Mancho, Chaos **19**, 013111 2009

LAGRANGIAN DESCRIPTORS: P-NORM

$$M(\mathbf{z}_0, \tau) = \int_{-\tau}^{\tau} \sum_{i=1}^{N} |\dot{z}_i(t)|^p dt$$

C. Lopesino, F. Balibrea-Iniesta, V. J. García-Garrido, S. Wiggins and A. M. Mancho, *Int. J. Bifur. and Chaos* **27**, 1730001 (2017)

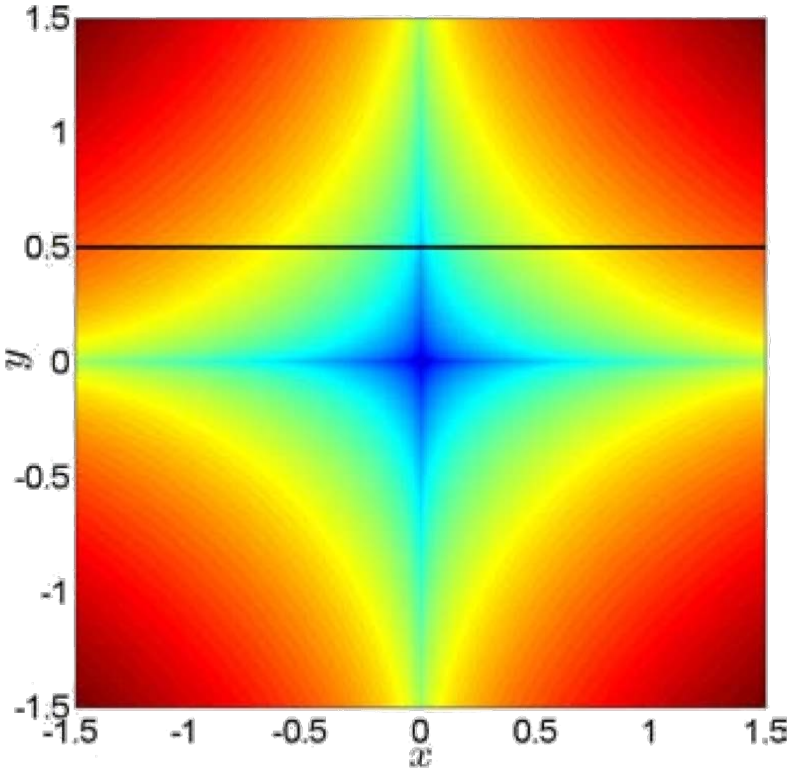
INVARIANT MANIFOLDS = SINGULARITIES

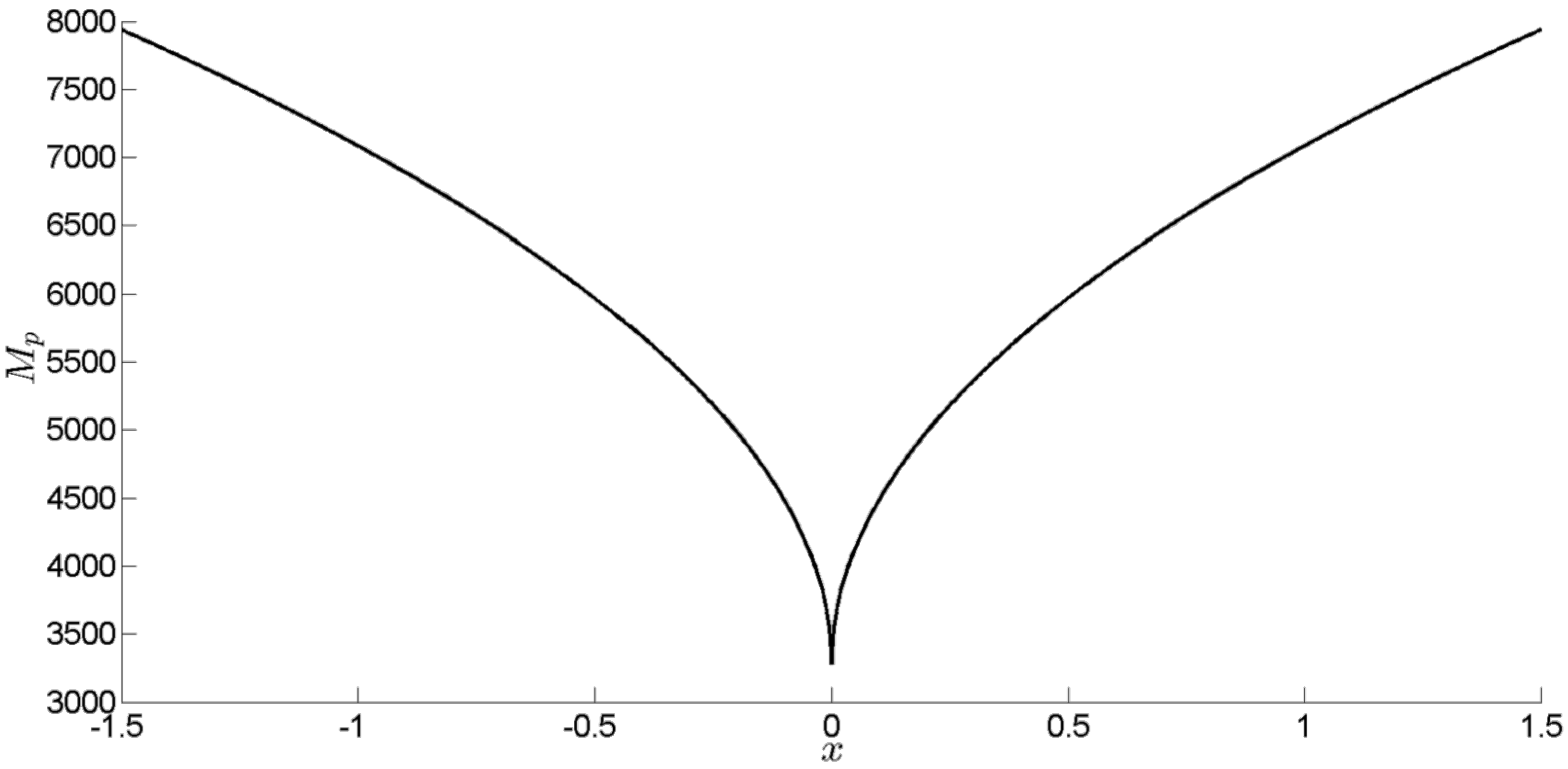


$$\begin{cases} \dot{x} = \lambda x \\ \dot{y} = -\lambda y \end{cases}, \quad \lambda > 0$$

C. Lopesino, F. Balibrea-Iniesta, V. J. García-Garrido, S. Wiggins and A. M. Mancho, *Int. J. Bifur. and Chaos* **27**, 1730001 (2017)

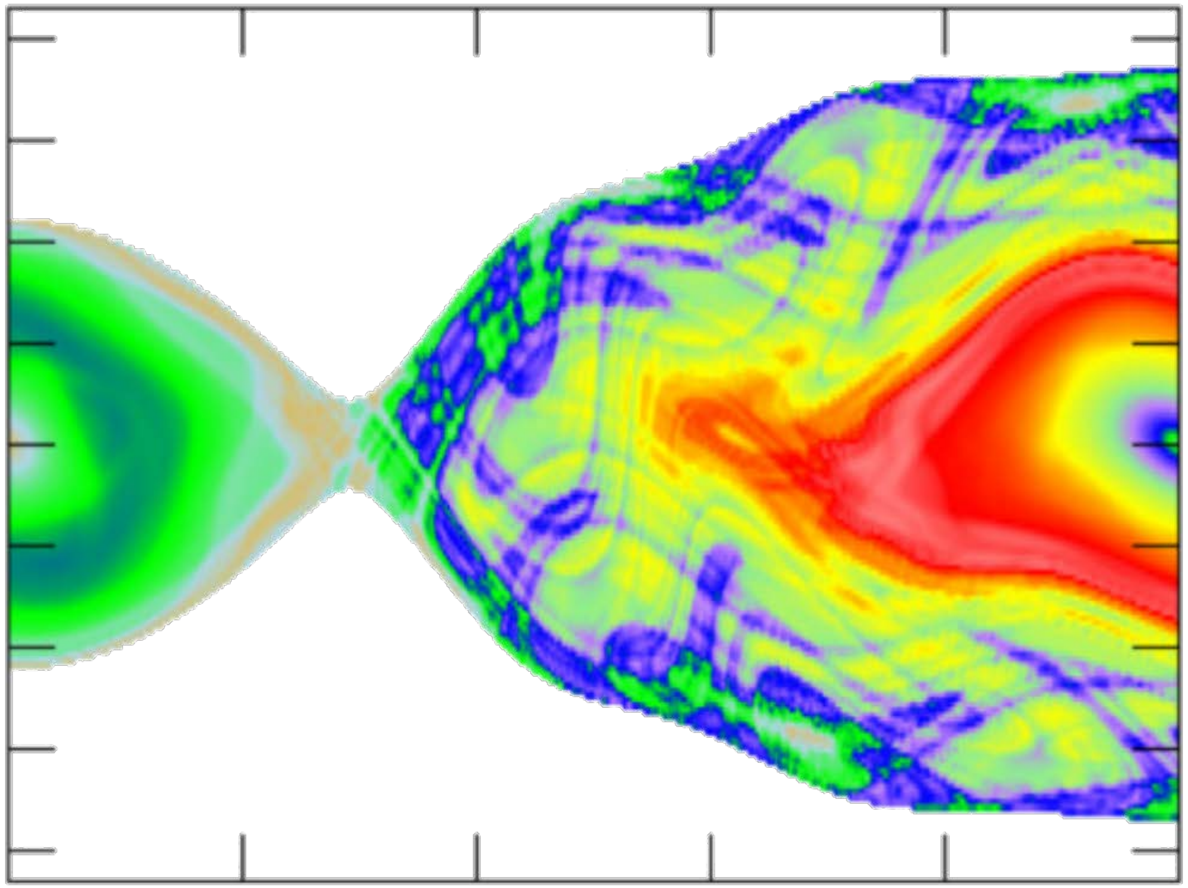
INVARIANT MANIFOLDS = SINGULARITIES





C. Lopesino, F. Balibrea-Iniesta, V. J. García-Garrido, S. Wiggins and A. M. Mancho, *Int. J. Bifur. and Chaos* **27**, 1730001 (2017)

Results

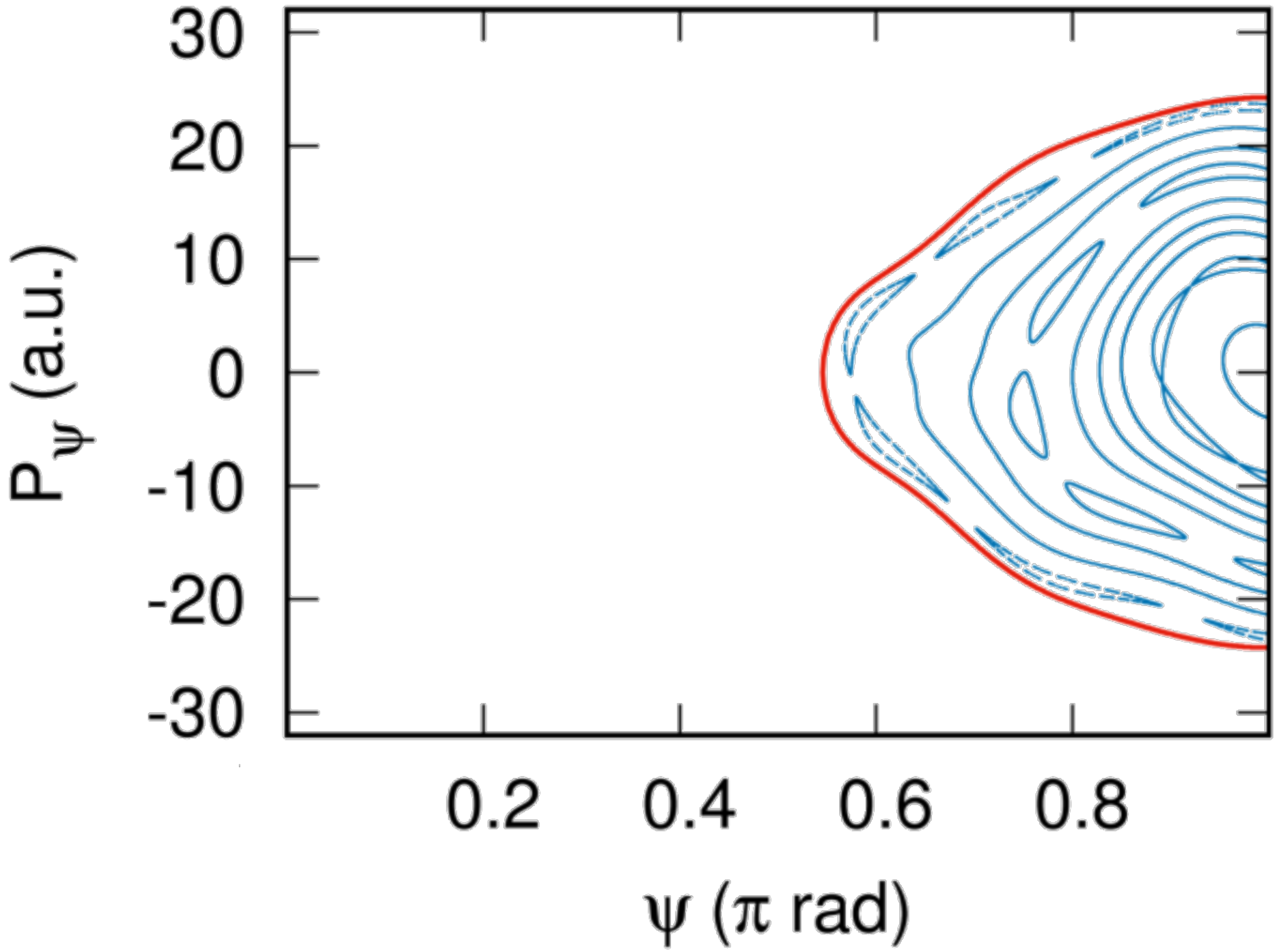


Results

1. System with 2 dof
2. Saddle-node bifurcation
3. System with 3 dof

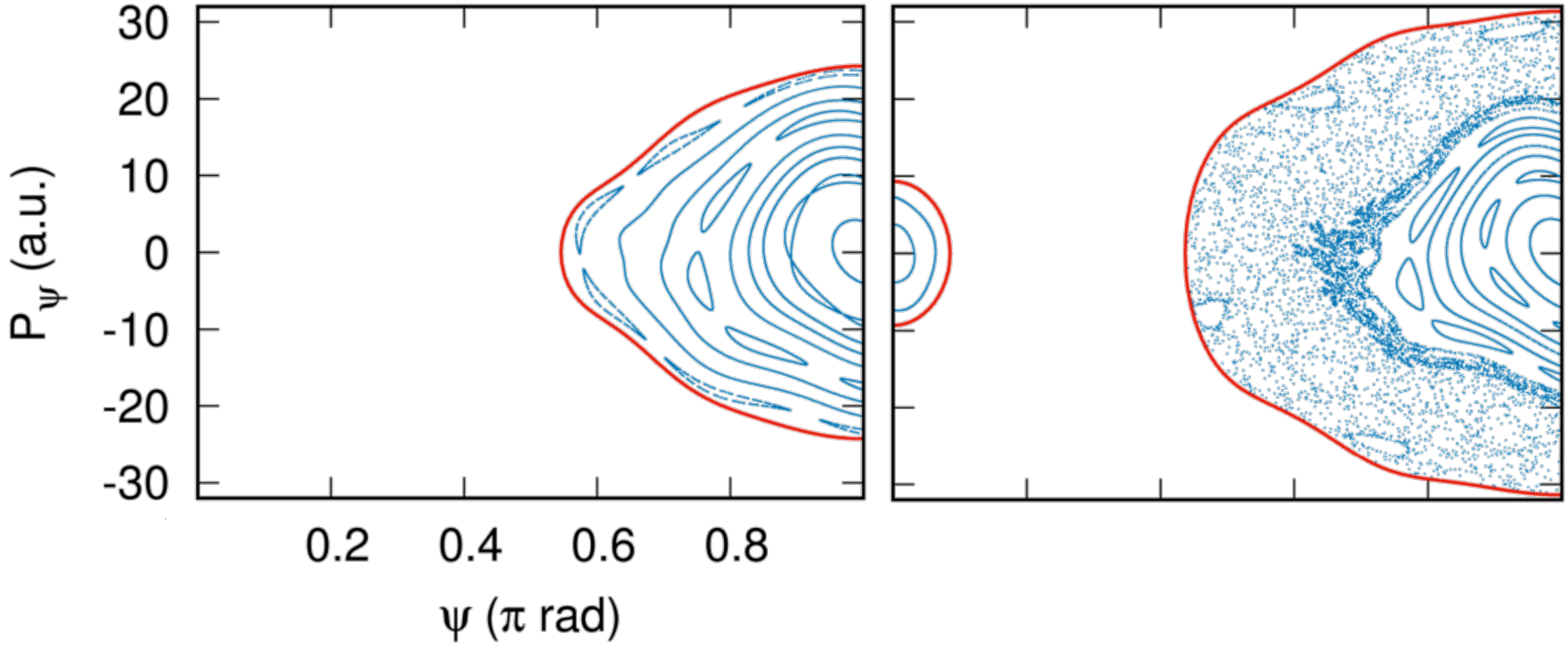
POINCARÉ SUPERFICIE OF SECTION

$E = 1500 cm^{-1}$



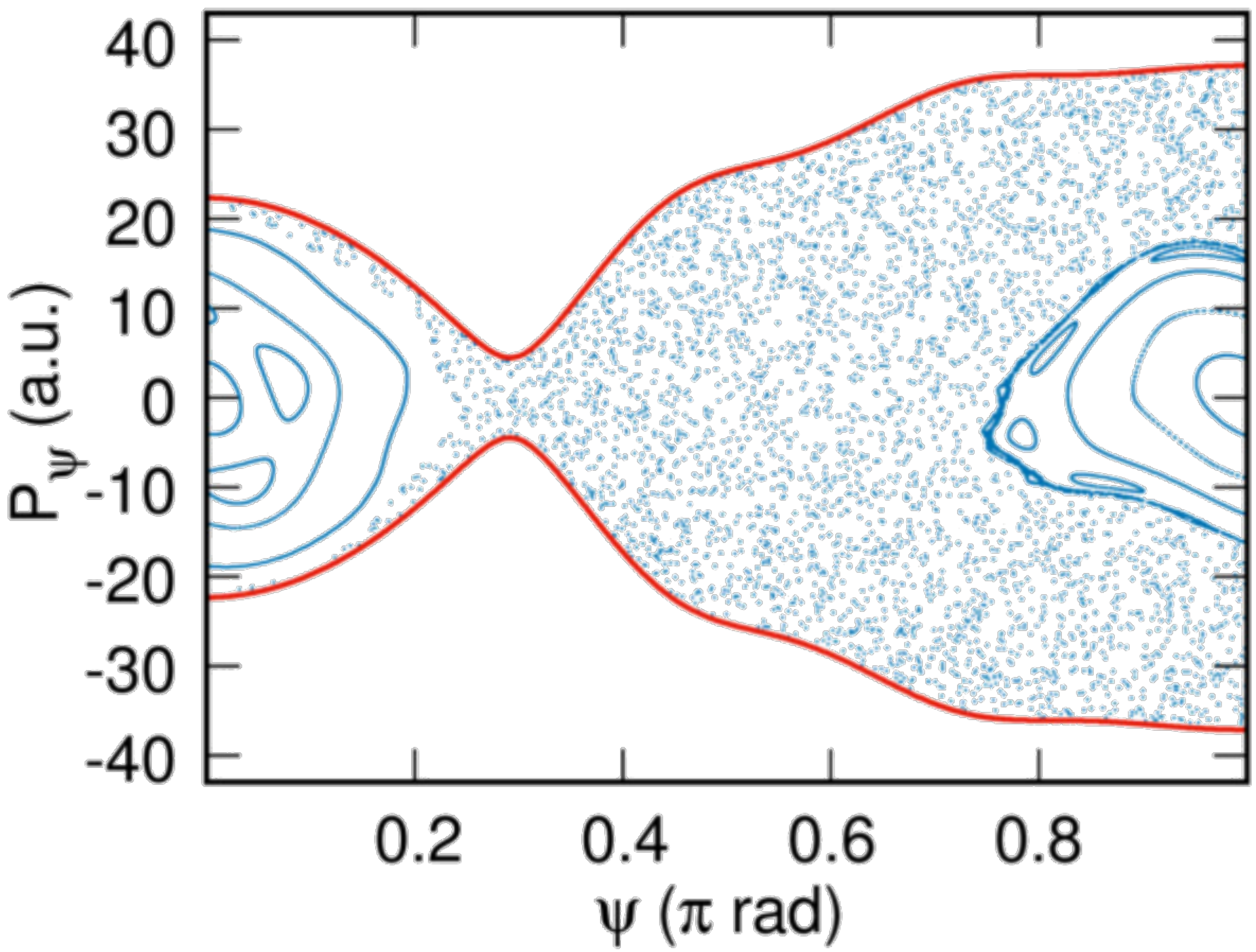
POINCARÉ SUPERFICIE OF SECTION

$E = 1500cm^{-1}$ $E = 2500cm^{-1}$

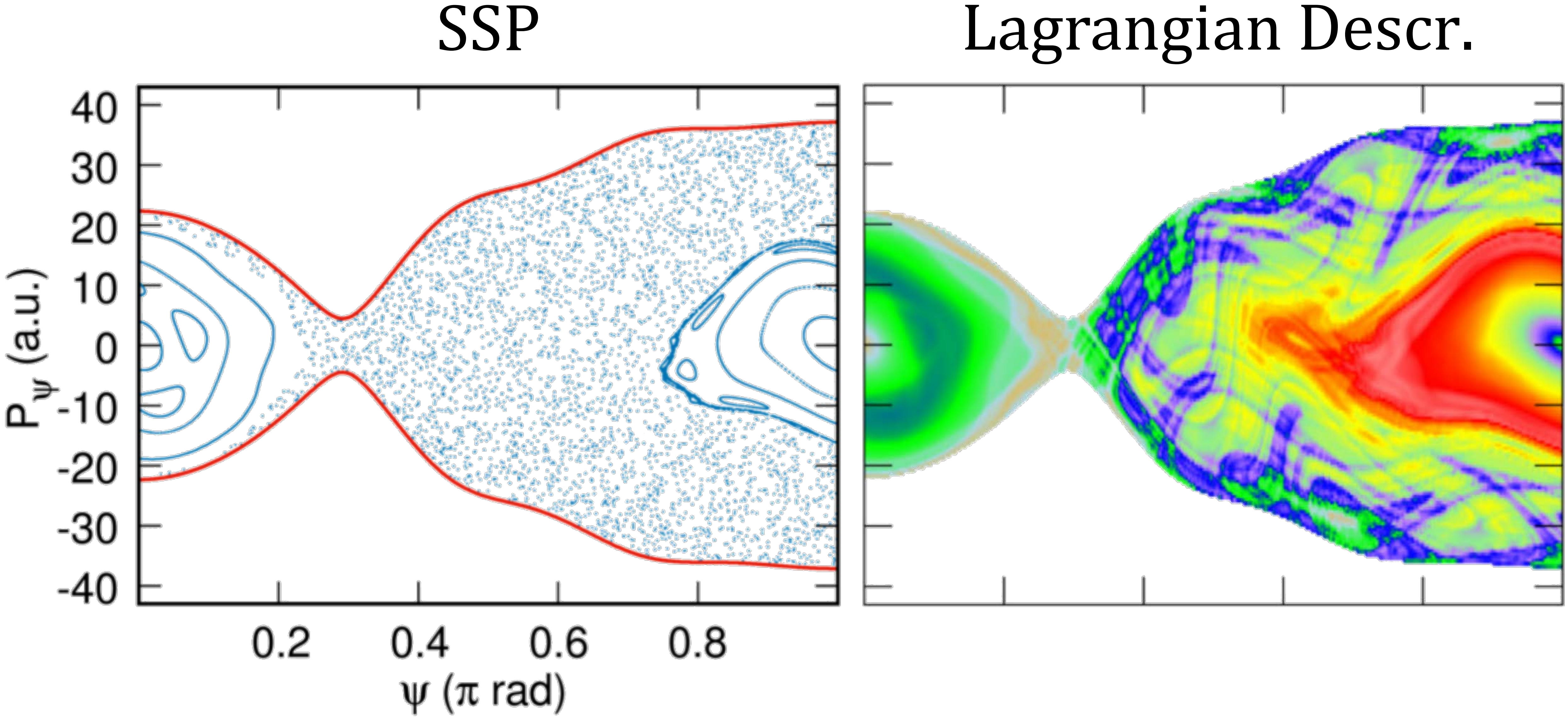


$$E = 3500cm^{-1}$$

SSP



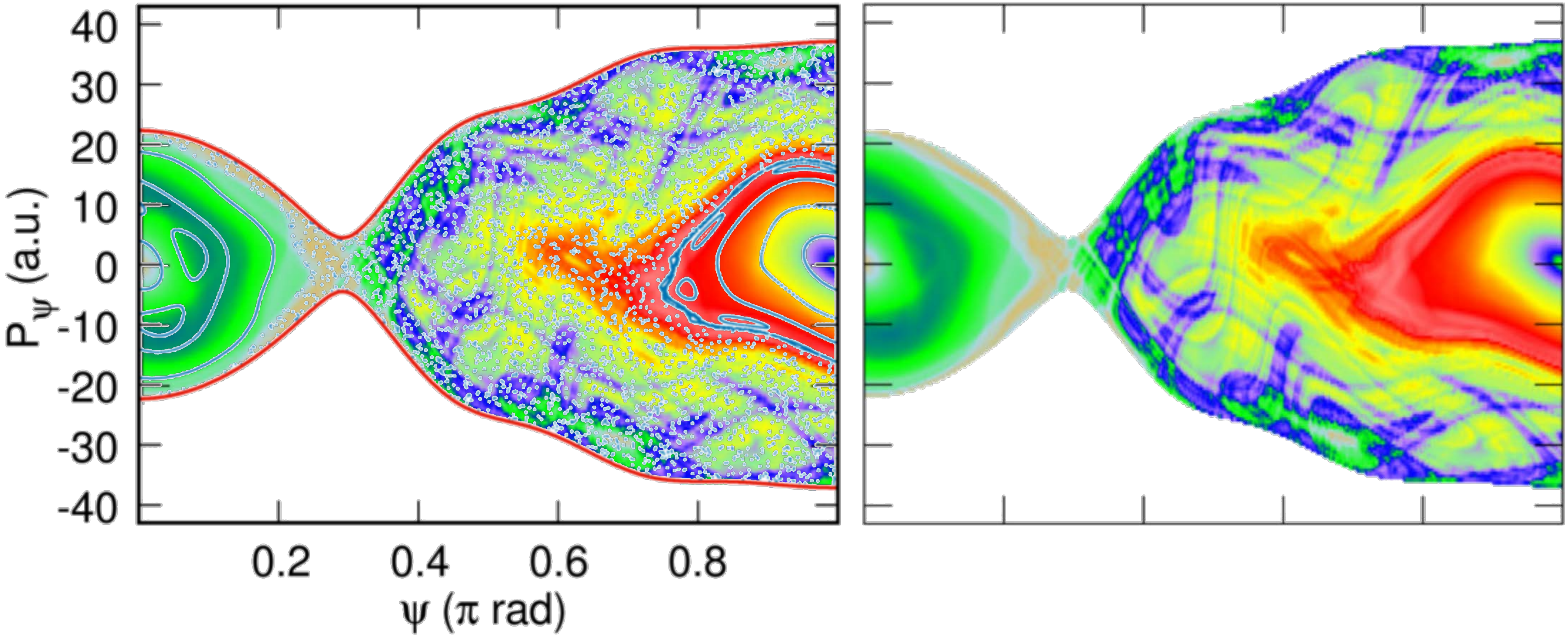
$$E = 3500 cm^{-1}$$



SSP
Lagrangian Descr.
40
30
20
10
0
-10
-20
-30
-40
P_ψ (a.u.)
0.2
0.4
0.6
0.8
ψ (π rad)

$$E = 3500cm^{-1}$$

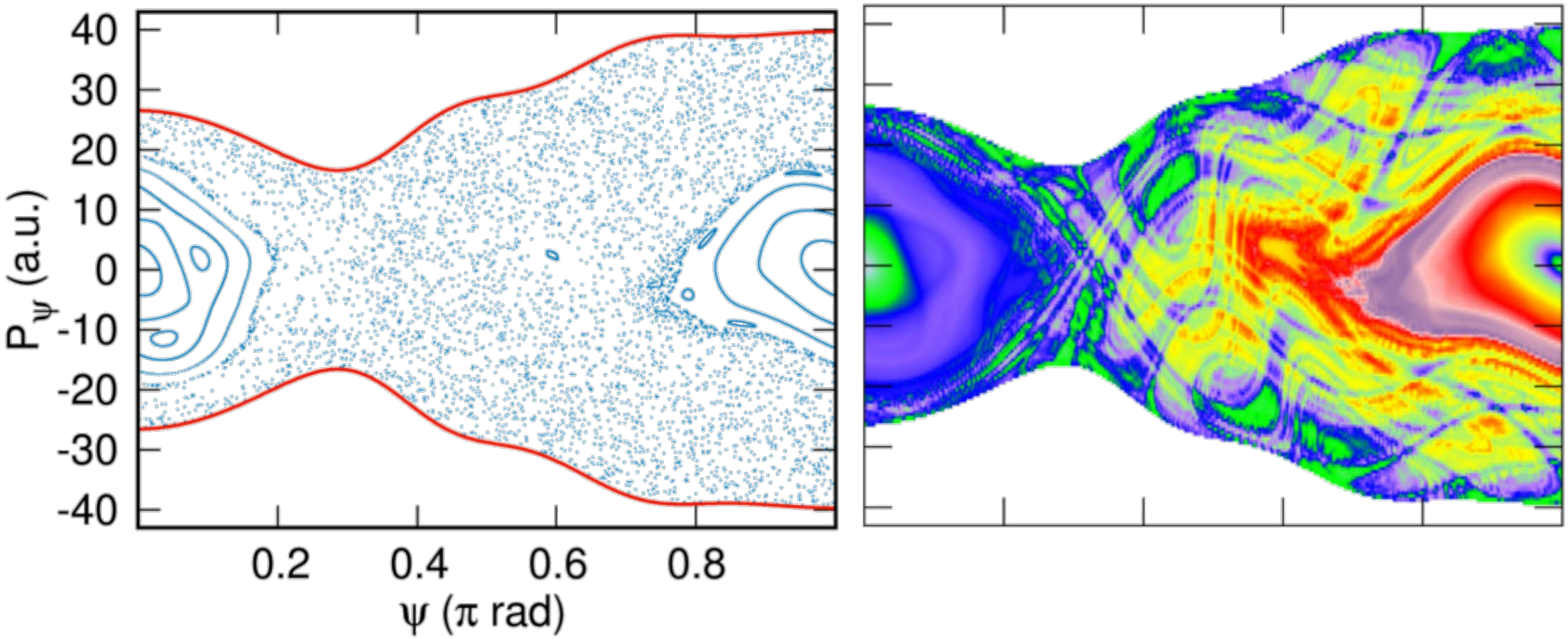
SSP | Lagrangian Descr.



$$E = 4000 cm^{-1}$$

SSP

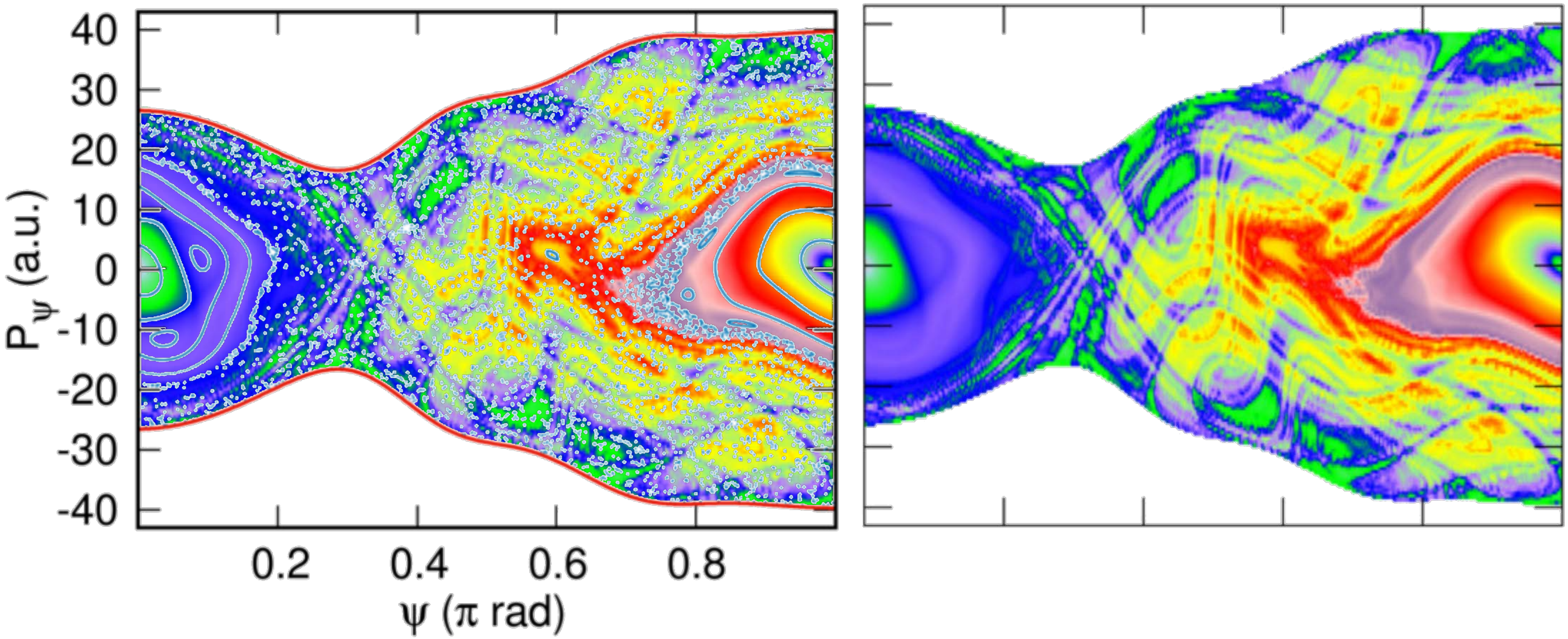
Lagrangian Descr.



$E = 4000cm^{-1}$

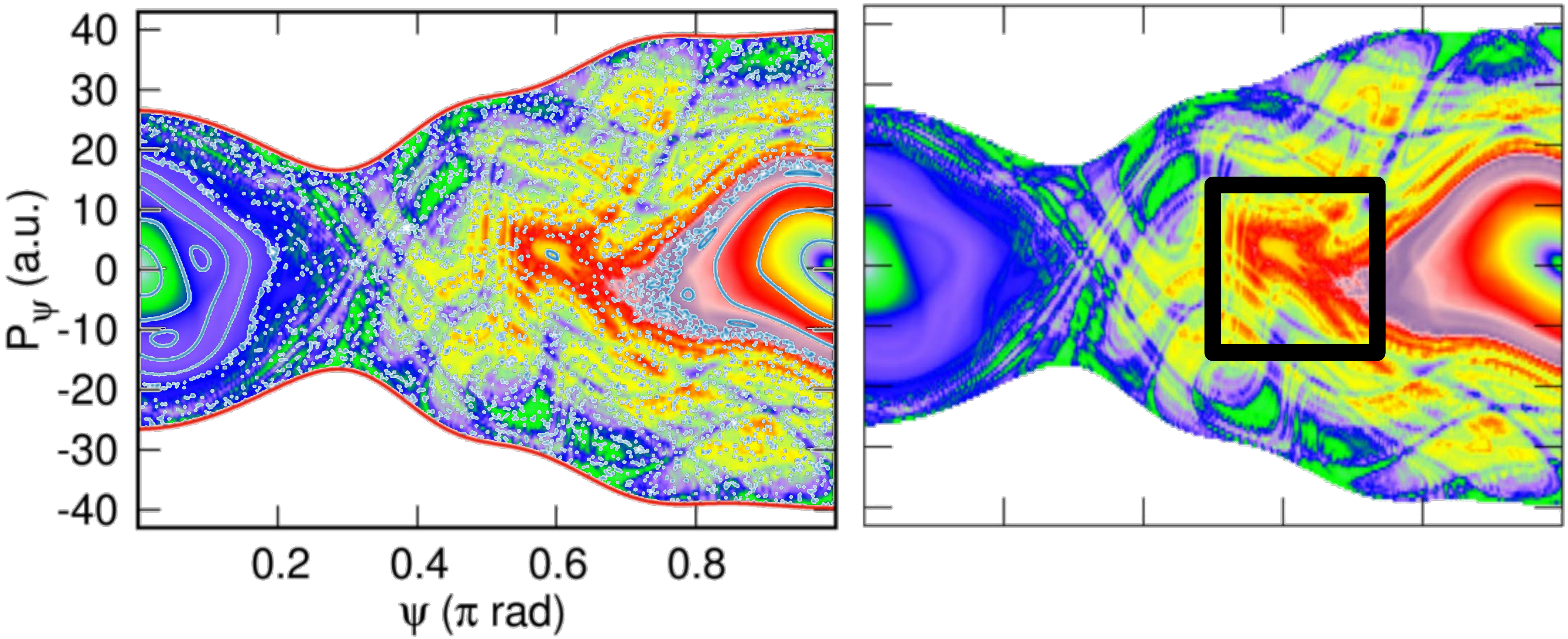
SSP

Lagrangian Descr.



$$E = 4000 cm^{-1}$$

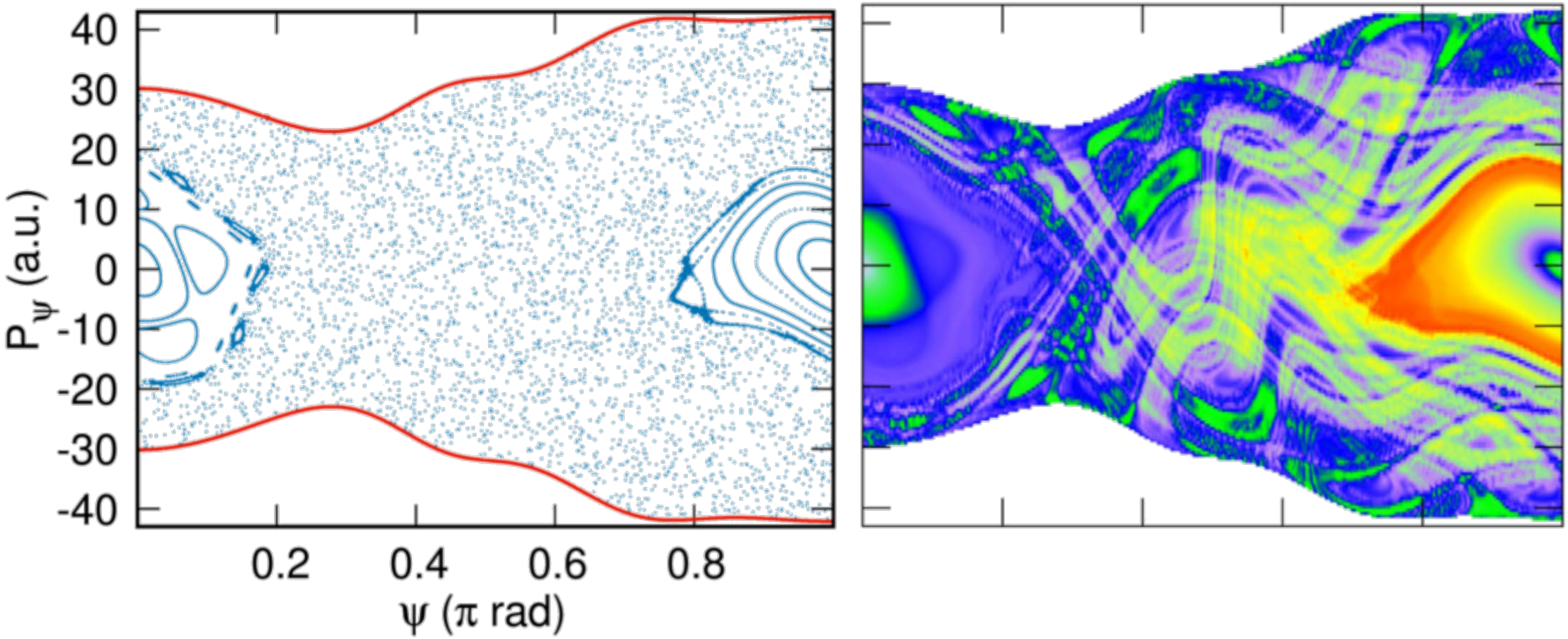
SSP Lagrangian Descr.



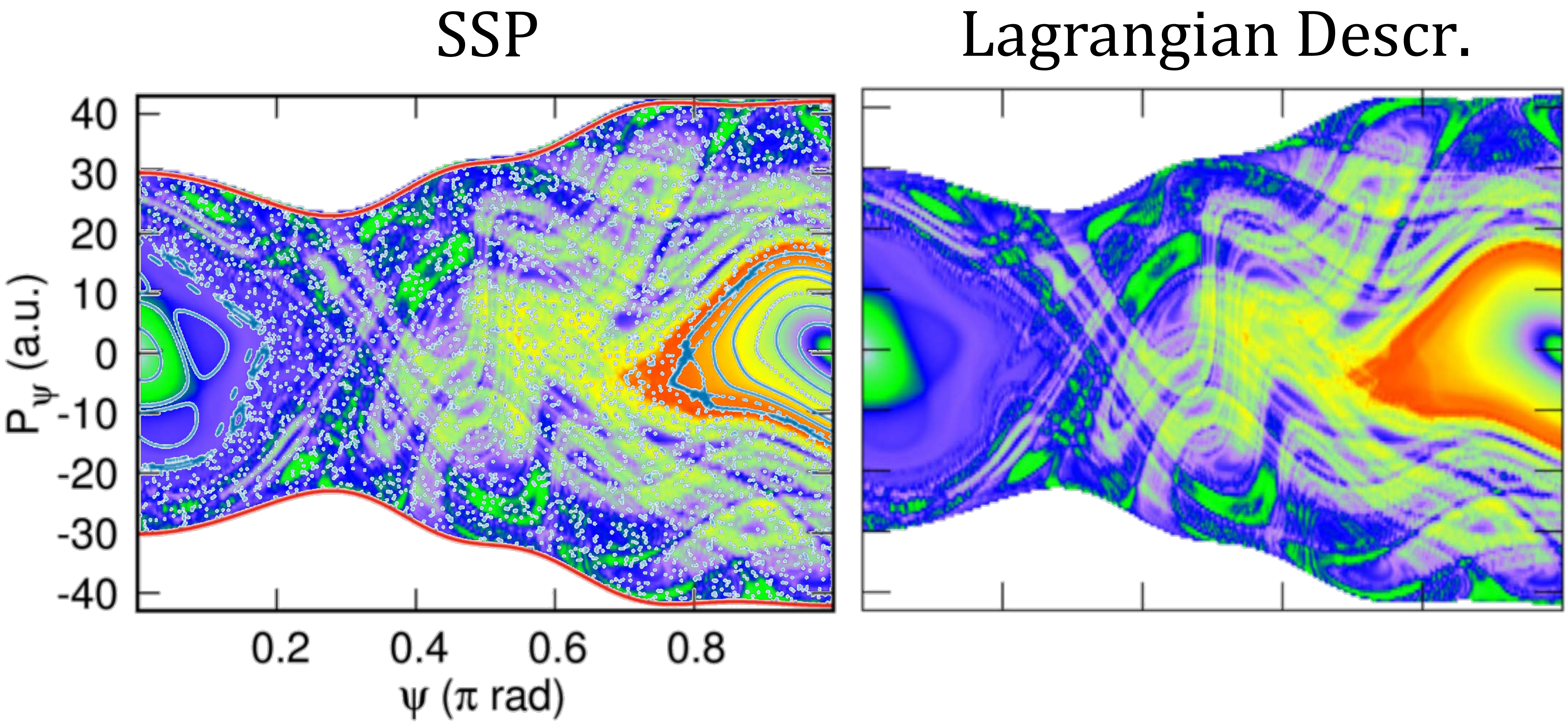
$$E = 4500cm^{-1}$$

SSP

Lagrangian Descr.

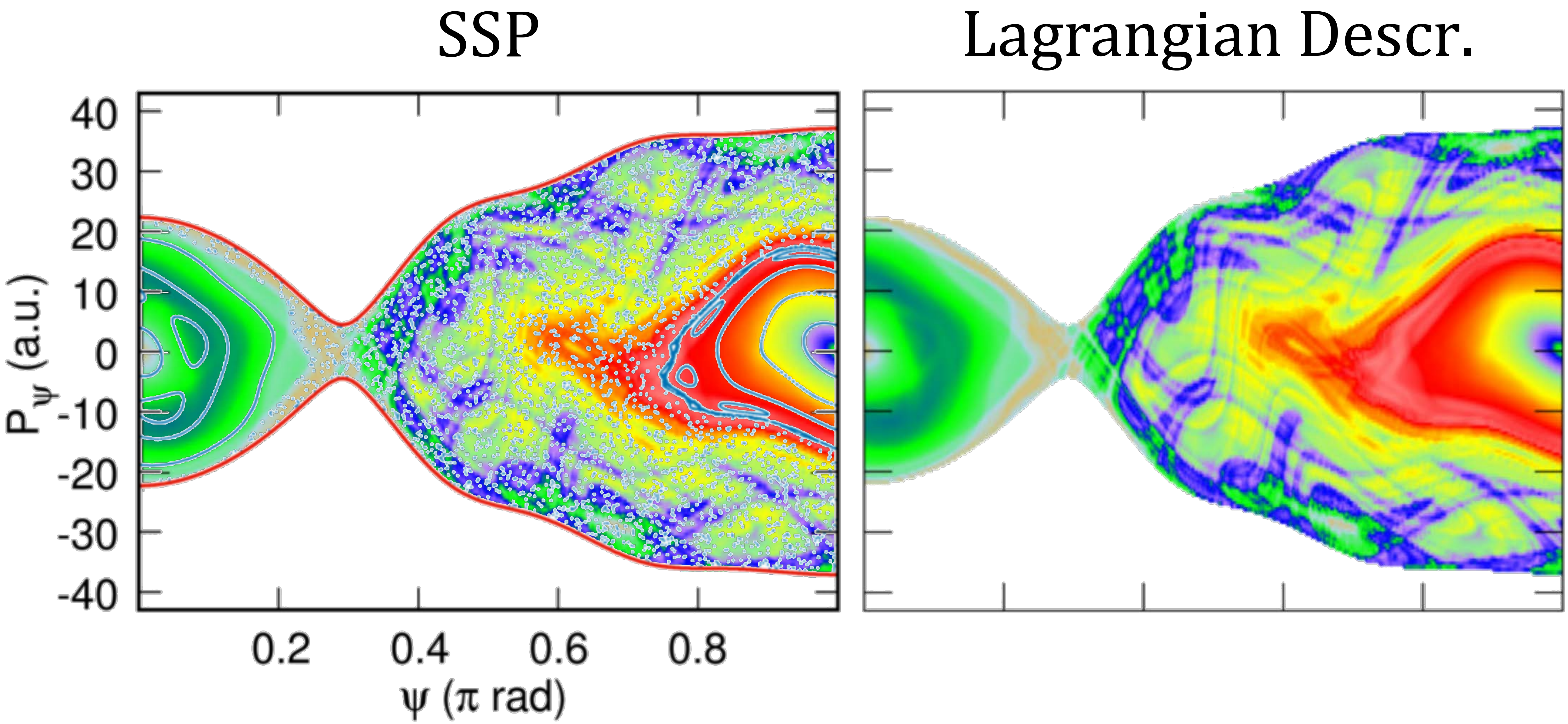


$$E = 4500 cm^{-1}$$



SSP
Lagrangian Descr.
40
30
20
10
0
-10
-20
-30
-40
P_ψ (a.u.)
0.2
0.4
0.6
0.8
ψ (π rad)

$$E = 3500 cm^{-1}$$



SSP
Lagrangian Descr.
40
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20
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0
-10
-20
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-40
P_ψ (a.u.)
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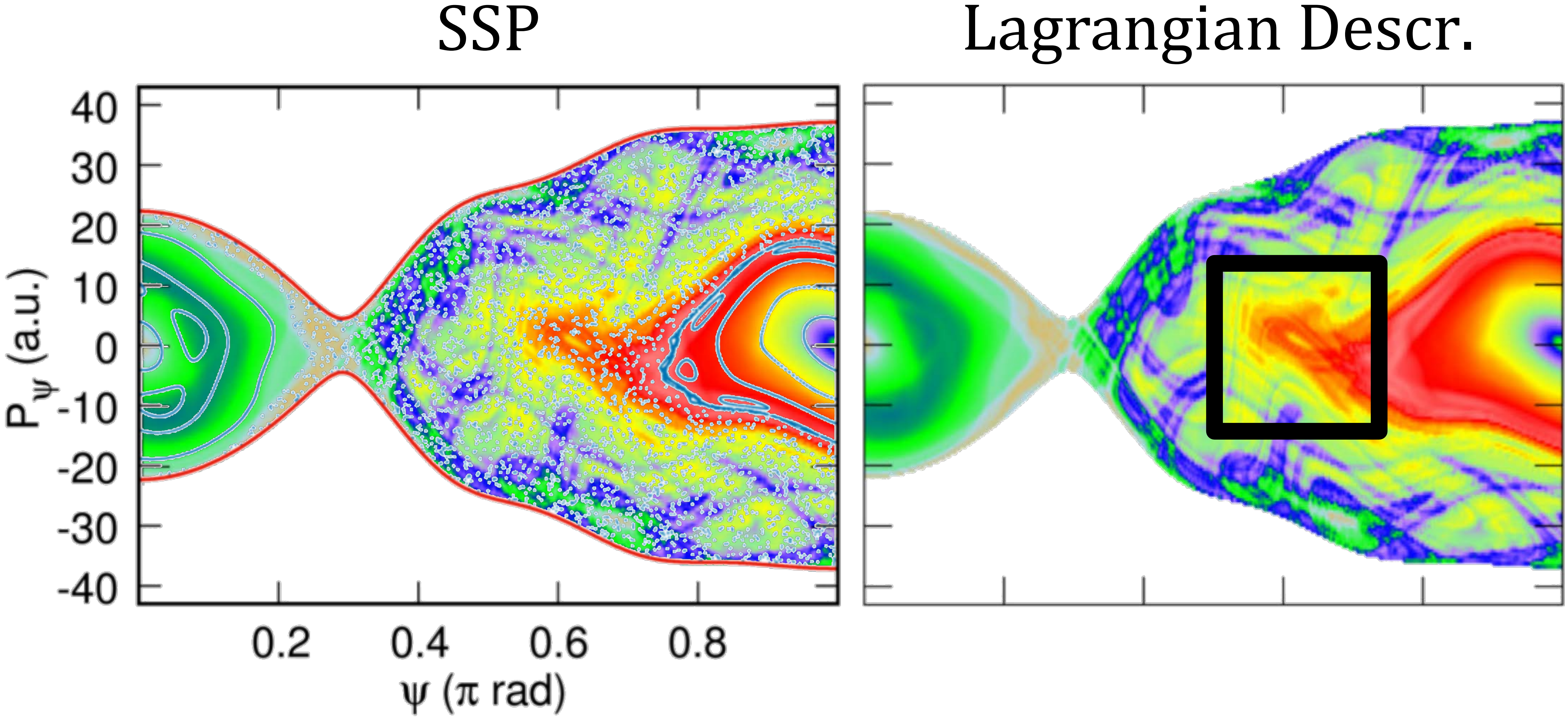
0.4
0.6
0.8
ψ (π rad)

$$E = 3500cm^{-1}$$


SSP
Lagrangian Descr.
40
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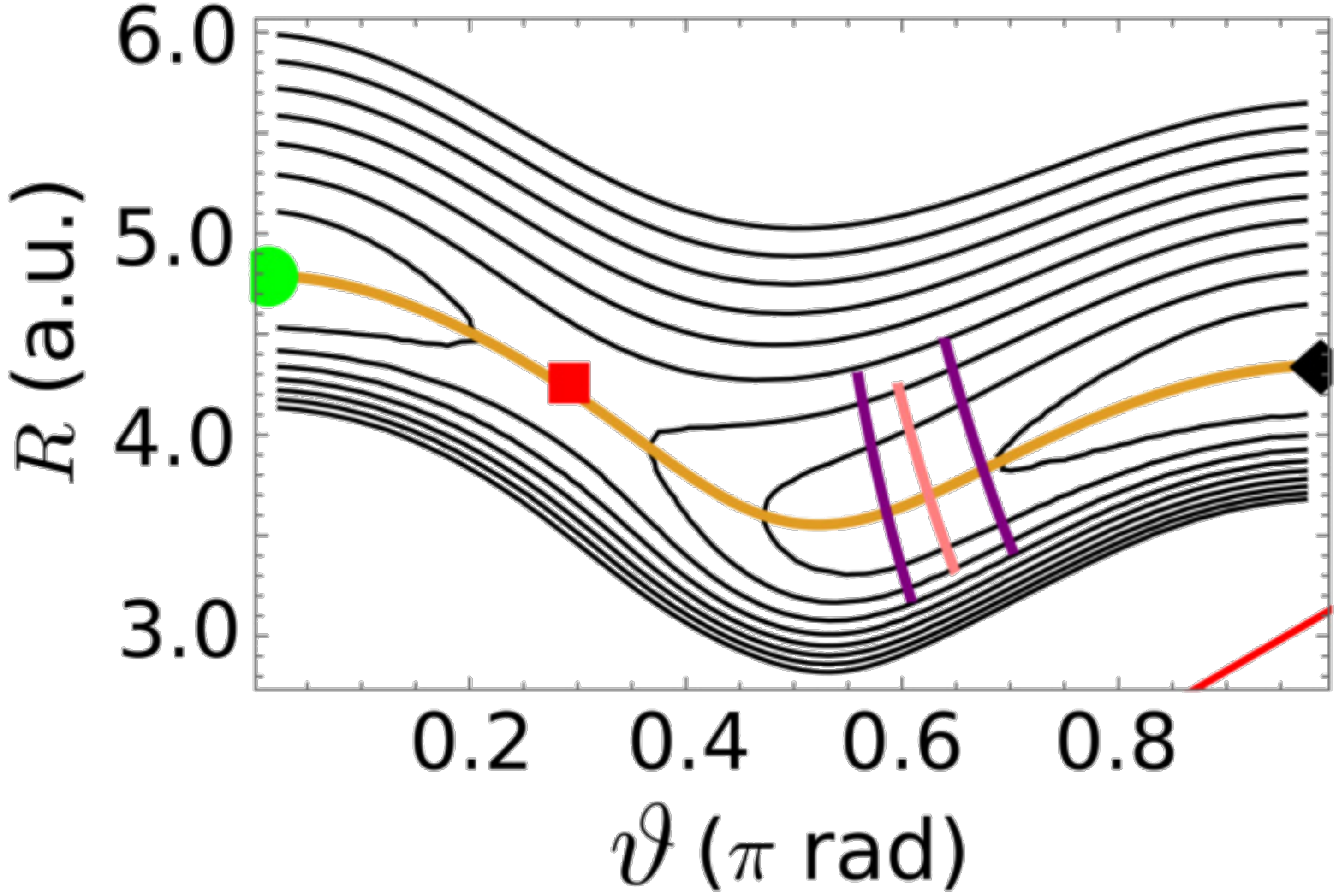
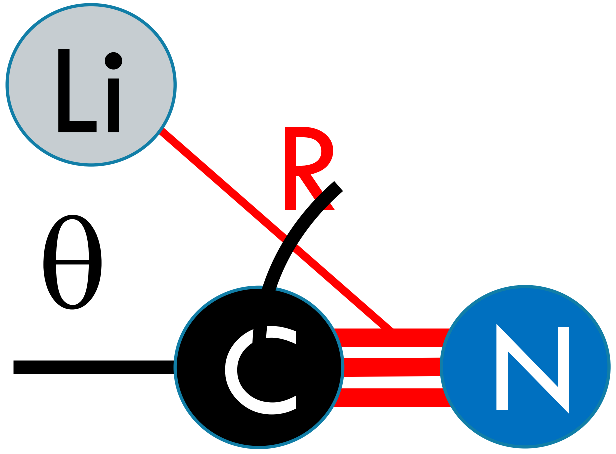
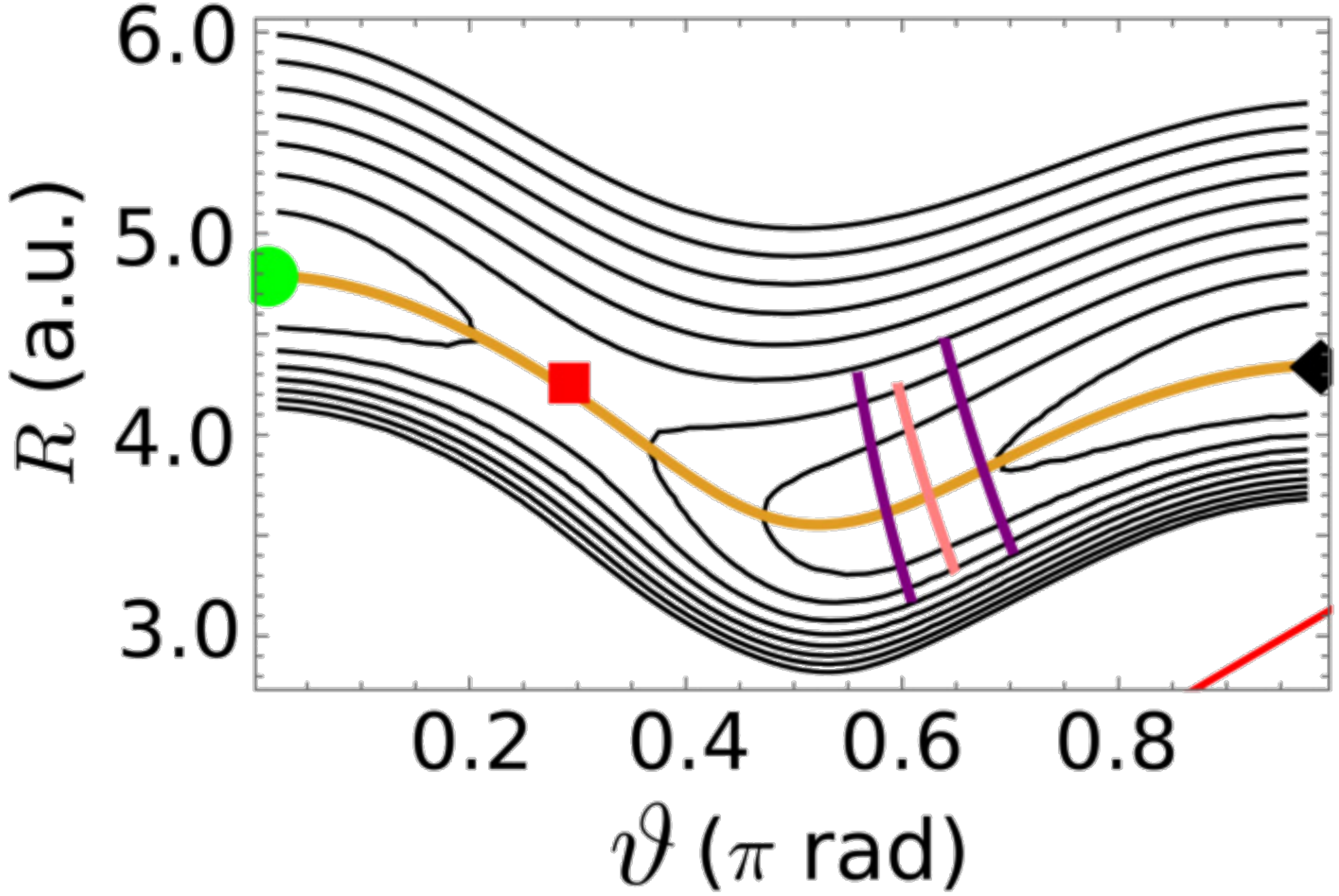
20
10
0
-10
-20
-30
-40
P_ψ (a.u.)
0.2
0.4
0.6
0.8
ψ (π rad)

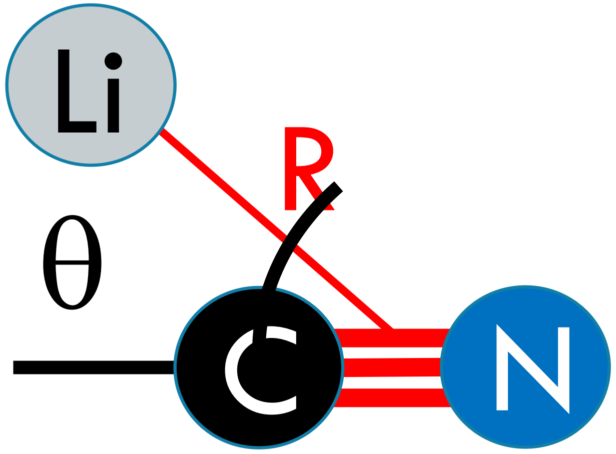
POTENTIAL ENERGY SURFACE





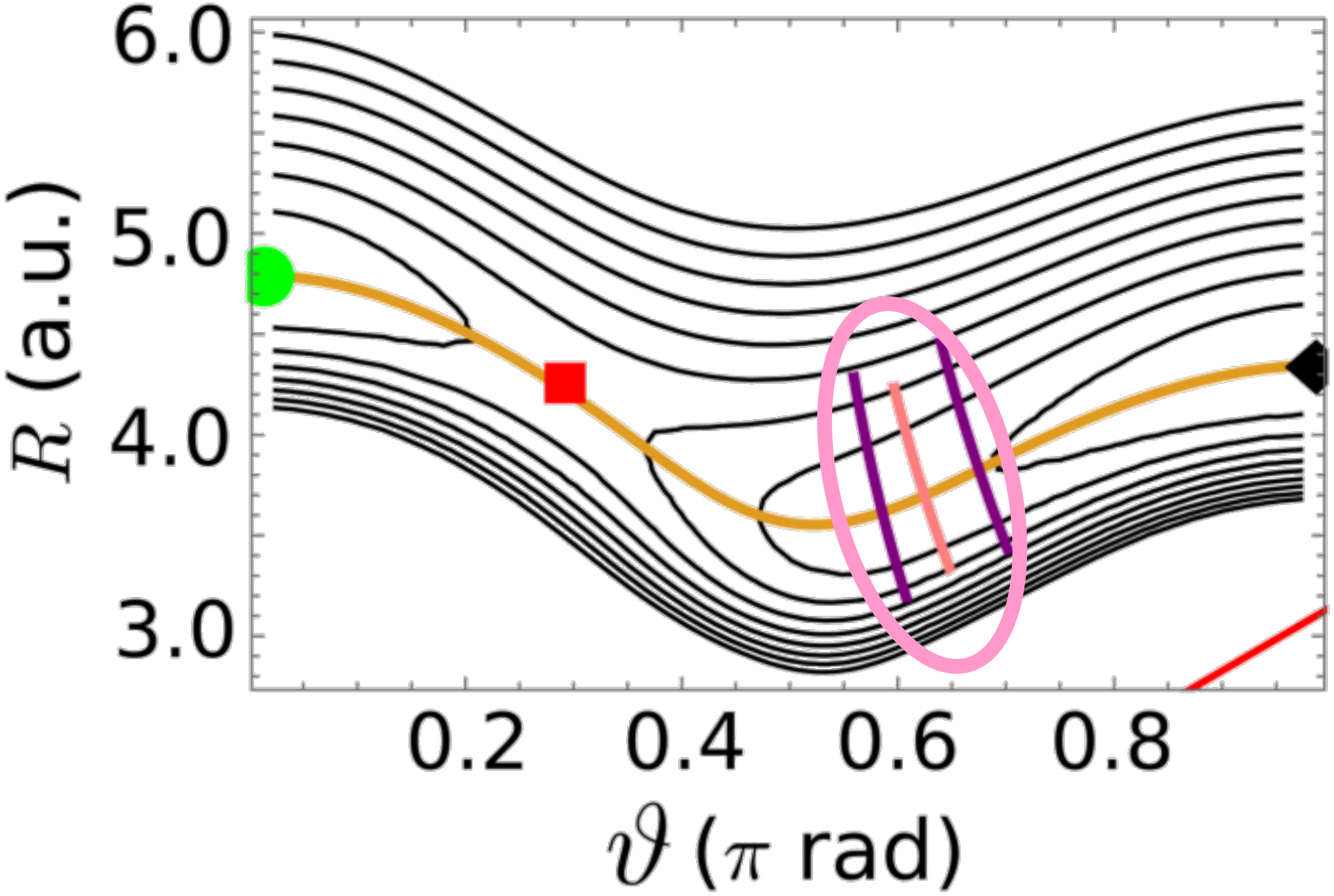
POTENTIAL ENERGY SURFACE

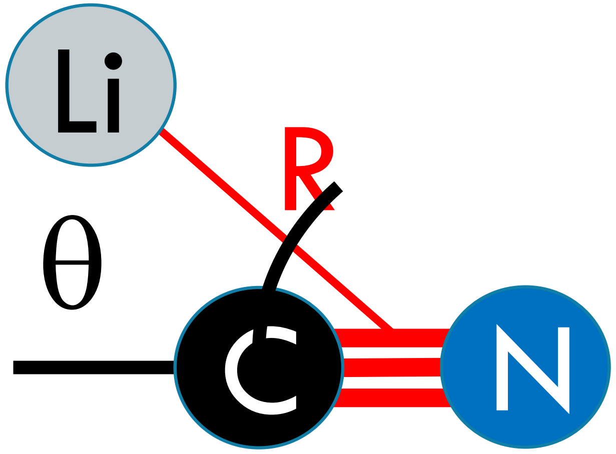




Periodic orbits

POTENTIAL ENERGY SURFACE

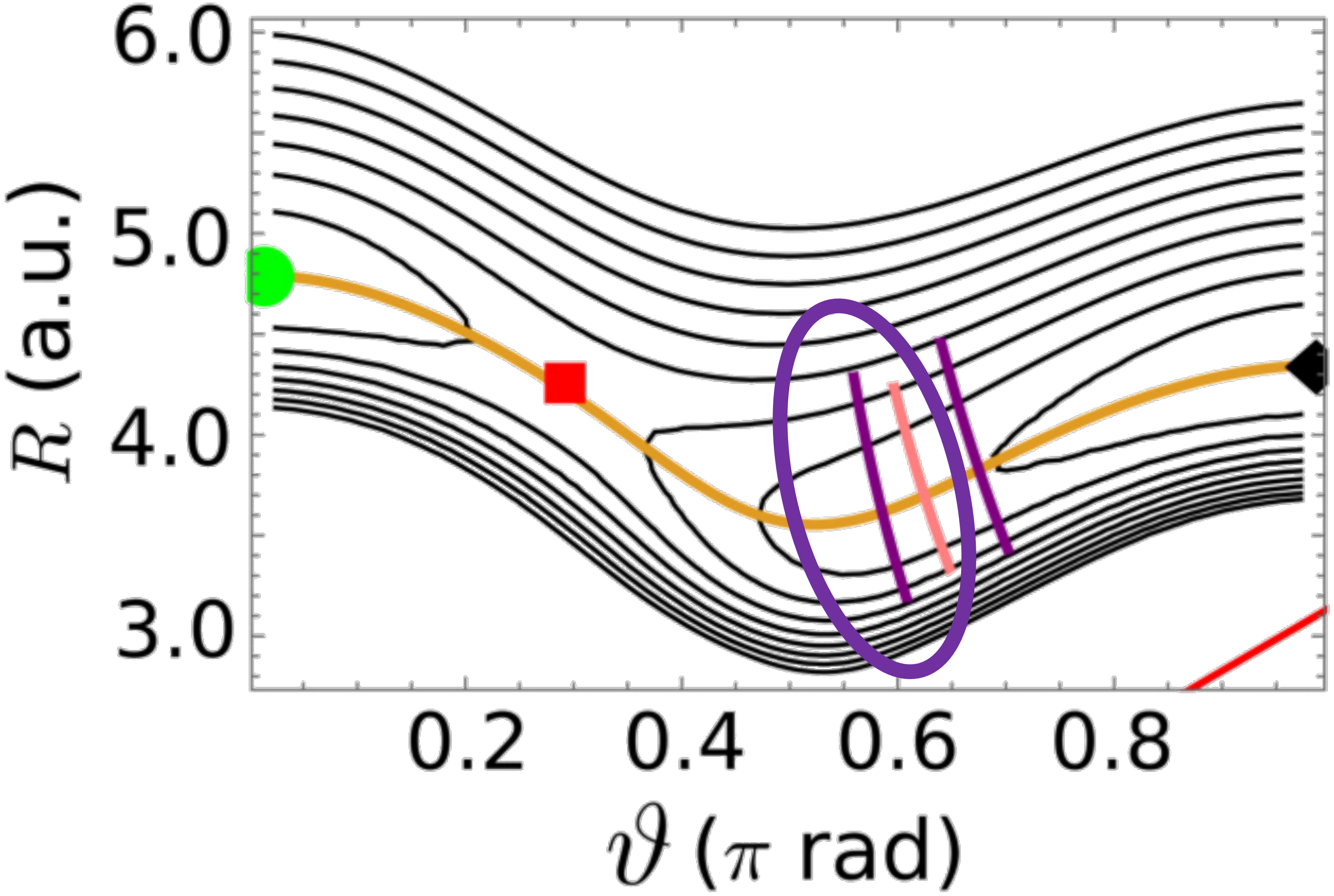


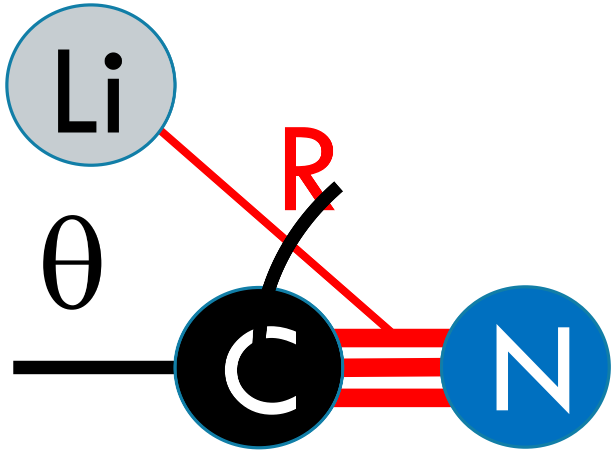


Periodic orbits

Center: marginallly stable

POTENTIAL ENERGY SURFACE



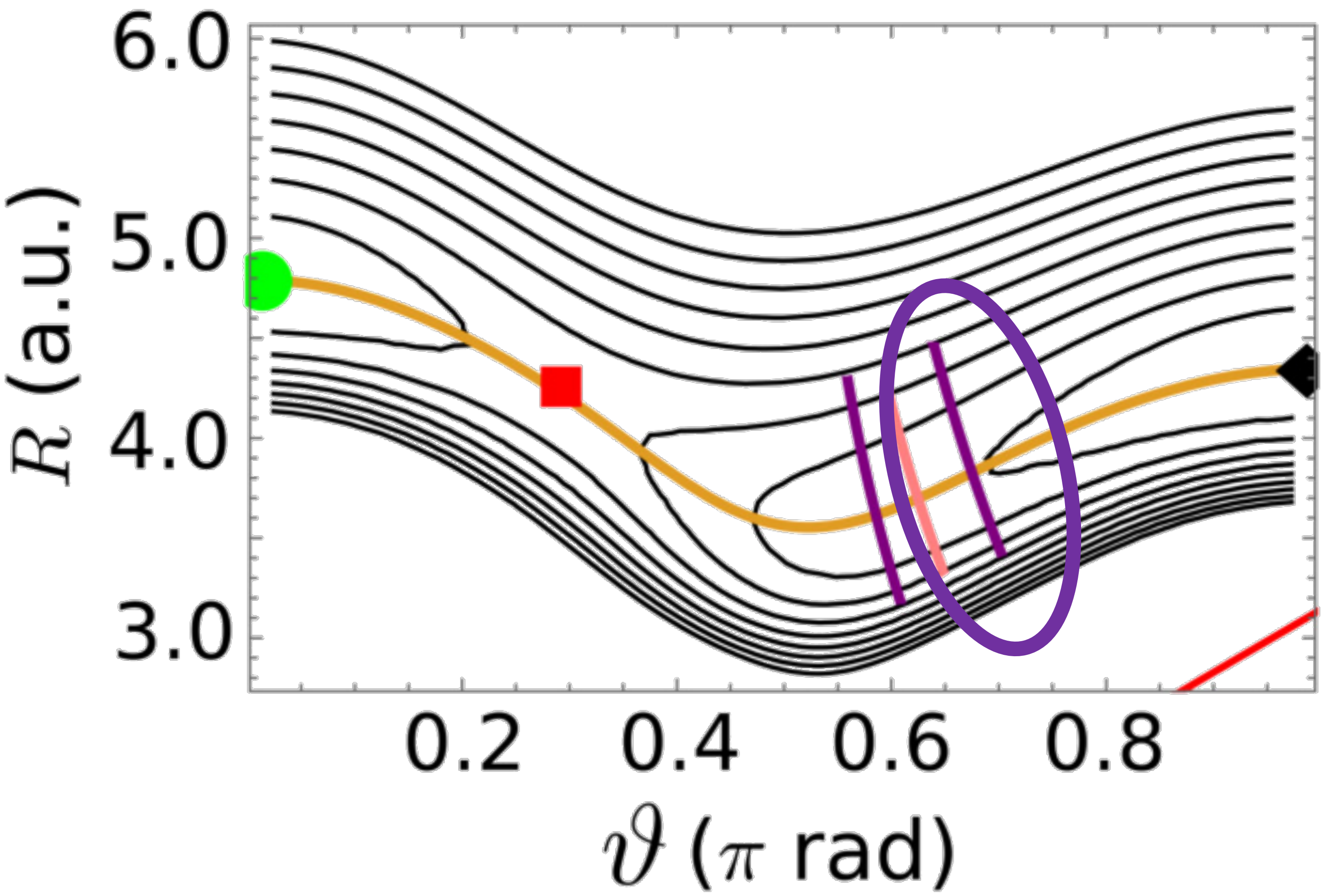


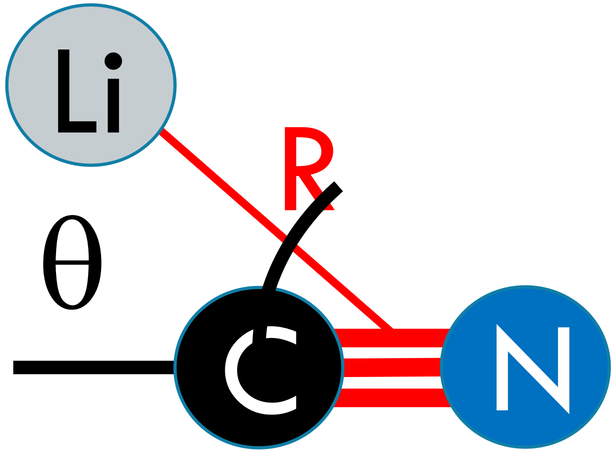
Periodic orbits

Center: marginallly stable

Left: Stable

POTENTIAL ENERGY SURFACE



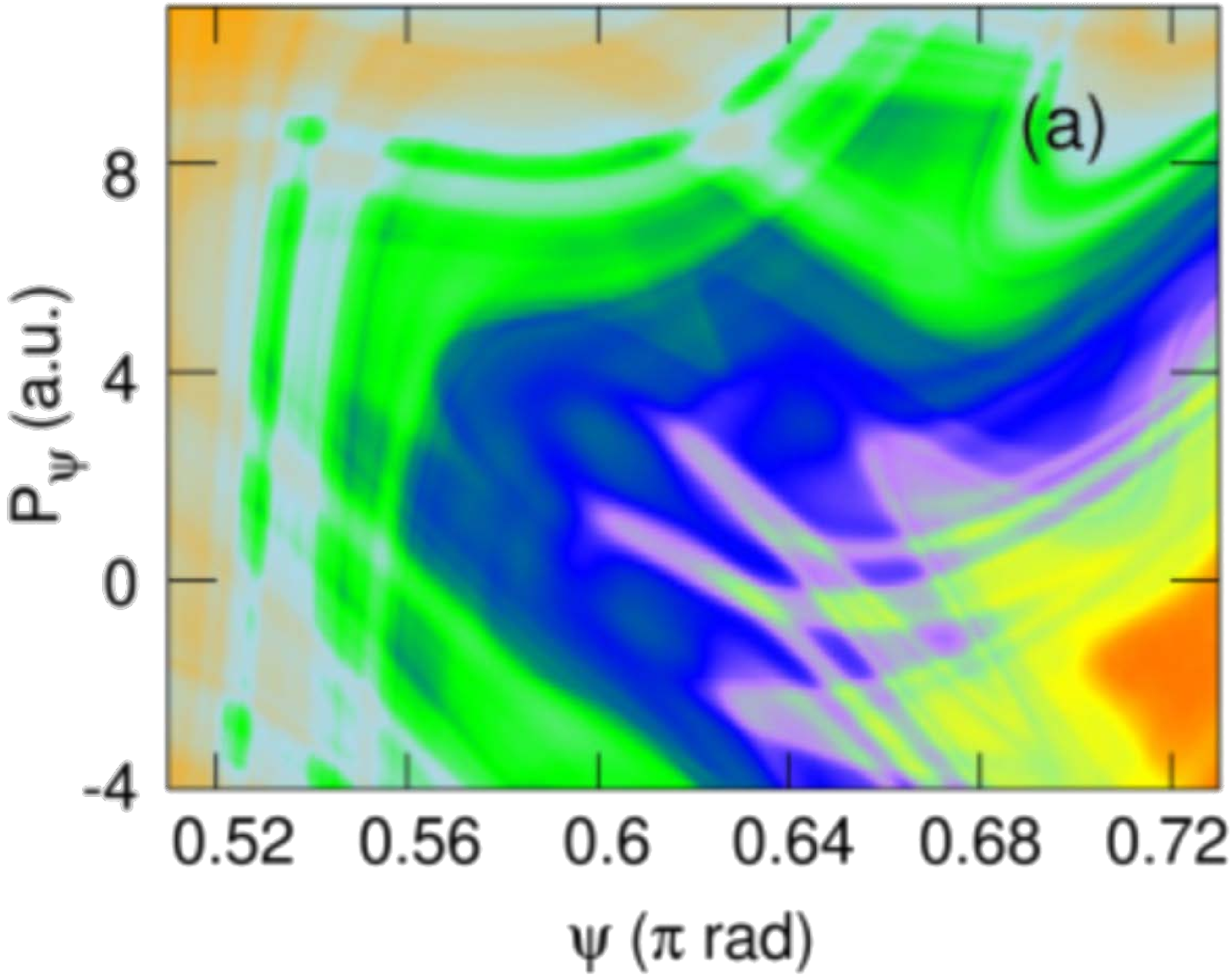


Periodic orbits

Center: marginallly stable

Left: Stable

Right: Unstable

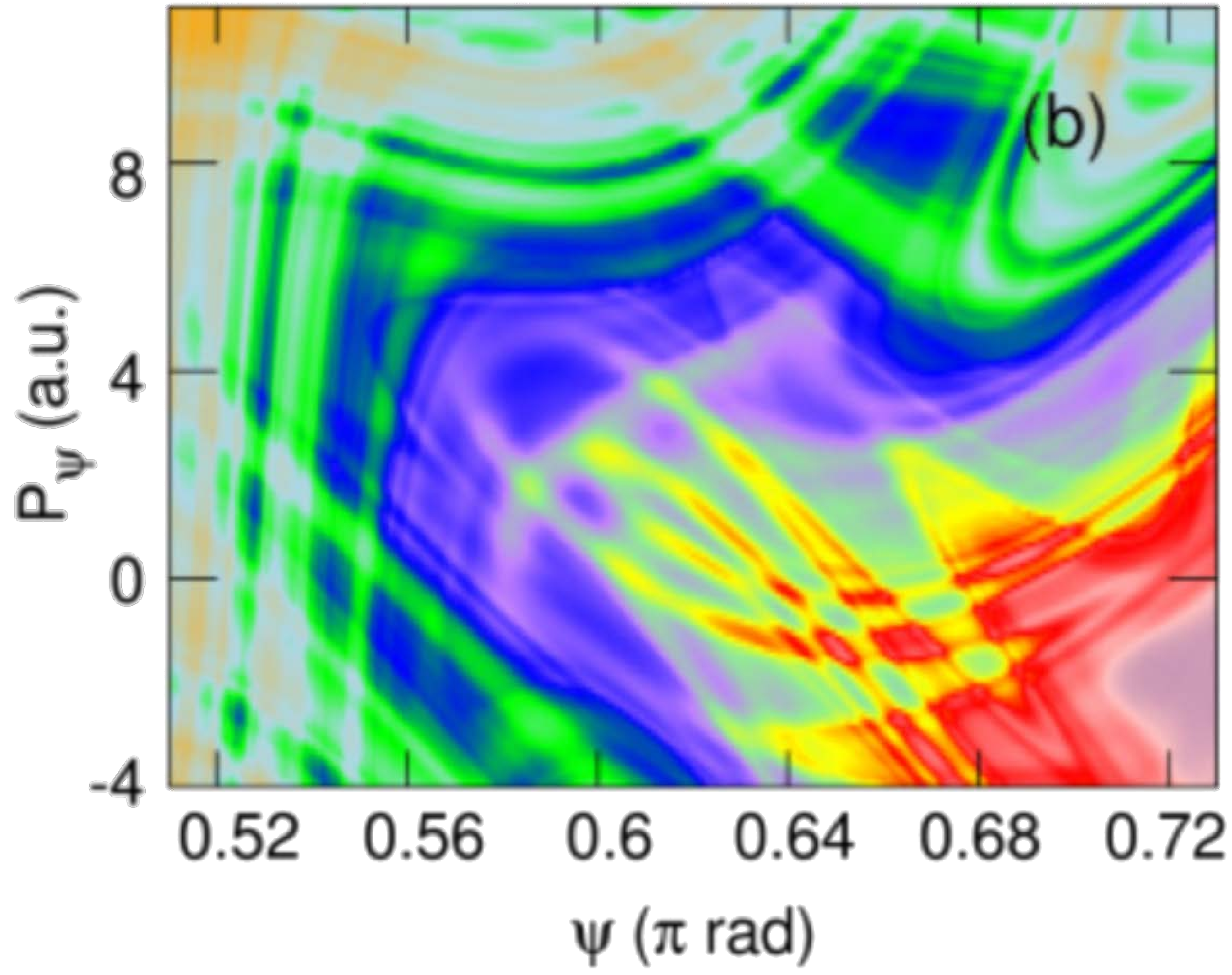


SADDLE-NODE BIFURCATION

$E = 3000\ cm^{-1}$

$p = 0.4$

$\tau = 2\,.\,10^4$

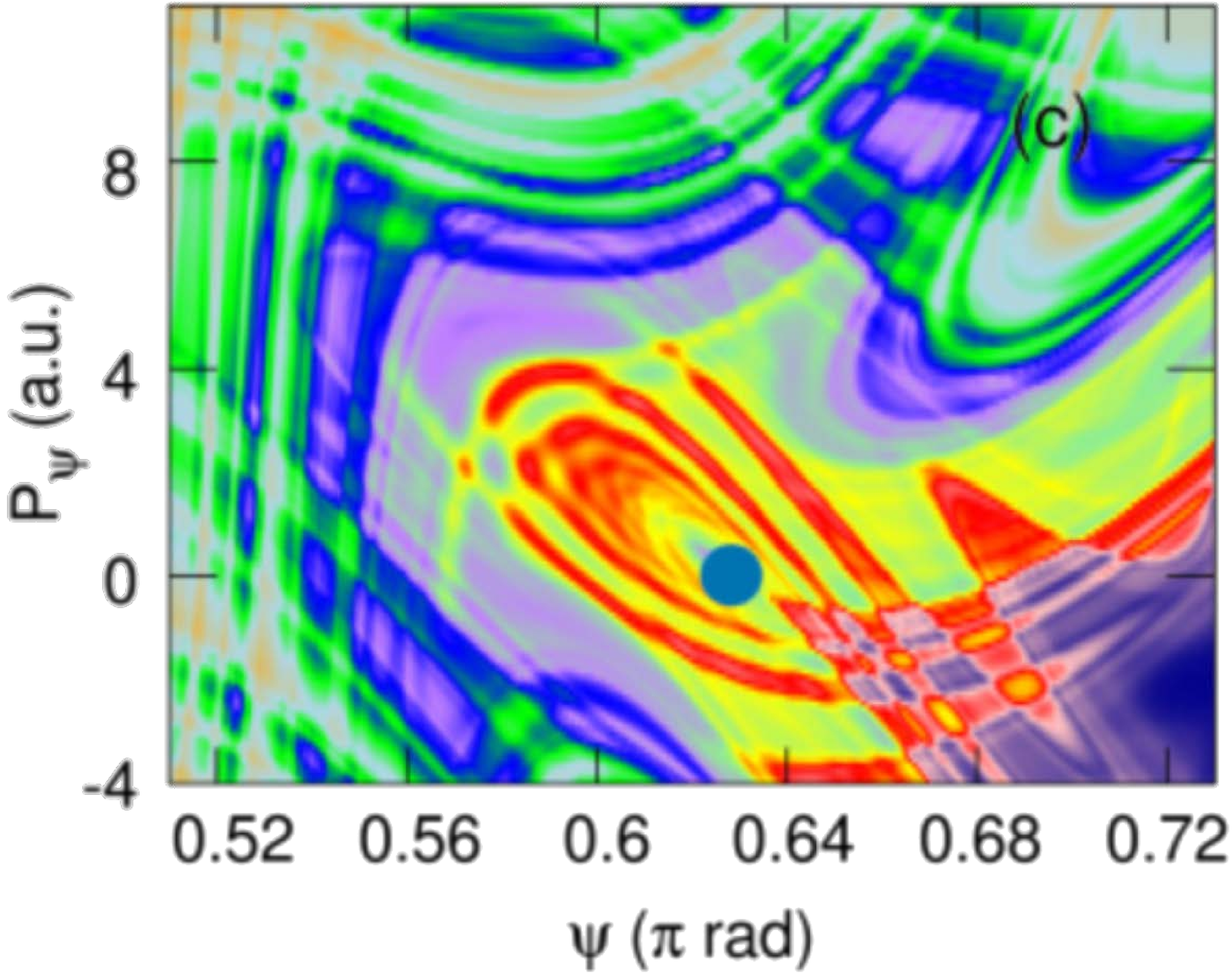


SADDLE-NODE BIFURCATION

$E = 3200\ cm^{-1}$

$p = 0.4$

$\tau = 2\,.\,10^4$

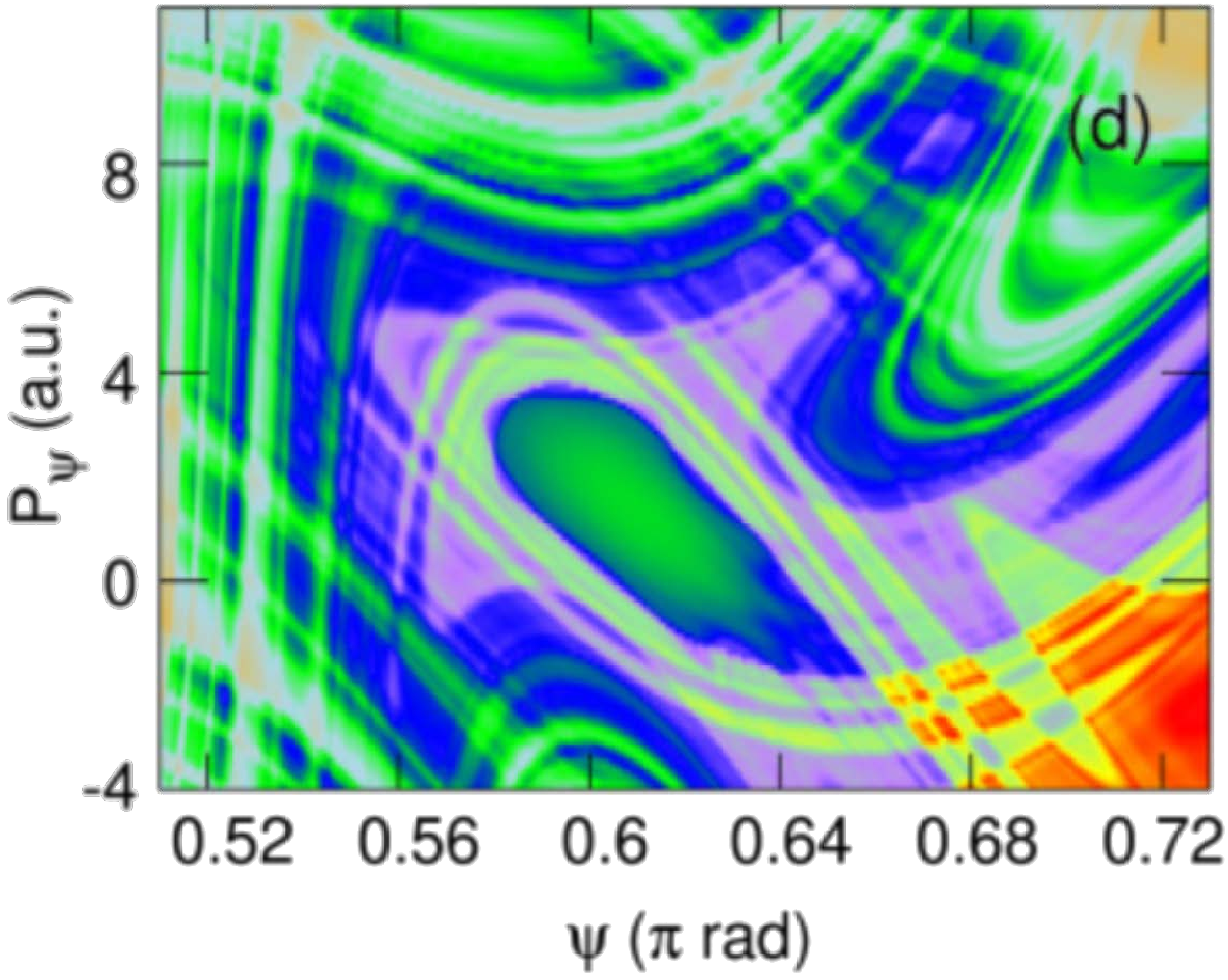


SADDLE-NODE BIFURCATION

$E \simeq 3441\ cm^{-1}$

$p = 0.4$

$\tau = 2\,.\,10^4$

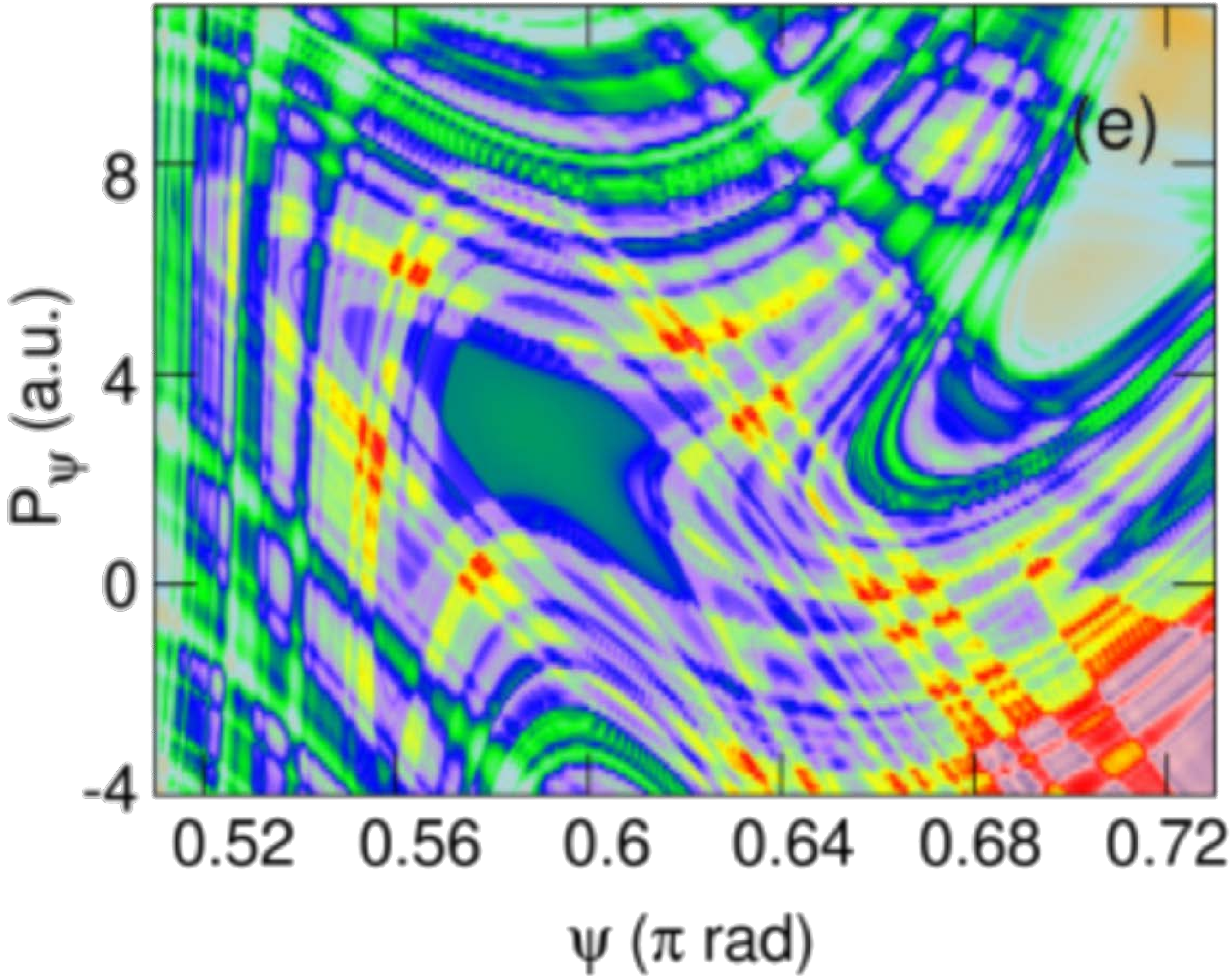


SADDLE-NODE BIFURCATION

$E = 3700\ cm^{-1}$

$p = 0.4$

$\tau = 2 \,.\, 10^4$

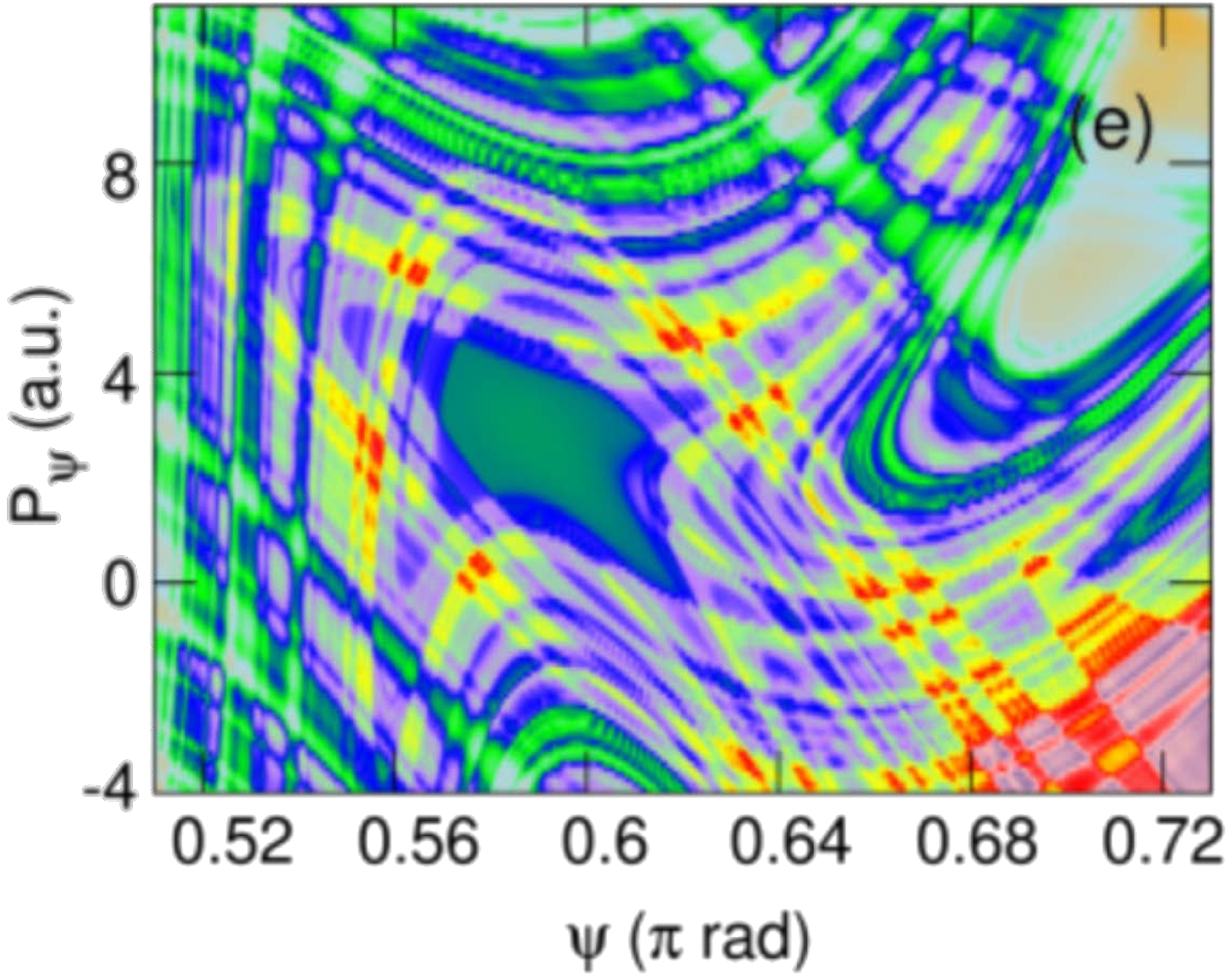


SADDLE-NODE BIFURCATION

$E \simeq 4162\ cm^{-1}$

$p = 0.4$

$\tau = 2\,.\,10^4$

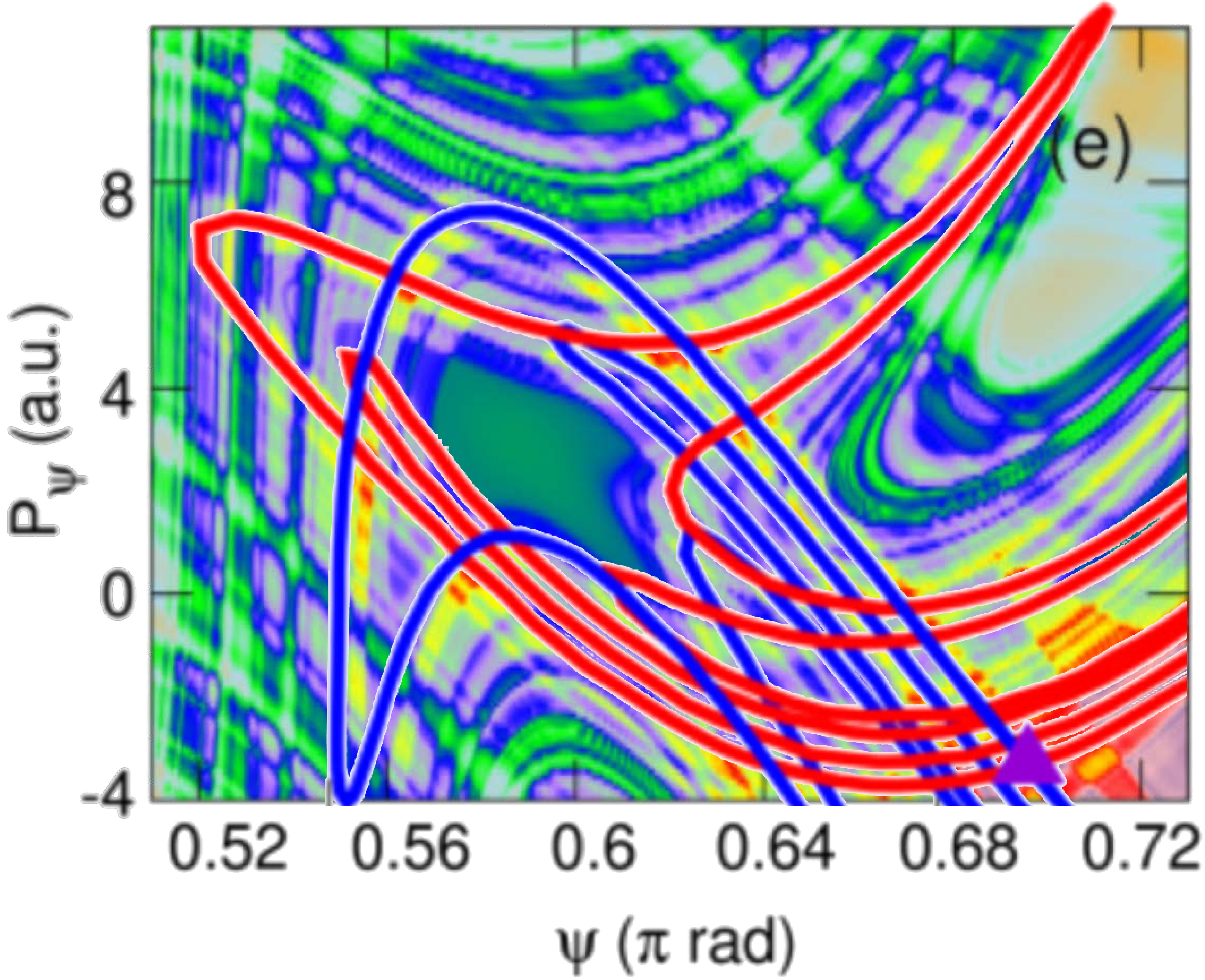


SADDLE-NODE BIFURCATION

$E \simeq 4162\ cm^{-1}$

$p = 0.4$

$\tau = 2\,.\,10^4$

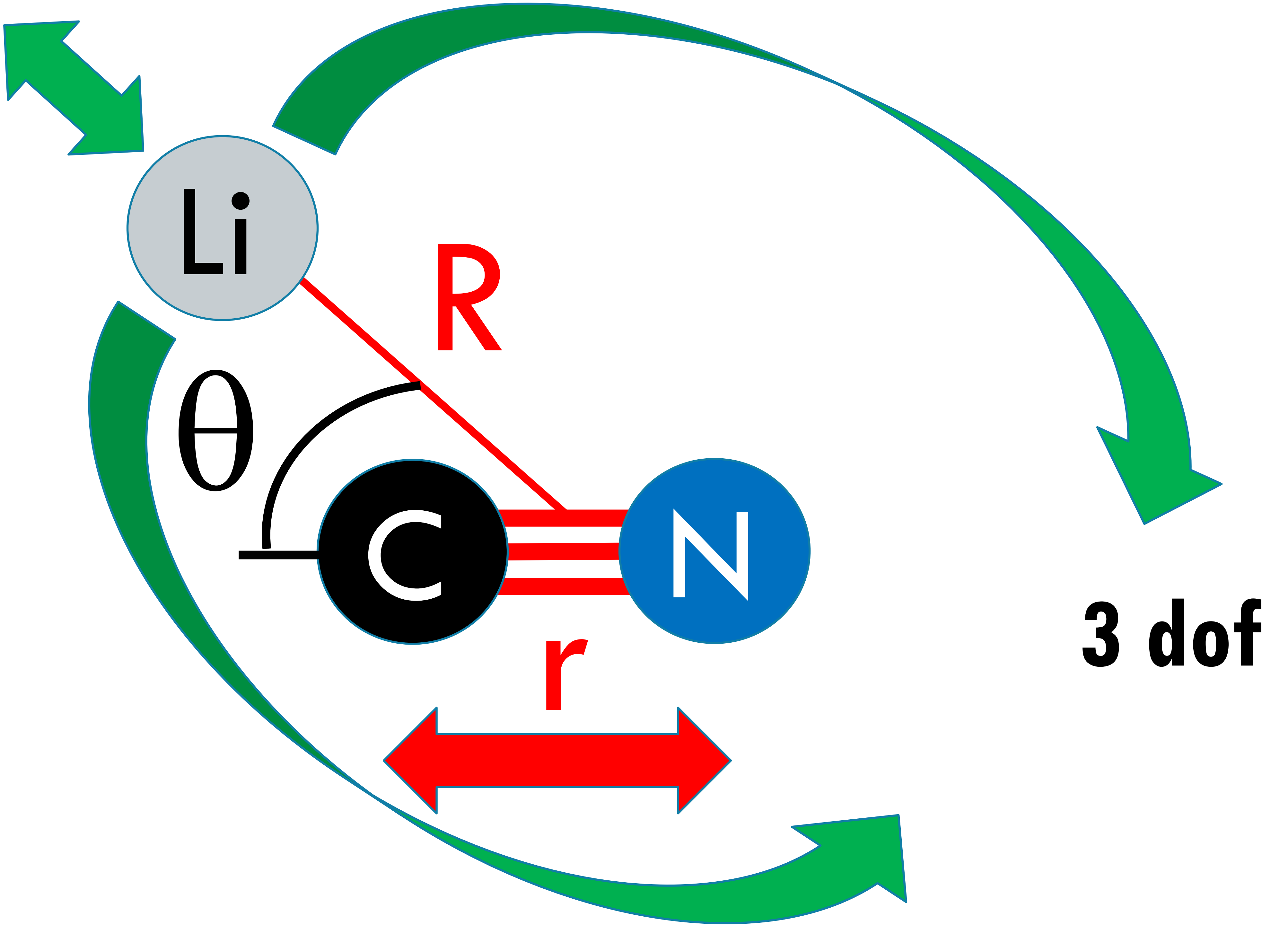


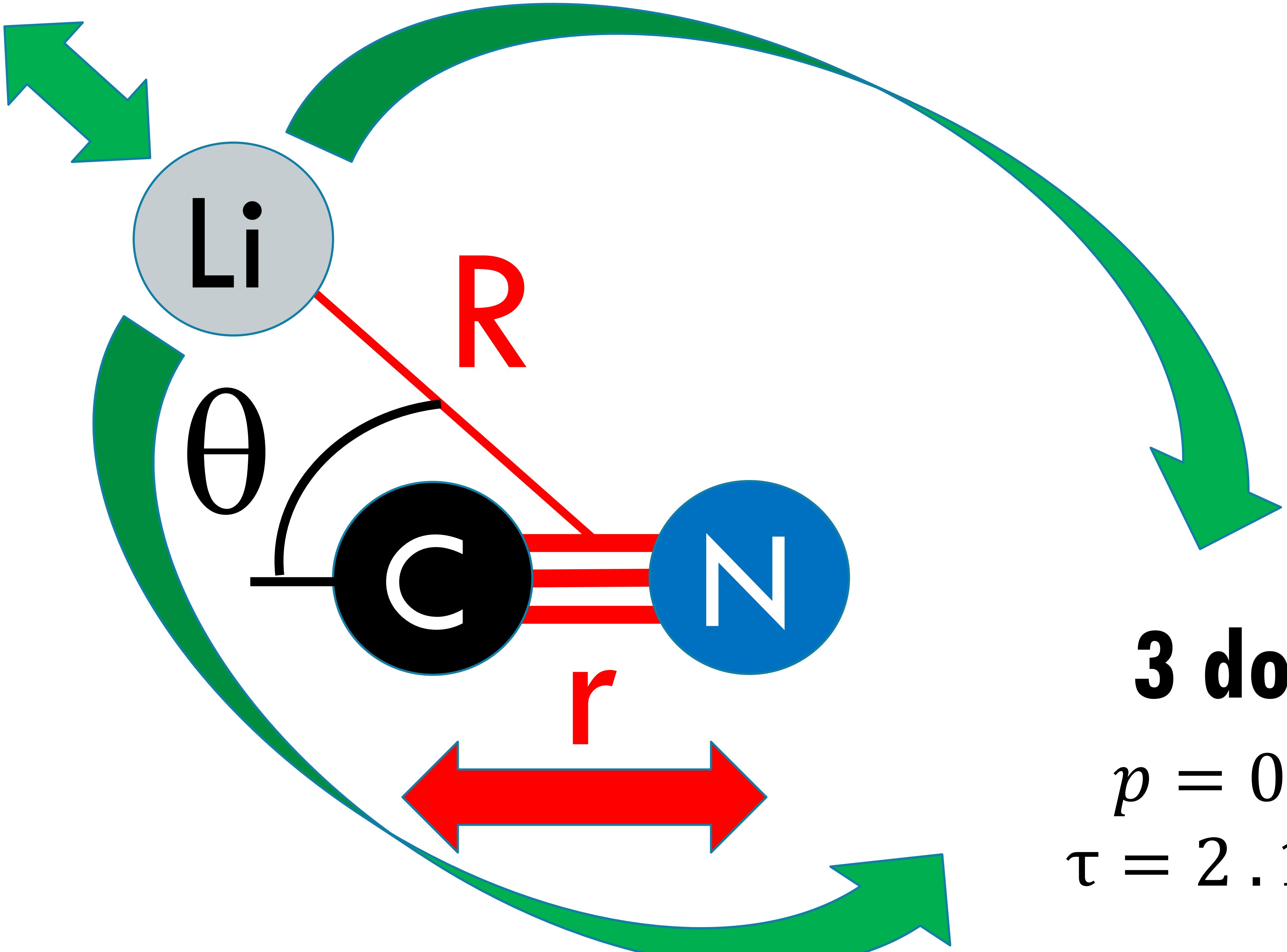
SADDLE-NODE BIFURCATION

$E \simeq 4162\ cm^{-1}$

$p = 0.4$

$\tau = 2\,.\,10^4$


Li
R
θ
C
N
r
3 dof



3 dof

$p = 0.4$

$\tau = 2 \,.\, 10^4$

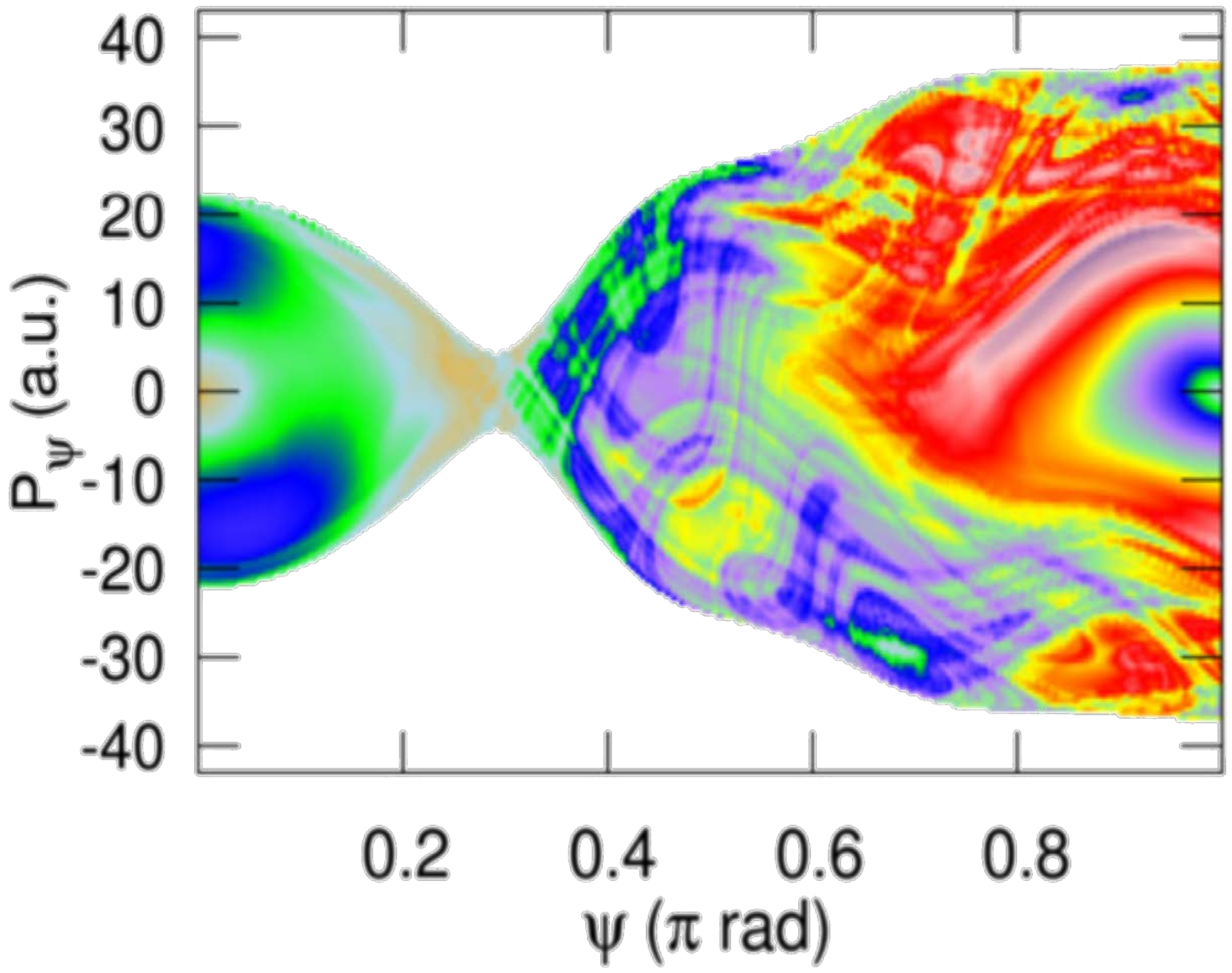
3-DOF SYSTEM

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

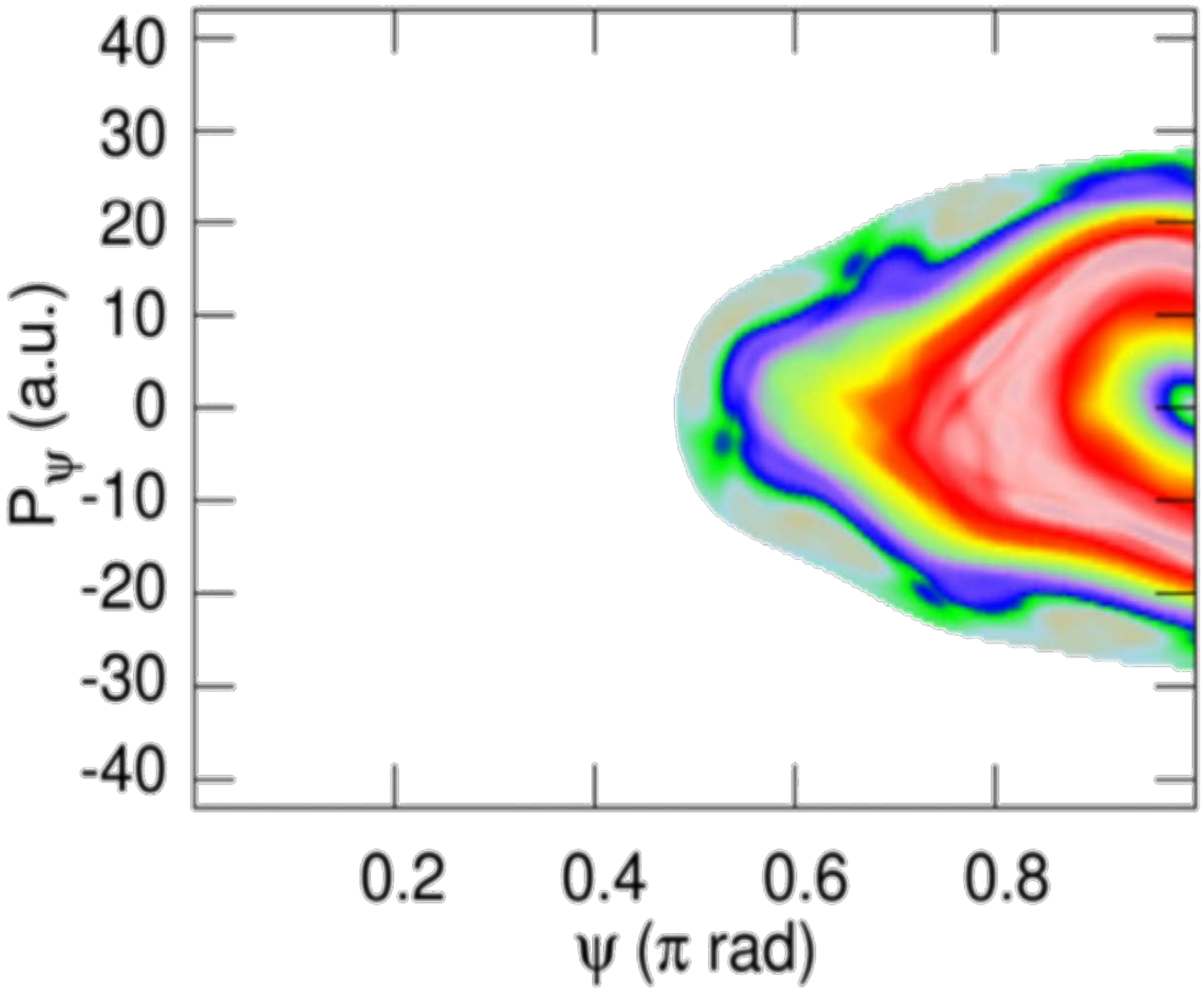
3-DOF SYSTEM

$$H = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{P_\theta^2}{2} + V(R, r, \theta)$$

The **more initial kinetic energy** is set in the r-dof, the more **regular** the phase space is in the other dofs’s



$$E = 3500\ cm^{-1}$$
$$T_{CN}^{kin} = 0\ cm^{-1}$$



$$E = 3500\ cm^{-1}$$
$$T_{CN}^{kin} = 1500\ cm^{-1}$$

CONCLUSIONS

CONCLUSIONS

Lagrangian descriptors allow the identification of the invariant manifolds in **molecular systems**

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NEW PERSPECTIVES INTO THE CHAOTIC DYNAMICS IN MOLECULES

Fabio Revuelta

Grupo de Sistemas Complejos

Universidad Politécnica de Madrid (Spain)

Dynamics Days Central Asia VI

5 June 2020

POINCARÉ SURFACE OF SECTION

$$\rho = R - R_{\mathrm{eq}}(\theta),$$

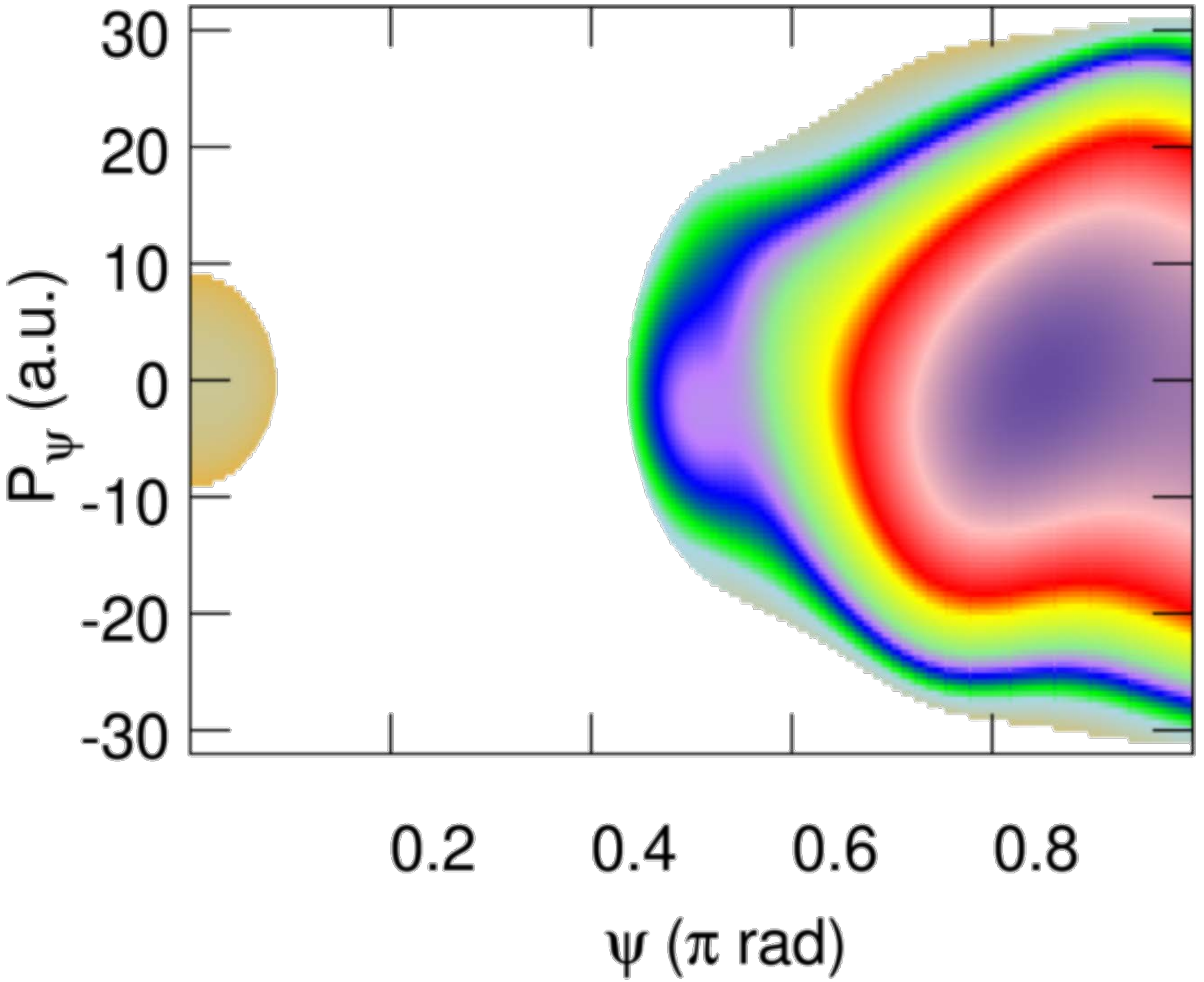
$$\vartheta = \theta,$$

$$P_\rho = P_R,$$

$$P_\vartheta = P_\theta + P_R \left(\frac{\mathrm{d}R_{\mathrm{eq}}(\theta)}{\mathrm{d}\theta} \right)$$

INFLUENCE OF THE INTEGRATION TIME

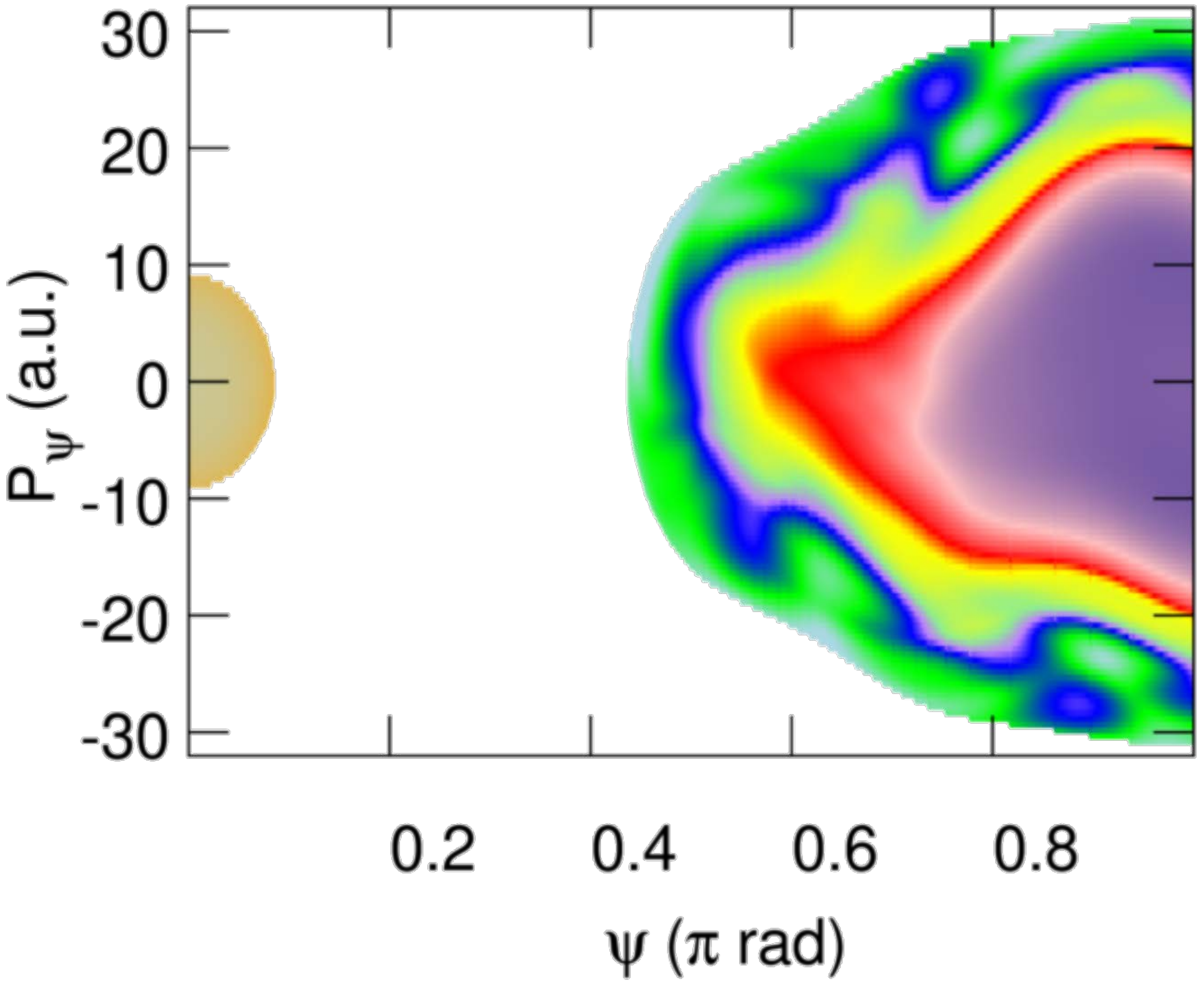
τ must be **long** enough… but **not** too **much**



LAGRANGIAN DESCRIPTORS

$Standard$

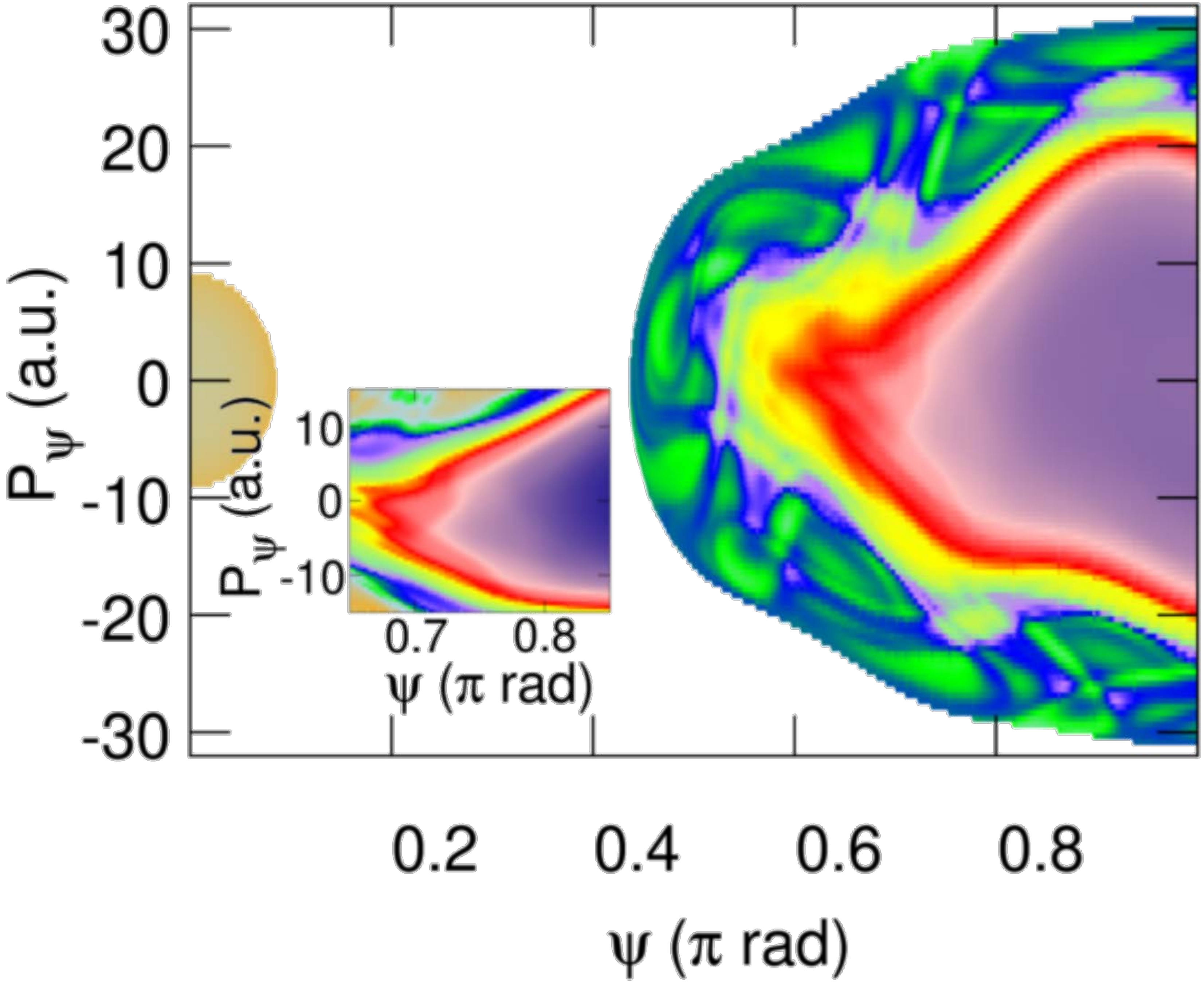
$\tau = 10^3$



LAGRANGIAN DESCRIPTORS

Standard

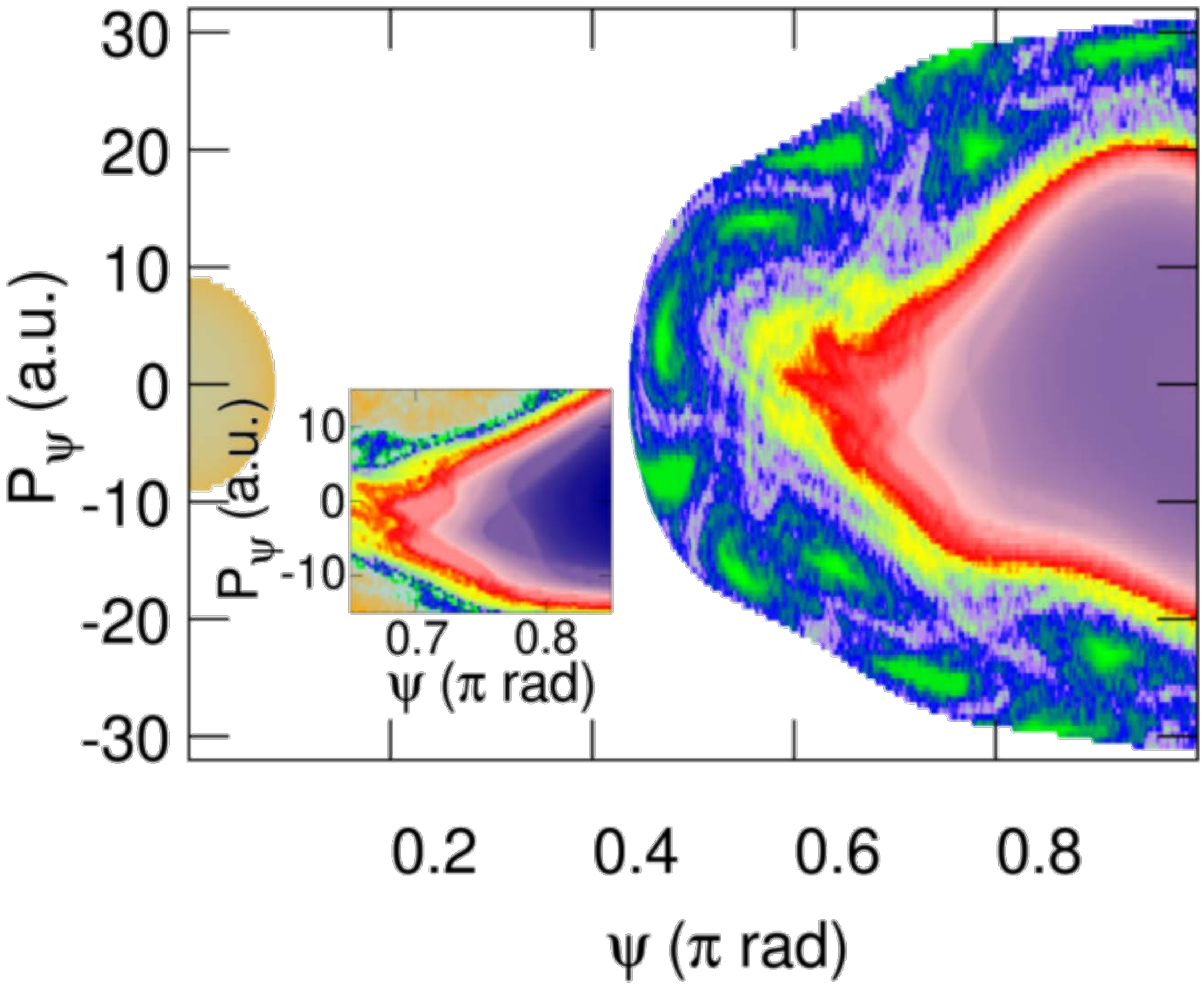
$\tau = 10^4$



LAGRANGIAN DESCRIPTORS

Standard

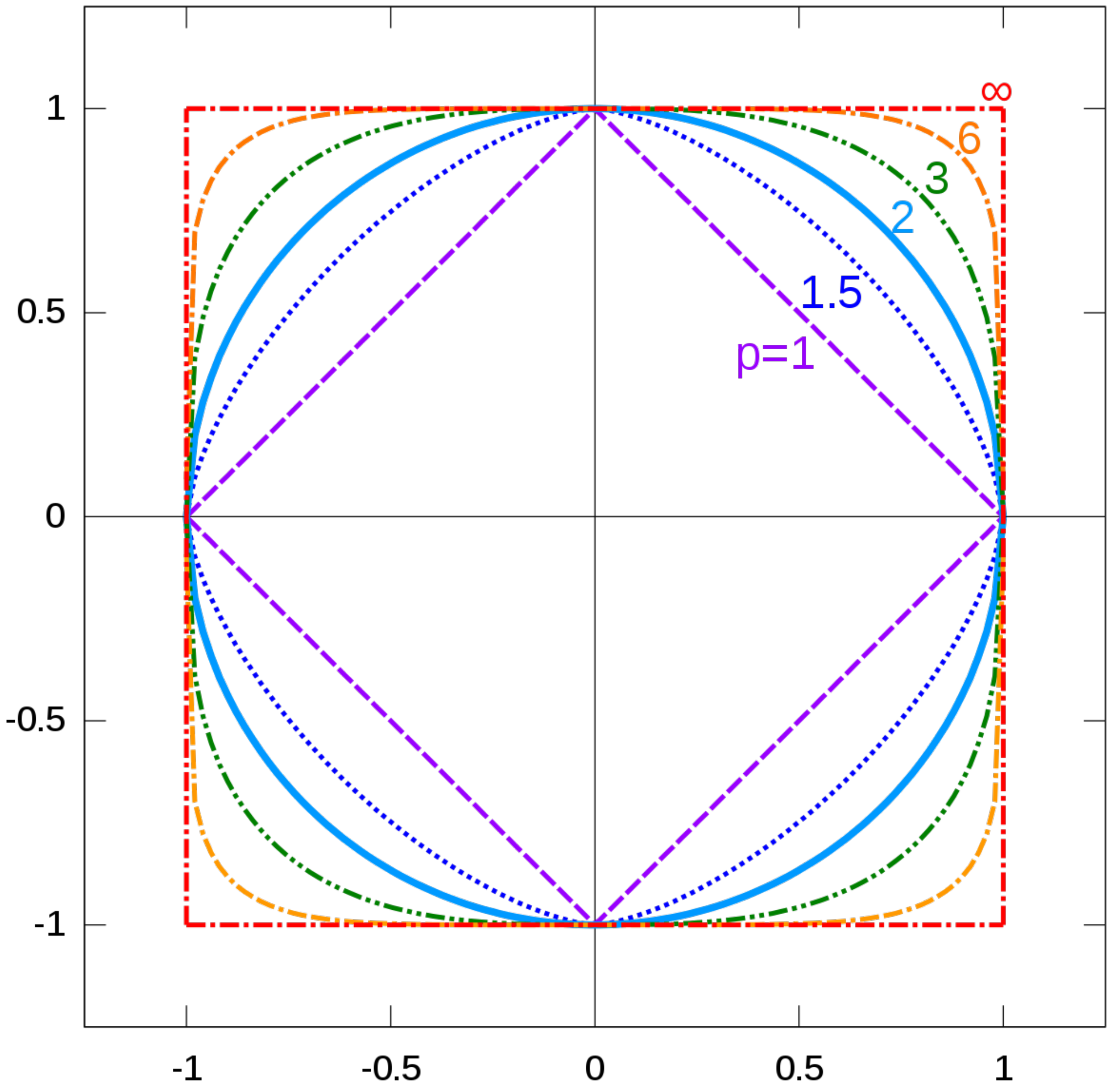
$\tau = 2 \, . \, 10^4$



LAGRANGIAN DESCRIPTORS

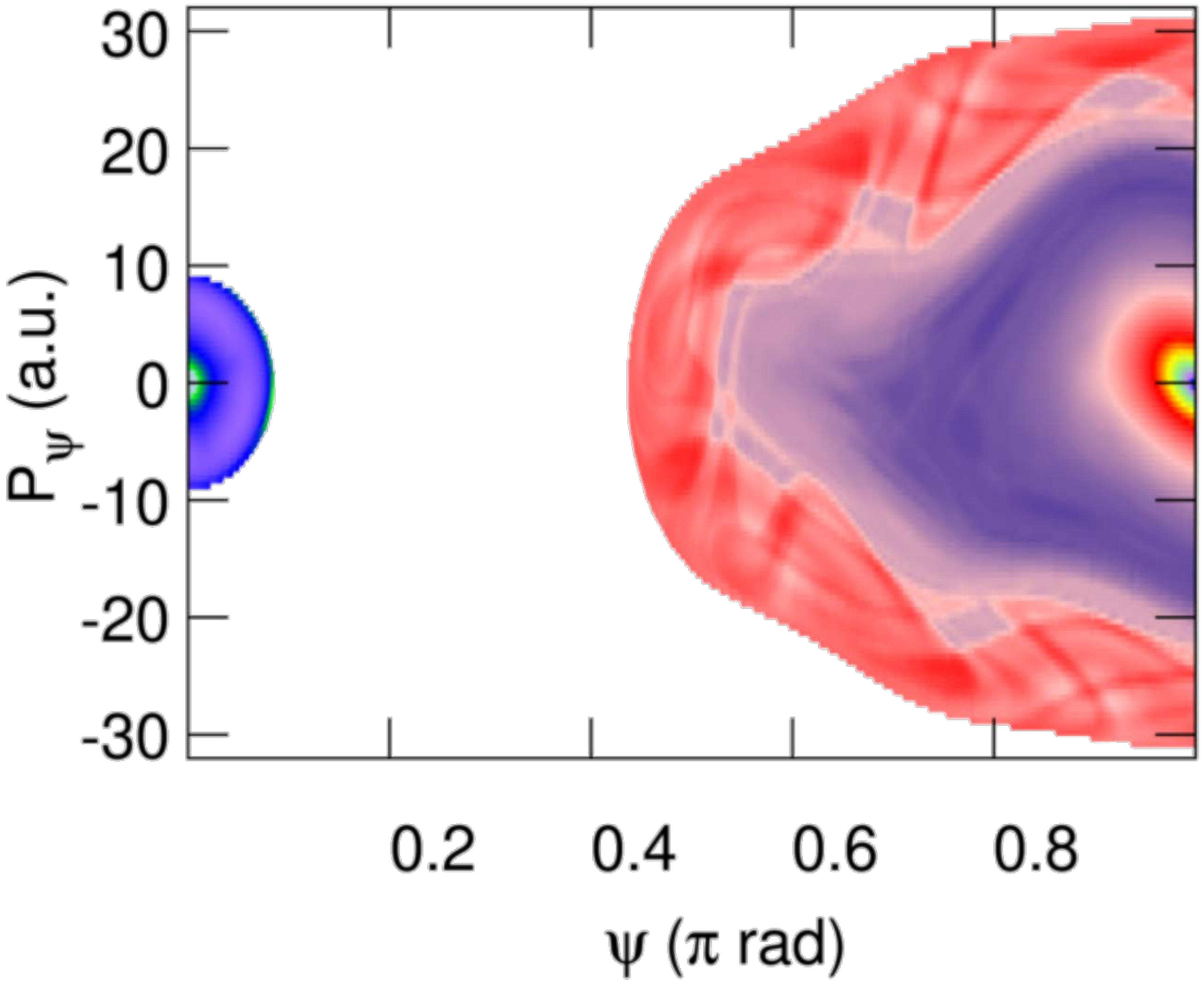
Standard

$\tau = 10^5$



INFLUENCE OF THE VALUE OF P IN THE NORM

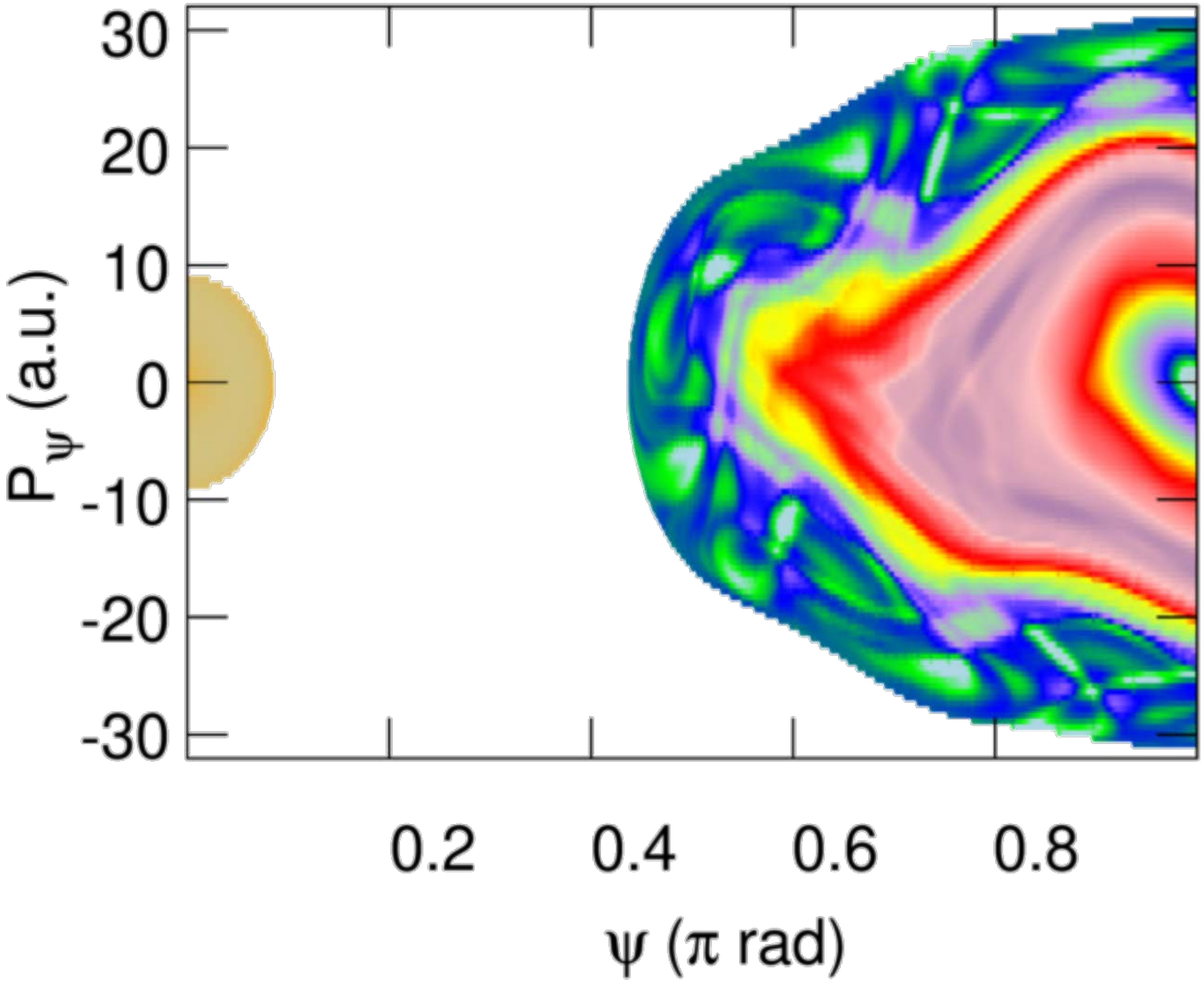
Image source:



LAGRANGIAN DESCRIPTORS

$p = 0.1$

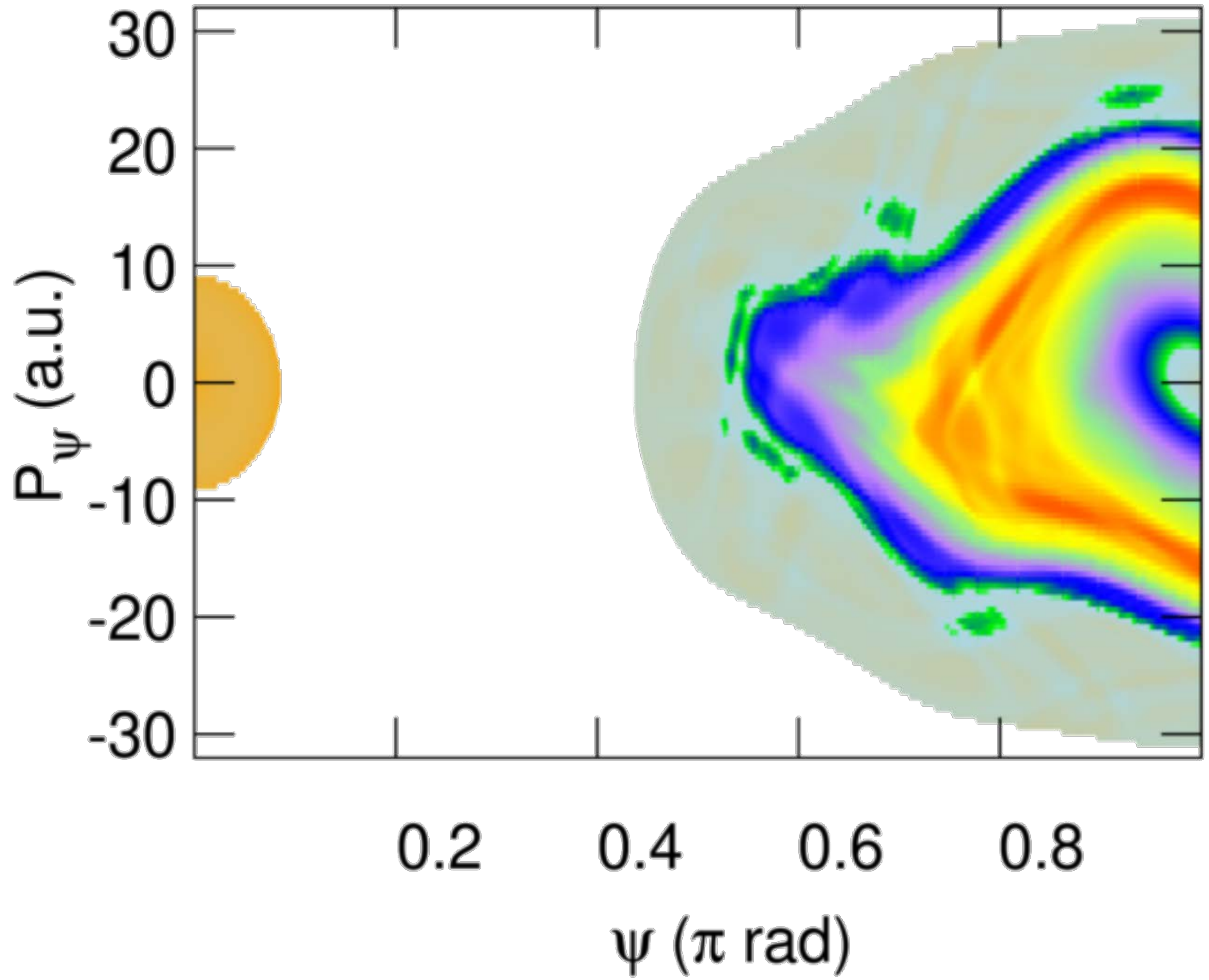
$\tau = 2\,.\,10^4$



LAGRANGIAN DESCRIPTORS

$p = 0.4$

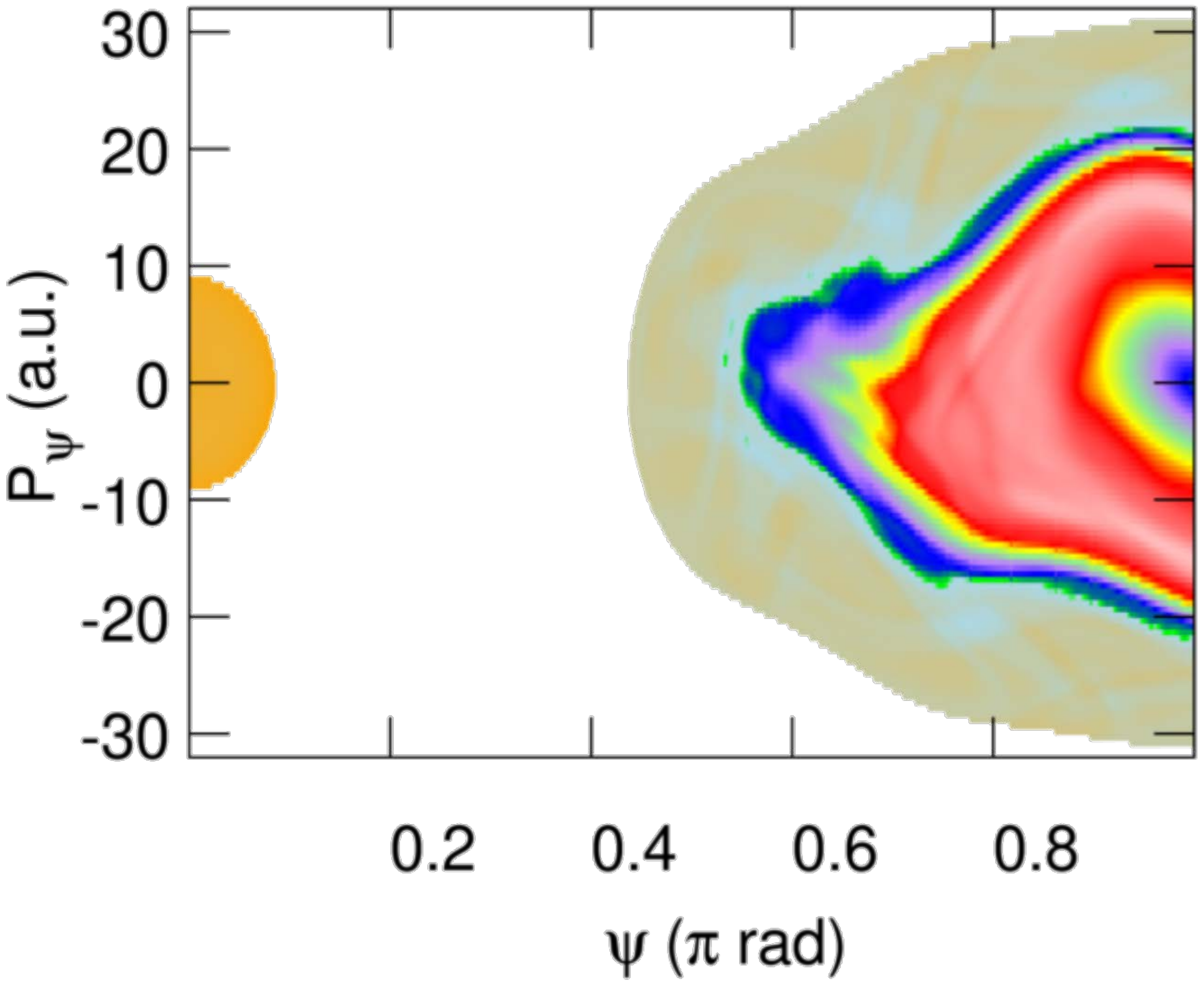
$\tau = 2\,.\,10^4$



LAGRANGIAN DESCRIPTORS

$p = 0.6$

$\tau = 2\,.\,10^4$

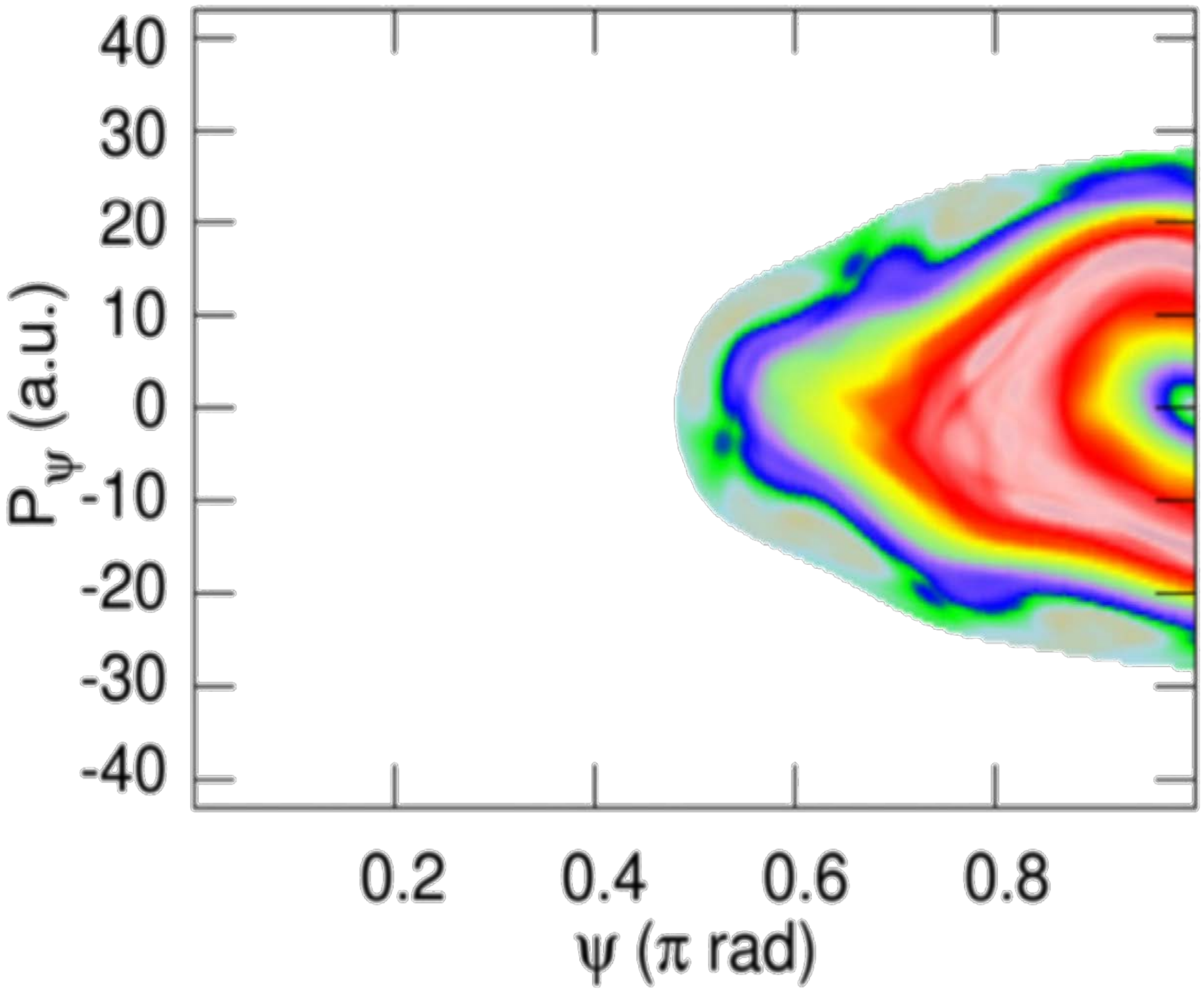


LAGRANGIAN DESCRIPTORS

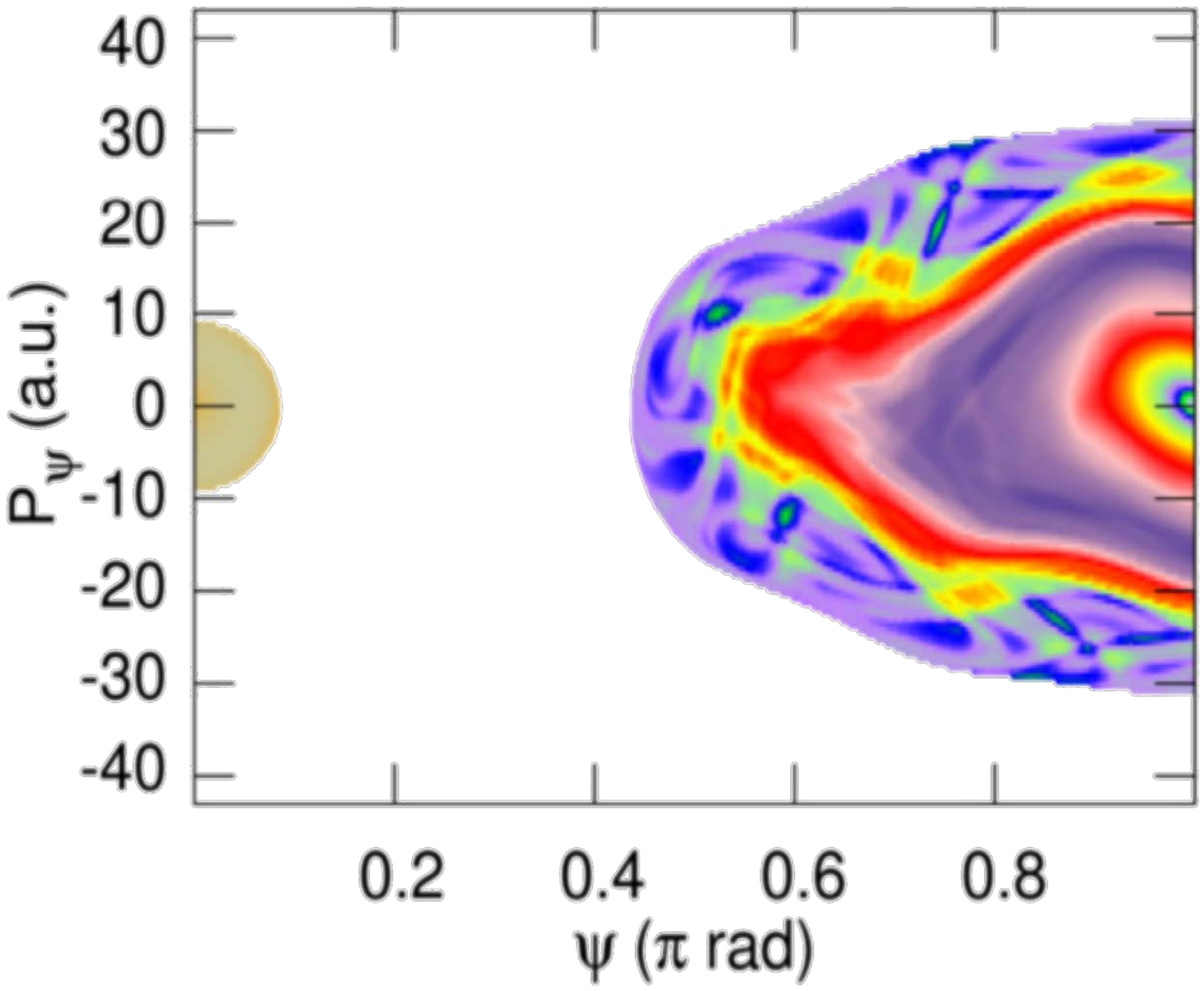
$p = 1$

$\tau = 2\,.\,10^4$

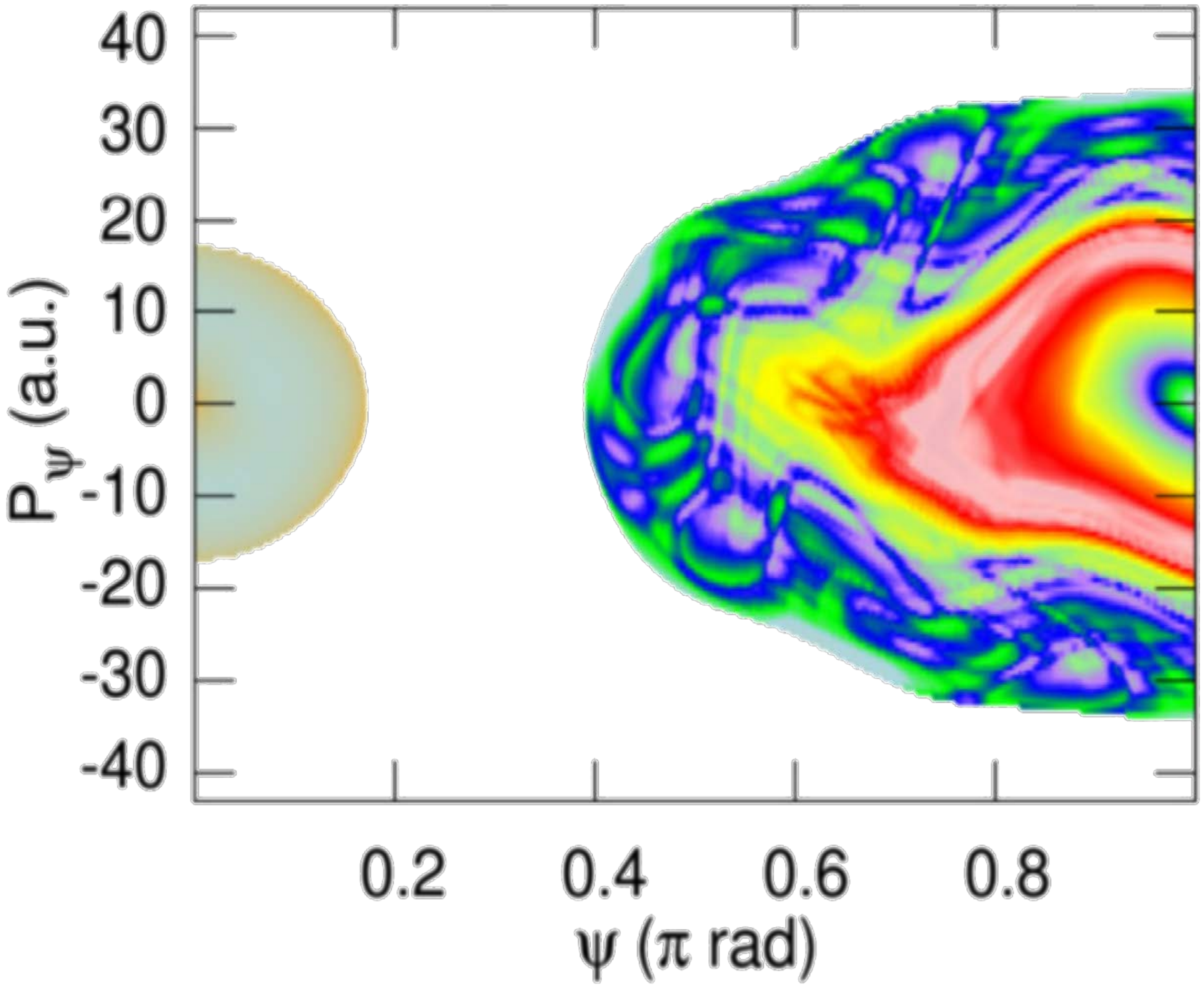
3 DOF



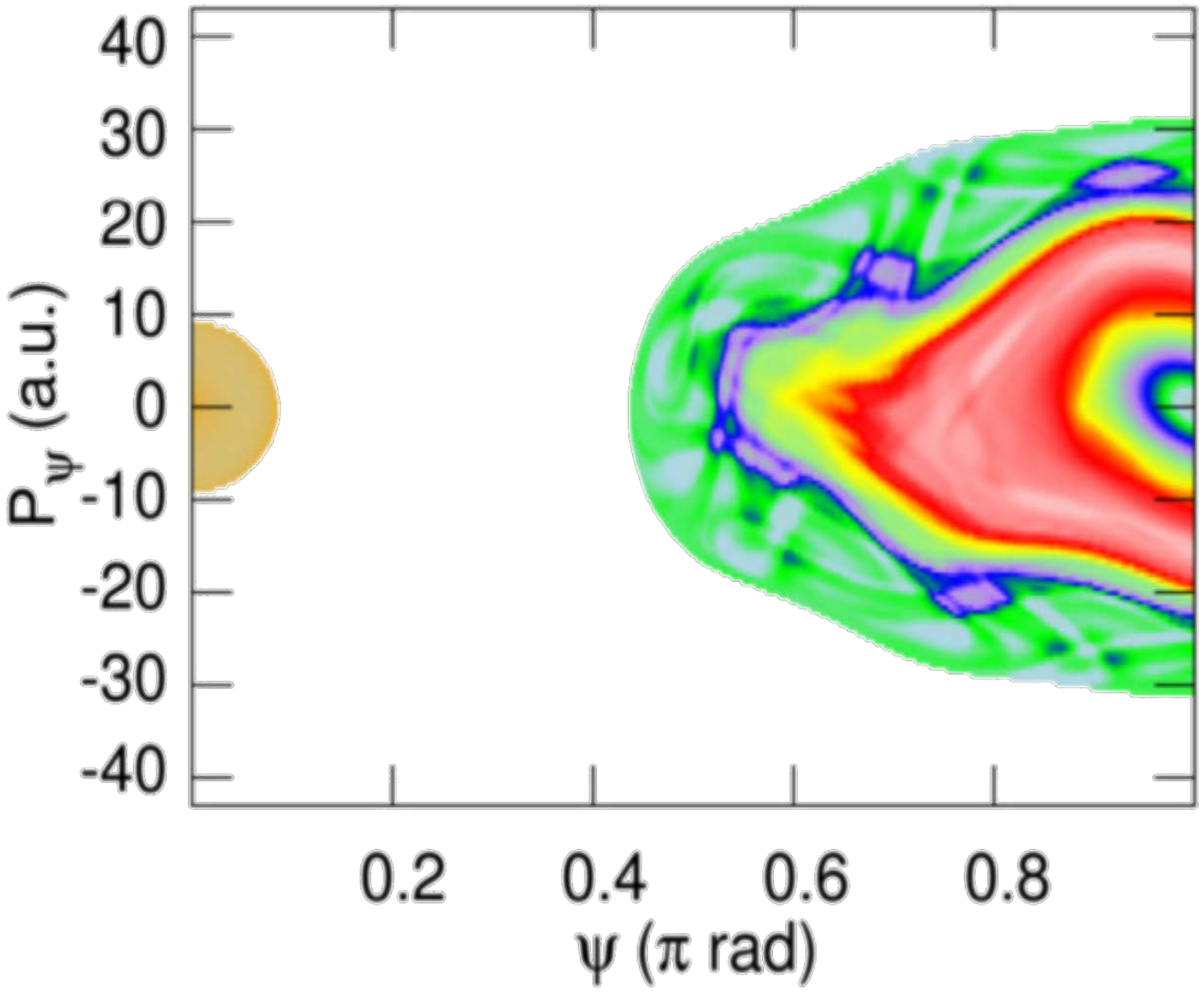
$$E = 3500\ cm^{-1}$$
$$T_{CN}^{kin} = 1500\ cm^{-1}$$



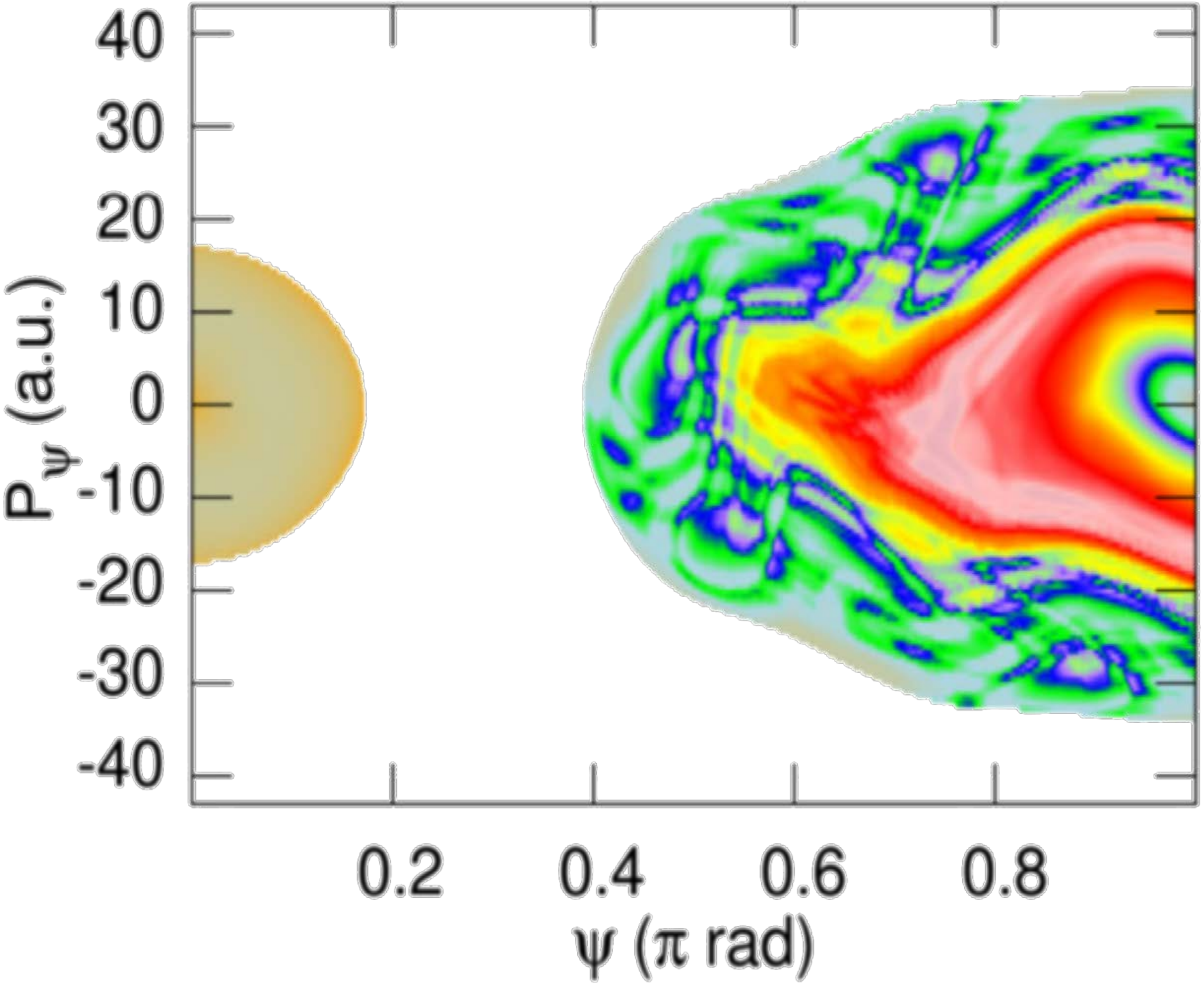
$E = 4000\ cm^{-1}$
$T_{CN}^{kin} = 1500\ cm^{-1}$



$$E = 4500\ cm^{-1}$$
$$T_{CN}^{kin} = 1500\ cm^{-1}$$

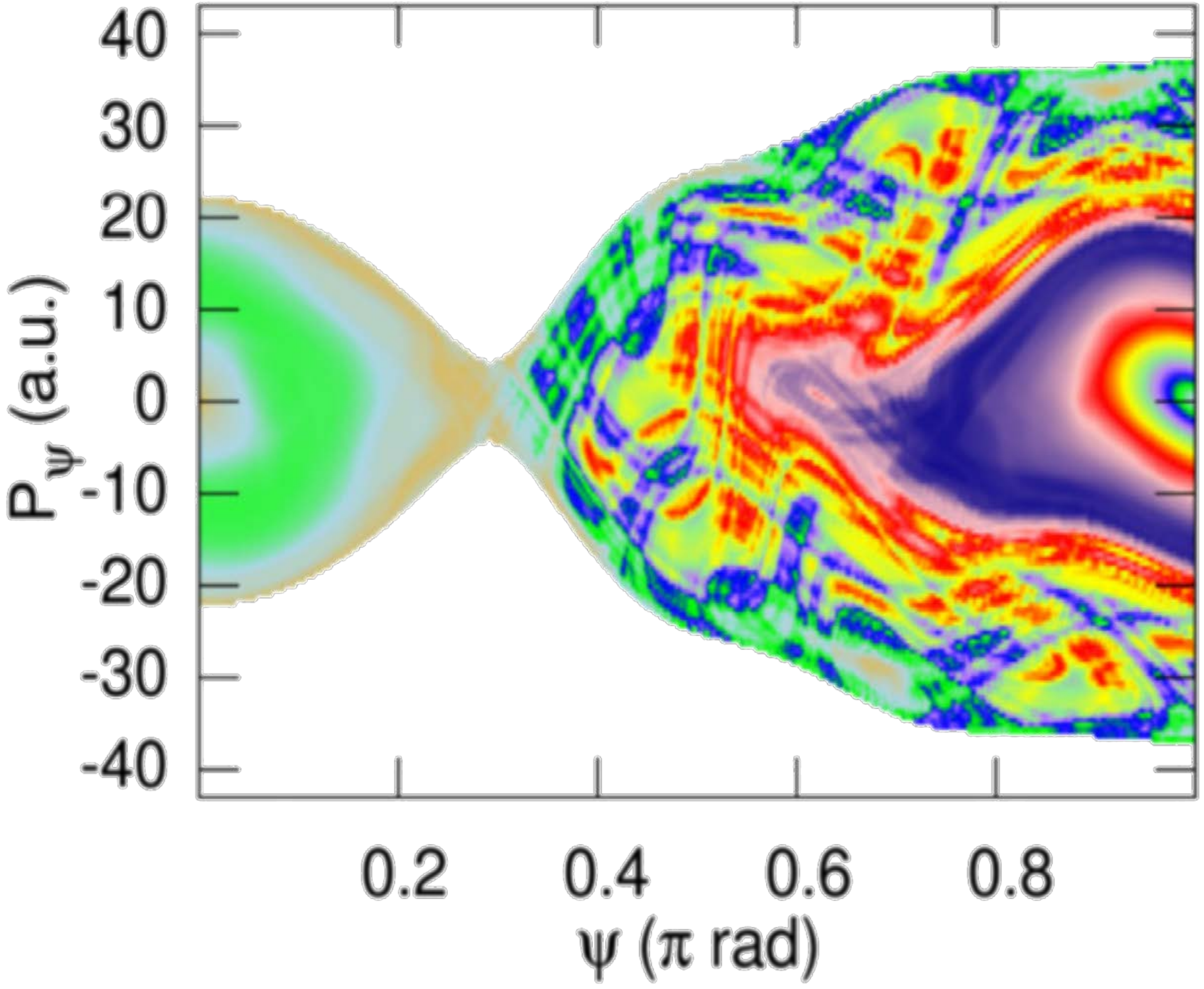


$$E = 3500\ cm^{-1}$$
$$T_{CN}^{kin} = 1000\ cm^{-1}$$

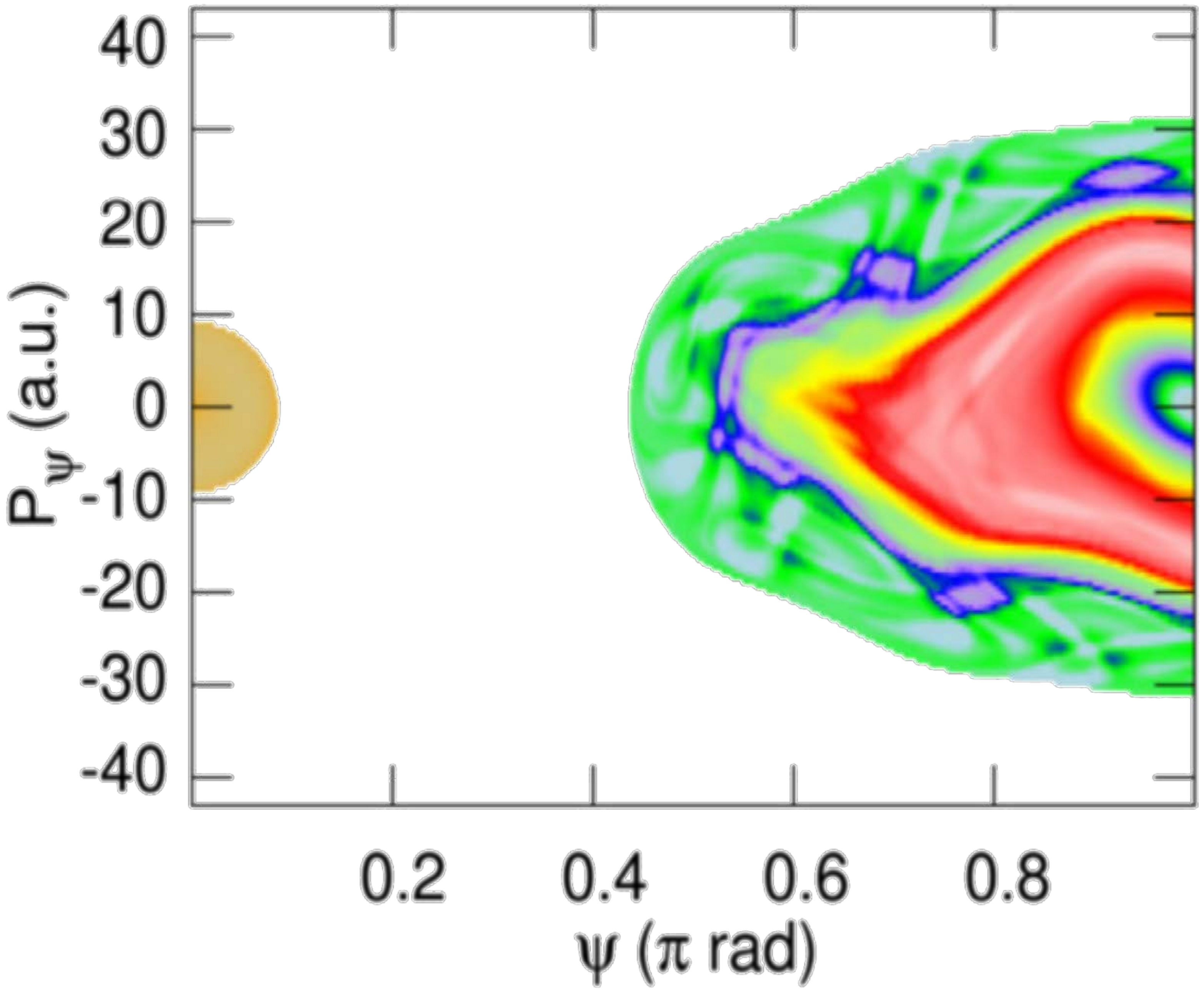


$E = 4000\ cm^{-1}$

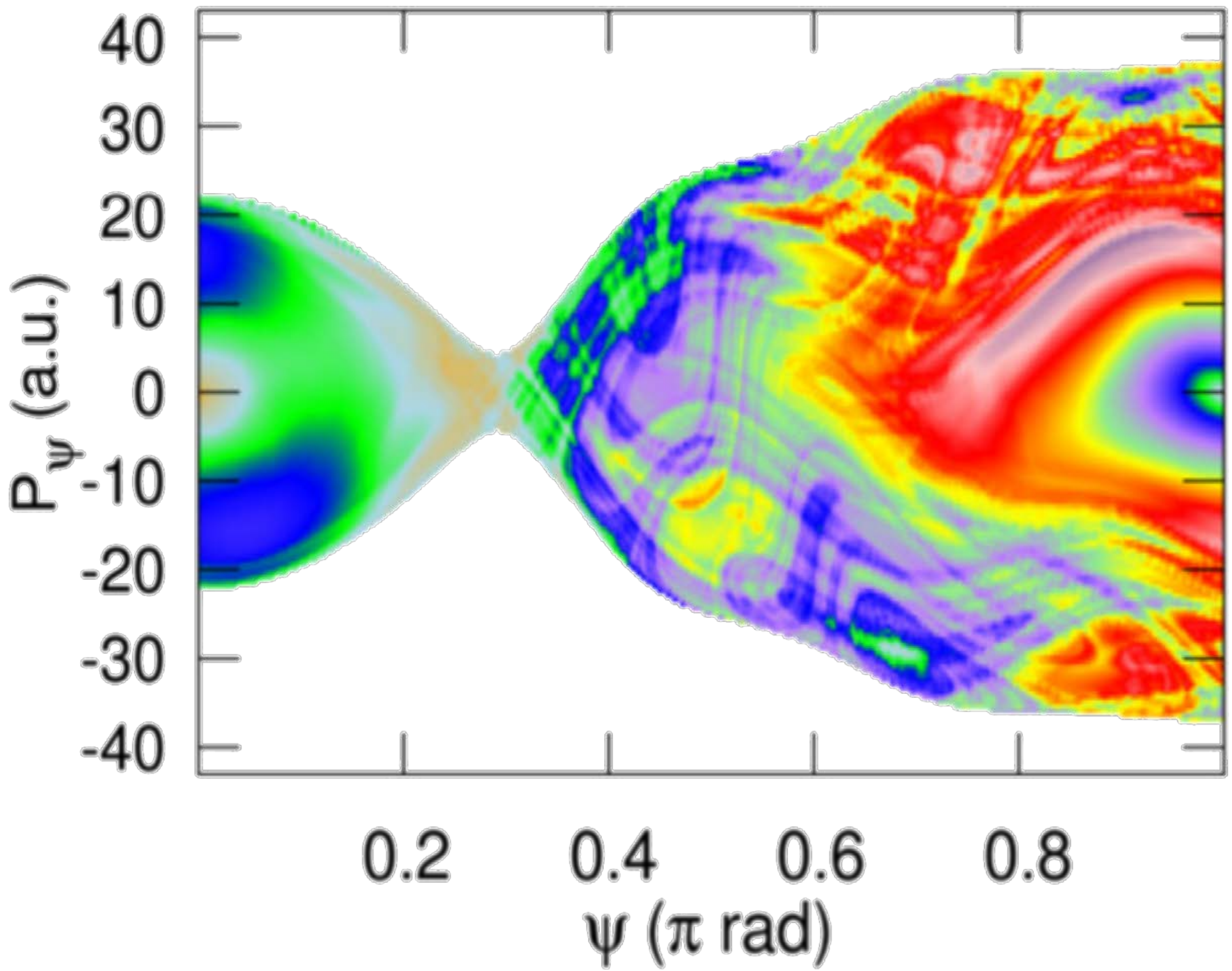
$T_{CN}^{kin} = 1000\ cm^{-1}$



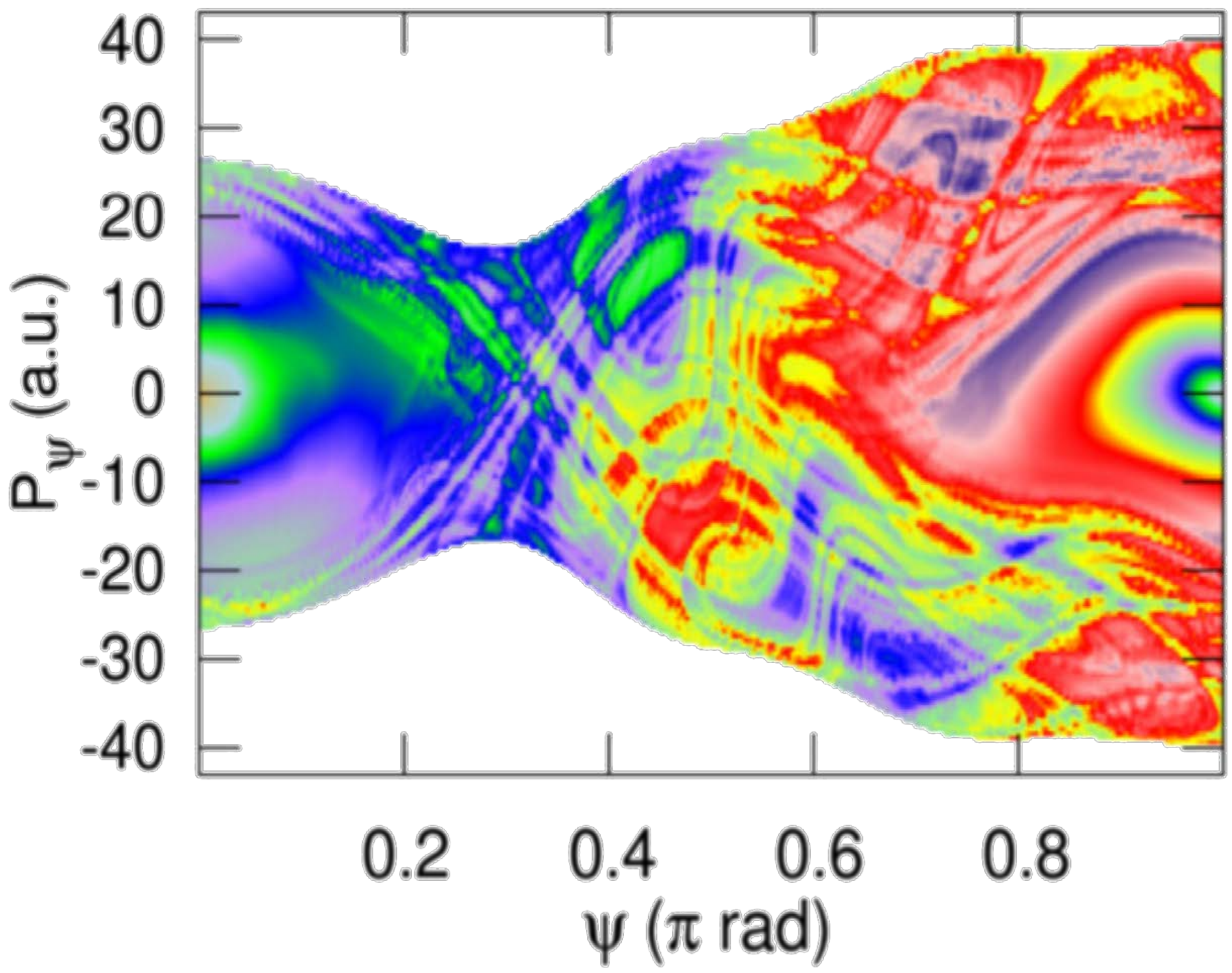
$$E = 4500\ cm^{-1}$$
$$T_{CN}^{kin} = 1000\ cm^{-1}$$



$$E = 3500\ cm^{-1}$$
$$T_{CN}^{kin} = 0\ cm^{-1}$$

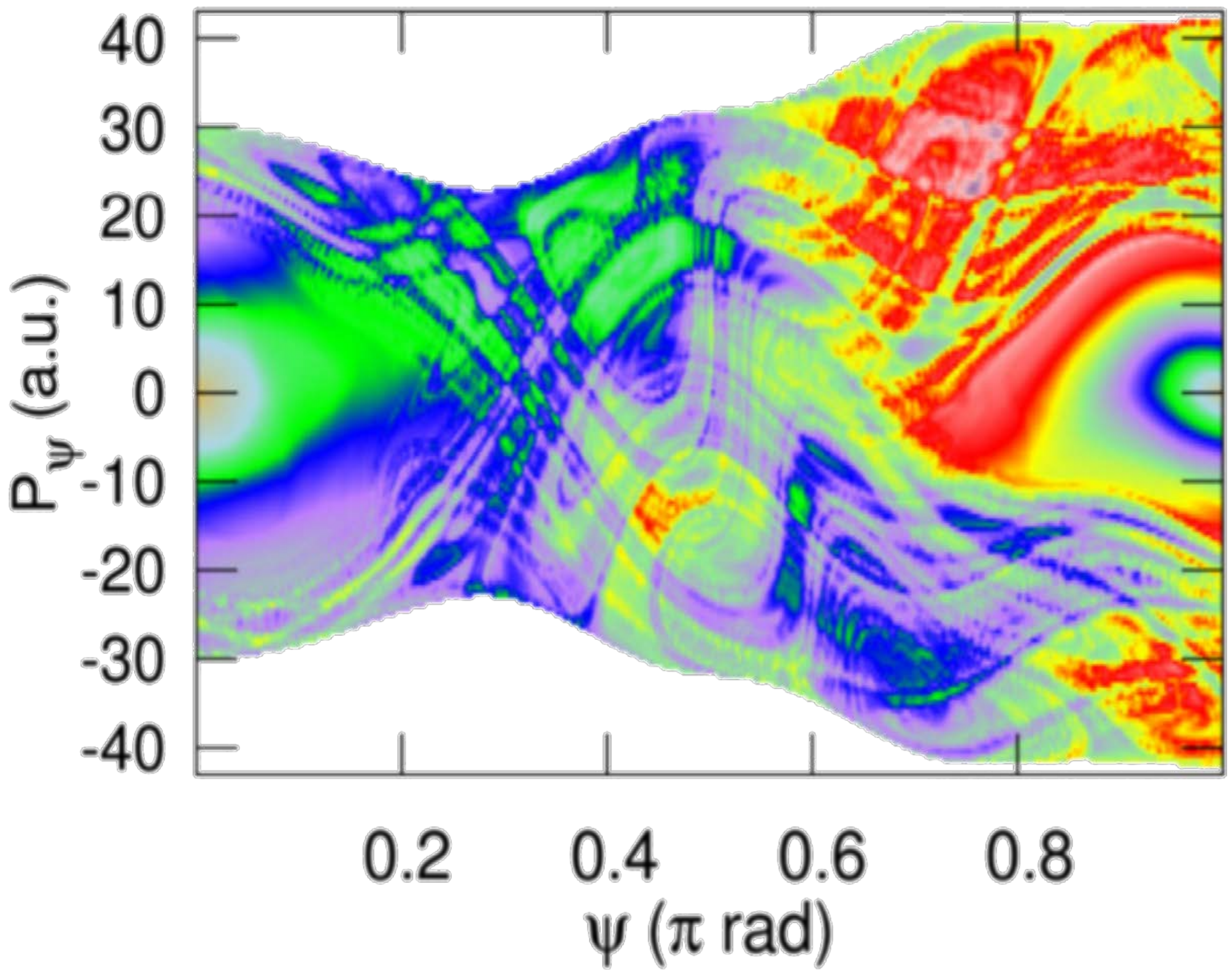


$$E = 3500\ cm^{-1}$$
$$T_{CN}^{kin} = 0\ cm^{-1}$$



$E = 4000\ cm^{-1}$

$T_{CN}^{kin} = 0\ cm^{-1}$



$$E = 4500\ cm^{-1}$$
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