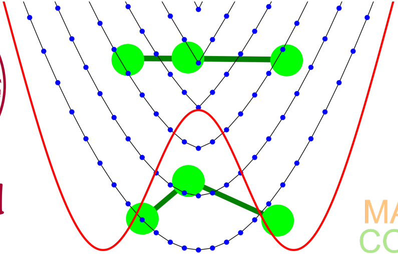
Transiciones de fase cuánticas de estados excitados en el límite bidimensional del modelo de vibrones

Jamil Khalouf-Rivera, Miguel Carvajal, Francisco Pérez-Bernal

Universidad de Huelva

January 25, 2022

Universidad de Huelva



FÍSICA MATEMÁTICAS COMPUTACIÓN

Table of Contents

2DVM

- 2D limit of the Vibron Model (2DVM)[a,b,c,d]
- Aplicación a moléculas [e,f,g]

---

[a] F. Iachello. *Chem. Phys. Lett.*, 78:581, 1981

[b] F. Iachello and S. Oss. *J. Chem. Phys.*, 104:6956–6963, 1996

[c] F. Pérez-Bernal and F. Iachello. *Phys. Rev. A*, 77:032–115, 2008

[d] F. Pérez-Bernal, L. F. Santos, P.H. Vaccaro, and F. Iachello. *Chem. Phys. Lett.*, 414:398 – 404, 2005

[e] F. Iachello, F. Pérez-Bernal, and P.H. Vaccaro. *Chem. Phys. Lett.*, 375:309 – 320, 2003

[f] D. Larese and F. Iachello. *J. Mol. Struct.*, 1006:611 – 628, 2011

[g] D. Larese, F. Pérez-Bernal, and F. Iachello. *J. Mol. Struct.*, 1051:310 – 327, 2013

2DVM

Boson Operators

$$\tau_x, \tau_x^\dagger, \tau_y, \tau_y^\dagger, \sigma, \sigma^\dagger$$

Circular Boson Operators

$$\tau_\pm^\dagger = \frac{\mp 1}{\sqrt{2}} \left(\tau_x^\dagger \pm i\tau_y^\dagger\right)$$
$$\tau_\pm = \frac{\mp 1}{\sqrt{2}} \left(\tau_x \mp i\tau_y\right)$$

2DVM

Boson Operators

$$\tau_x, \tau_x^\dagger, \tau_y, \tau_y^\dagger, \sigma, \sigma^\dagger$$

Circular Boson Operators

$$\tau_\pm^\dagger = \frac{\mp 1}{\sqrt{2}} \left(\tau_x^\dagger \pm i\tau_y^\dagger\right)$$
$$\tau_\pm = \frac{\mp 1}{\sqrt{2}} \left(\tau_x \mp i\tau_y\right)$$

U(3) Algebra Generators

$$U(3) = \left\langle \tau_i^\dagger \tau_j, \tau_i^\dagger \sigma, \sigma^\dagger \tau_i, \sigma^\dagger \sigma;\ i, j = x, y \right\rangle$$
$$= \left\langle \hat{n}, \hat{n}_s, \hat{\ell}, \hat{Q}_\pm, \hat{R}_\pm, \hat{D}_\pm \right\rangle$$

$$\hat{n} = \tau_+^\dagger \tau_+ + \tau_-^\dagger \tau_-$$
$$\hat{\ell} = \tau_+^\dagger \tau_+ - \tau_-^\dagger \tau_-$$

$$\hat{W}^2 = \frac{1}{2} \left(\hat{D}_+ \hat{D}_- + \hat{D}_- \hat{D}_+\right) + \hat{\ell}^2$$
$$\hat{D}_\pm = \sqrt{2} \left(\pm \tau_\pm^\dagger \sigma \mp \sigma^\dagger \tau_\mp\right)$$

2DVM

$$
\begin{array}{ccccc}
 & & \begin{array}{c} U(2) \\ \hat{n} \end{array} & & \\
\begin{array}{c} U(3) \\ [N] \end{array} & \begin{array}{c} \nearrow \\ \searrow \end{array} & & \begin{array}{c} \searrow \\ \nearrow \end{array} & \begin{array}{c} SO(2) \\ \hat{\ell} \end{array} \\
 & & \begin{array}{c} SO(3) \\ \hat{W}^2 \end{array} & &
\end{array}
$$

2DVM

$$
\begin{array}{ccccc}
 & & \begin{array}{c} U(2) \\ \hat{n} \end{array} & & \\
\begin{array}{c} U(3) \\ [N] \end{array} & \begin{array}{c} \nearrow \\ \searrow \end{array} & & \begin{array}{c} \searrow \\ \nearrow \end{array} & \begin{array}{c} SO(2) \\ \hat{\ell} \end{array} \\
 & & \begin{array}{c} SO(3) \\ \hat{W}^2 \end{array} & &
\end{array}
$$

Cadena I

$$\left| \begin{array}{ccccc} U(3) & \supset & U(2) & \supset & SO(2) \\ [N] & & n & & \ell \end{array} \right\rangle$$

Cadena II

$$\left| \begin{array}{ccccc} U(3) & \supset & SO(3) & \supset & SO(2) \\ [N] & & \omega & & \ell \end{array} \right\rangle$$

$$\nu_b = \frac{N-\omega}{2}$$

2DVM

$$
\begin{array}{ccccc}
 & \nearrow & \begin{array}{c} U(2) \\ \hat{n} \end{array} & \searrow & \\
\begin{array}{c} U(3) \\ [N] \end{array} & & & & \begin{array}{c} SO(2) \\ \hat{\ell} \end{array} \\
 & \searrow & \begin{array}{c} SO(3) \\ \hat{W}^2 \end{array} & \nearrow &
\end{array}
$$

Cadena I

$$\left| \begin{array}{ccccc} U(3) & \supset & U(2) & \supset & SO(2) \\ [N] & & n & & \ell \end{array} \right\rangle$$

Cadena II

$$\left| \begin{array}{ccccc} U(3) & \supset & SO(3) & \supset & SO(2) \\ [N] & & \omega & & \ell \end{array} \right\rangle$$

$$\nu_b = \frac{N-\omega}{2}$$

2DVM

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- GSQPT de segundo orden
- ESQPT, transición a la linealidad
- Monodromía cuántica

2DVM

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- ESQPT no asociada a una GSQPT
- Isomerización

- GSQPT de segundo orden
- ESQPT, transición a la linealidad
- Monodromía cuántica

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}\,(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

2DVM

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- ESQPT no asociada a una GSQPT
- Isomerización

$$\hat{\mathcal{H}}(\eta) = (1-\eta)\hat{n} + \eta\left[\frac{\hat{n}^2+\hat{W}^2}{N-1} - 2\frac{\hat{n}\hat{W}^2+\hat{W}^2\hat{n}}{(N-1)(N-2)}\right]$$

- GSQPT de segundo orden
- ESQPT, transición a la linealidad
- Monodromía cuántica

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}\,(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- GSQPT primer orden
- Doble pozo

2DVM

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- ESQPT no asociada a una GSQPT
- Isomerización

$$\hat{\mathcal{H}}(\eta) = (1-\eta)\hat{n} + \eta\left[\frac{\hat{n}^2+\hat{W}^2}{N-1} - 2\frac{\hat{n}\hat{W}^2+\hat{W}^2\hat{n}}{(N-1)(N-2)}\right]$$

- Descripción de niveles vibracionales
- Predicción de niveles

- GSQPT de segundo orden
- ESQPT, transición a la linealidad
- Monodromía cuántica

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}\,(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- GSQPT primer orden
- Doble pozo

$$\begin{aligned}\hat{H}_{4b} = \; & P_{11}\hat{n} + P_{21}\hat{n}^2 + P_{22}\hat{\ell}^2 + P_{23}\hat{W}^2 + \\ & P_{31}\hat{n}^3 + P_{32}\hat{n}\hat{\ell}^2 + P_{33}\left(\hat{n}\hat{W}^2 + \hat{W}^2\hat{n}\right) + \\ & P_{41}\hat{n}^4 + P_{42}\hat{n}^2\hat{\ell}^2 + P_{43}\hat{\ell}^4 + P_{44}\hat{\ell}^2\hat{W}^2 + \\ & P_{45}\left(\hat{n}^2\hat{W}^2 + \hat{W}^2\hat{n}^2\right) + P_{46}\hat{W}^4\end{aligned}$$

Modelo Hamiltoniano

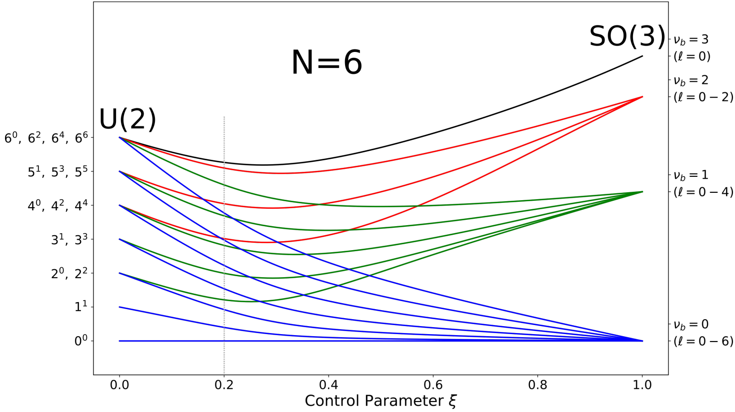
$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- $\xi_c = 0.2$
- $E^{\mathrm{ESQPT}}(\xi) = \frac{(5\xi-1)^2}{16\xi}, \; \xi > \xi_c$

Modelo Hamiltoniano

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

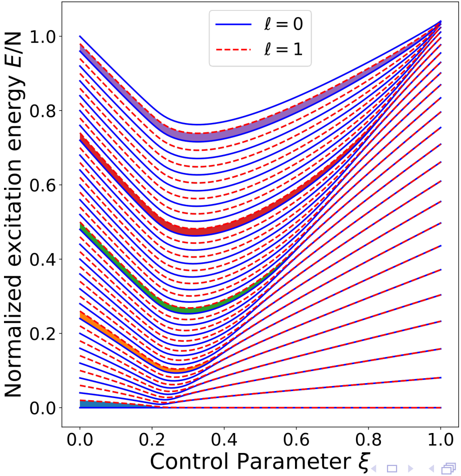
- $\xi_c = 0.2$
- $E^{\text{ESQPT}}(\xi) = \frac{(5\xi-1)^2}{16\xi}, \ \xi > \xi_c$



Modelo Hamiltoniano

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

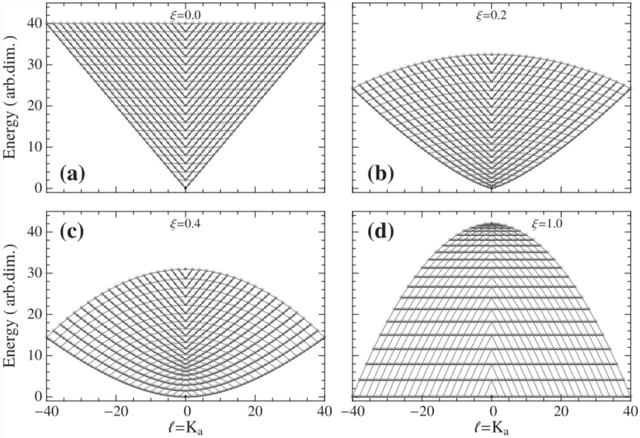
- $\xi_c = 0.2$
- $E^{\text{ESQPT}}(\xi) = \frac{(5\xi-1)^2}{16\xi}, \;\; \xi > \xi_c$



Modelo Hamiltoniano

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- $\xi_c = 0.2$
- $E^{\text{ESQPT}}(\xi) = \frac{(5\xi-1)^2}{16\xi}, \; \xi > \xi_c$

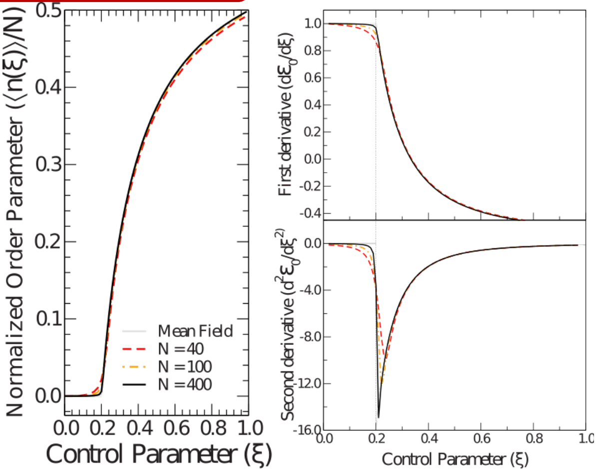


D. Larese and F. Iachello. *J. Mol. Struct.*, 1006:611 – 628, 2011

Modelo Hamiltoniano

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

- $\xi_c = 0.2$
- $E^{\mathrm{ESQPT}}(\xi) = \frac{(5\xi-1)^2}{16\xi}, \; \xi > \xi_c$

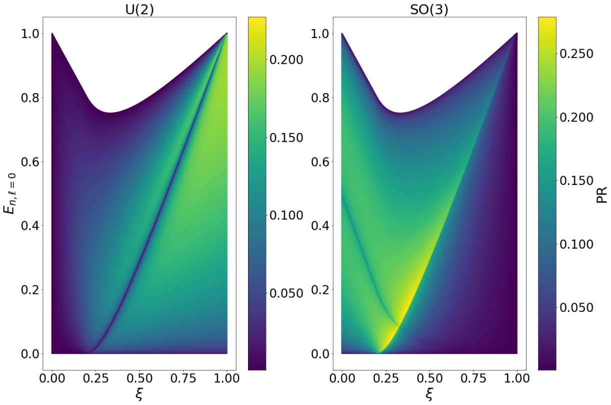


F. Pérez-Bernal and F. Iachello. *Phys. Rev. A*, 77:032–115, 2008

Modelo Hamiltoniano

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

$$PR(\psi) = \frac{1}{\sum_{j,\ell}\left|c_{j,\ell}\right|^4}$$

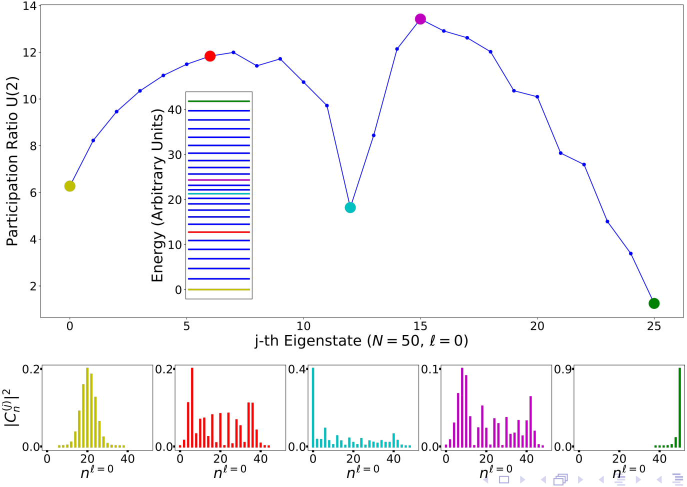


JKR, Francisco Pérez-Bernal, and Miguel Carvajal. *J. Quant. Spectrosc. and Rad. Transfer*, 216:107436, 2020

Modelo Hamiltoniano

$$\hat{\mathcal{H}}(\xi) = (1-\xi)\,\hat{n} - \frac{\xi}{N-1}\hat{W}^2$$

$$PR(\psi) = \frac{1}{\sum_{j,\ell}\left|c_{j,\ell}\right|^4}$$



$$\hat{H}_{Si_2C} = P_{11}\hat{n} + P_{21}\hat{n}^2 + P_{22}\hat{\ell}^2 + P_{23}\hat{W}^2$$

P_{11}	P_{21}	P_{22}	P_{23}	N	rms	σ_{exp}	N_{data}
63.8(5)	-0.108(18)	0.98(5)	-0.8117(17)	49	1.48	2	37

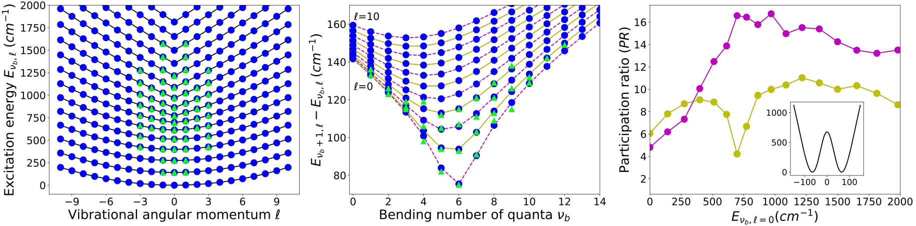
P_{ij}, rms and σ in cm^{-1} units.

Si_2C

$$\hat{H}_{Si_2C} = P_{11}\hat{n} + P_{21}\hat{n}^2 + P_{22}\hat{\ell}^2 + P_{23}\hat{W}^2$$

P_{11}	P_{21}	P_{22}	P_{23}	N	rms	σ_{exp}	N_{data}
63.8(5)	-0.108(18)	0.98(5)	-0.8117(17)	49	1.48	2	37

P_{ij}, rms and σ in cm^{-1} units.



JKR, Francisco Pérez-Bernal, and Miguel Carvajal. *J. Quant. Spectrosc. and Rad. Transfer*, 216:107436, 2020

Término anarmónico (arXiv:2106.11044, 2021)

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- $E_1(\xi,\alpha) = \frac{(5\xi-1)^2}{4(4\xi+\alpha)},\ \xi > \xi_c$
- $E_2(\xi,\alpha) = \begin{cases} 1+\alpha-\xi, & \xi \leq \xi_c \\ \frac{(1+2\alpha+3\xi)^2}{4(4\xi+\alpha)}, & \xi > \xi_c \end{cases}$

Fase no simétrica $\xi > \xi_c$

F. Pérez-Bernal and O. Álvarez-Bajo. *Phys. Rev. A*, 81:050–101, 2010

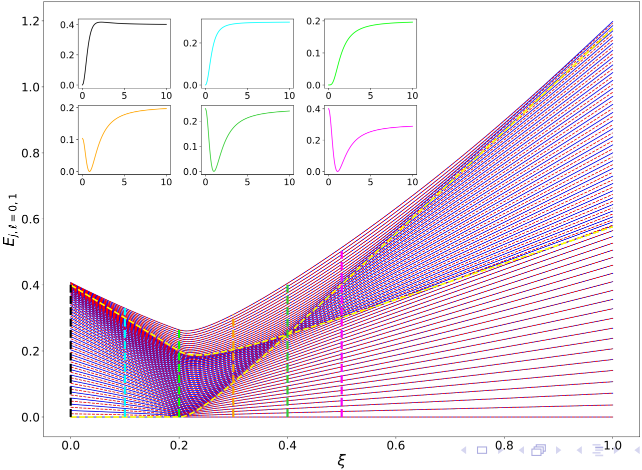
Fase simétrica $\xi < \xi_c$

JKR, Francisco Pérez-Bernal, and Miguel Carvajal. *arXiv:2106.11044*, 2021

Término anarmónico (arXiv:2106.11044, 2021)

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- $E_1(\xi,\alpha) = \frac{(5\xi-1)^2}{4(4\xi+\alpha)},\ \xi > \xi_c$
- $E_2(\xi,\alpha) = \begin{cases} 1+\alpha-\xi, & \xi \le \xi_c \\ \frac{(1+2\alpha+3\xi)^2}{4(4\xi+\alpha)}, & \xi > \xi_c \end{cases}$

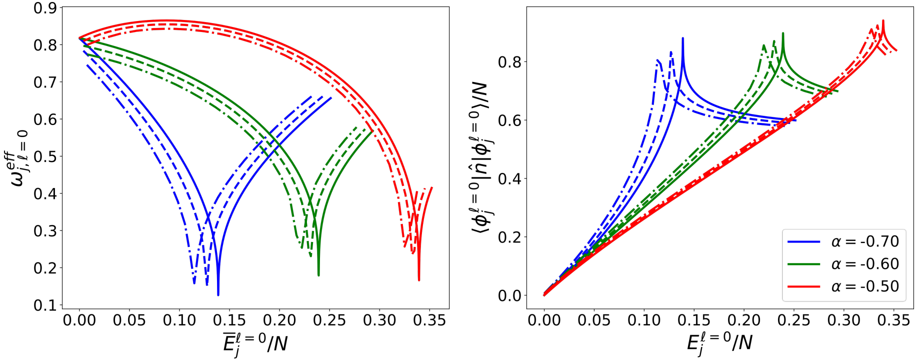


Término anarmónico (arXiv:2106.11044, 2021)

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- $E_1(\xi,\alpha) = \frac{(5\xi-1)^2}{4(4\xi+\alpha)},\ \xi > \xi_c$
- $E_2(\xi,\alpha) = \begin{cases} 1+\alpha-\xi, & \xi \leq \xi_c \\ \frac{(1+2\alpha+3\xi)^2}{4(4\xi+\alpha)}, & \xi > \xi_c \end{cases}$

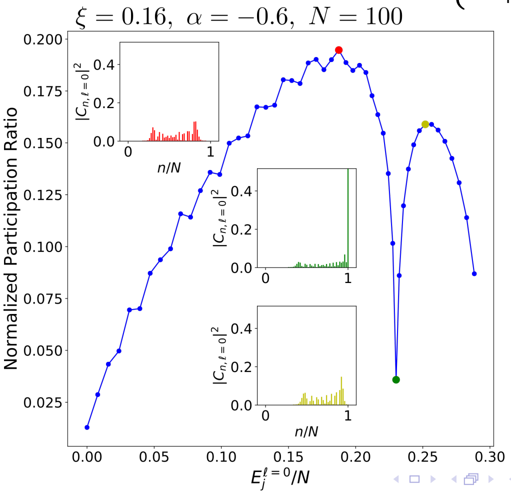
$\xi = 0.16,\ N = 50, 100, 1000$



Término anarmónico (arXiv:2106.11044, 2021)

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- $E_1(\xi,\alpha) = \frac{(5\xi-1)^2}{4(4\xi+\alpha)},\ \xi > \xi_c$
- $E_2(\xi,\alpha) = \begin{cases} 1+\alpha-\xi, & \xi \le \xi_c \\ \frac{(1+2\alpha+3\xi)^2}{4(4\xi+\alpha)}, & \xi > \xi_c \end{cases}$

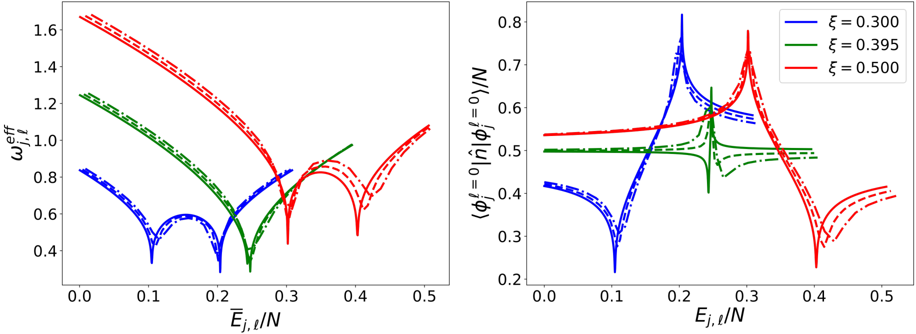


Término anarmónico (arXiv:2106.11044, 2021)

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- $E_1(\xi,\alpha) = \frac{(5\xi-1)^2}{4(4\xi+\alpha)},\ \xi > \xi_c$
- $E_2(\xi,\alpha) = \begin{cases} 1+\alpha-\xi, & \xi \le \xi_c \\ \frac{(1+2\alpha+3\xi)^2}{4(4\xi+\alpha)}, & \xi > \xi_c \end{cases}$

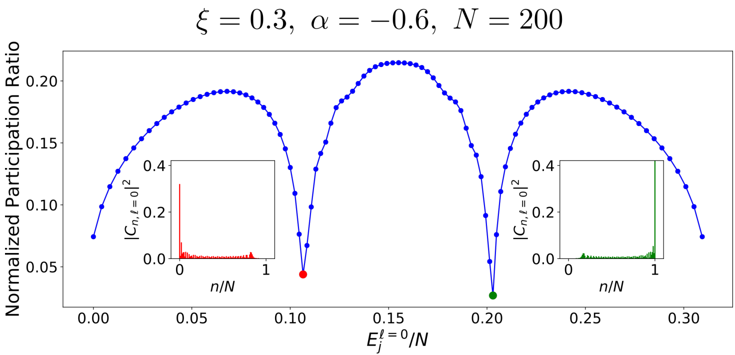
$\alpha = -0.6,\ \ N = 50, 100, 1000$



Término anarmónico (arXiv:2106.11044, 2021)

$$\hat{\mathcal{H}}(\xi,\alpha) = (1-\xi)\,\hat{n} + \frac{\alpha}{N-1}\hat{n}(\hat{n}+1) - \frac{\xi}{N-1}\hat{W}^2$$

- $E_1(\xi,\alpha) = \frac{(5\xi-1)^2}{4(4\xi+\alpha)},\ \xi > \xi_c$
- $E_2(\xi,\alpha) = \begin{cases} 1+\alpha-\xi, & \xi \le \xi_c \\ \frac{(1+2\alpha+3\xi)^2}{4(4\xi+\alpha)}, & \xi > \xi_c \end{cases}$



Isomerización: HCN-HNC

$$\hat{H} = P_{11}\hat{n} + P_{21}\hat{n}^2 + P_{22}\hat{\ell}^2 + P_{23}\hat{W}^2 + P_{45}\left[\hat{W}^2\hat{n}^2 + \hat{n}^2\hat{W}^2\right]$$

P_{11}	P_{21}	P_{22}	P_{23}	P_{45}	N	rms
2308.3(6)	-39.947(14)	21.810(6)	-10.635(3)	$-1.311(3)\times10^{-4}$	50	19.37
1024.9(1.4)	-18.59(4)	13.362(23)	-5.085(11)	-	40	14.91

P_{ij} and *rms* in cm^{-1} units.

JKR, M. Carvajal, L. F. Santos, and F. Pérez-Bernal. *J. Phys. Chem. A*, 123:9544–9551, 2019

Isomerización: HCN-HNC

$$\hat{H} = P_{11}\hat{n} + P_{21}\hat{n}^2 + P_{22}\hat{\ell}^2 + P_{23}\hat{W}^2 + P_{45}\left[\hat{W}^2\hat{n}^2 + \hat{n}^2\hat{W}^2\right]$$

P_{11}	P_{21}	P_{22}	P_{23}	P_{45}	N	rms
2308.3(6)	-39.947(14)	21.810(6)	-10.635(3)	$-1.311(3)\times10^{-4}$	50	19.37
1024.9(1.4)	-18.59(4)	13.362(23)	-5.085(11)	-	40	14.91

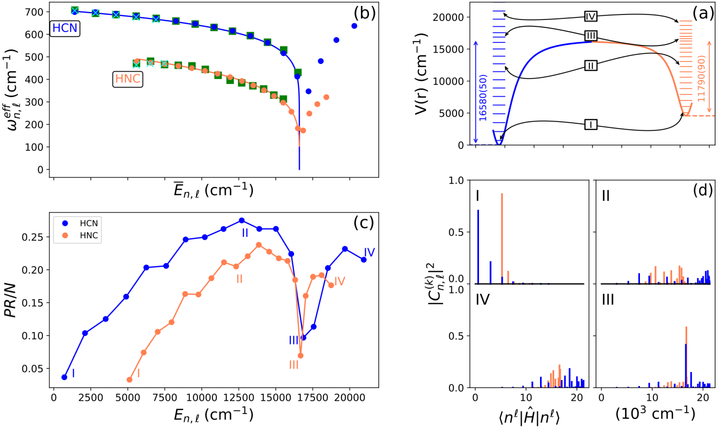
P_{ij} and *rms* in cm^{-1} units.

JKR, M. Carvajal, L. F. Santos, and F. Pérez-Bernal. *J. Phys. Chem. A*, 123:9544–9551, 2019

$$\omega_{\text{eff}}\left(\overline{E}\right) = \omega_0\left(1 - \frac{\overline{E}}{E_{TS}}\right)^{1/m}$$

J.H. Baraban, P.B. Changala, G.Ch. Mellau, et al. *Science*, 350:1338–1342, 2015

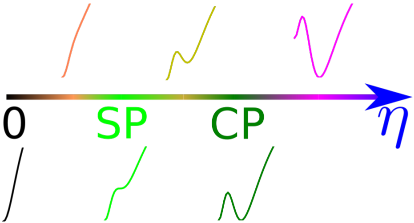
Isomerización: HCN-HNC

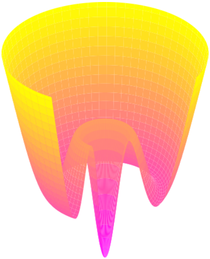


Energía de transición E_{TS} (cm^{-1})					
Molécula	2DVM-I	2DVM-II	Baraban *et al.*	Mourik *et al.*	Makhnev *et al.*
HCN($\ell = 0$)	16580(50)	16599(15)	16695(17)	16798	16809.4
HNC($\ell = 0$)	11790(90)	11977(15)	11533(124)	11517	11496.6

Doble pozo

$$\hat{\mathcal{H}} = (1-\eta)\hat{n} + \eta\left[\frac{\hat{n}^2+\hat{W}^2}{N-1} - 2\frac{\hat{n}\hat{W}^2+\hat{W}^2\hat{n}}{(N-1)(N-2)}\right]$$

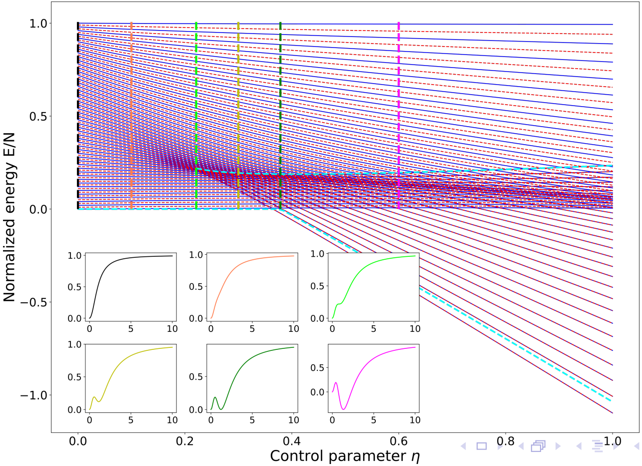




- $\eta \in [0, 48/217)$: pozo central.
- $\eta = 48/217$: punto de inflexión.
- $\eta \in (48/217, 64/169)$: doble pozo y estado fundamental en el origen.
- $\eta = 64/169$: ambos mínimos toman el mismo valor de energía.
- $\eta \in (64/169, 1]$: doble pozo y estado fundamental fuera del origen.

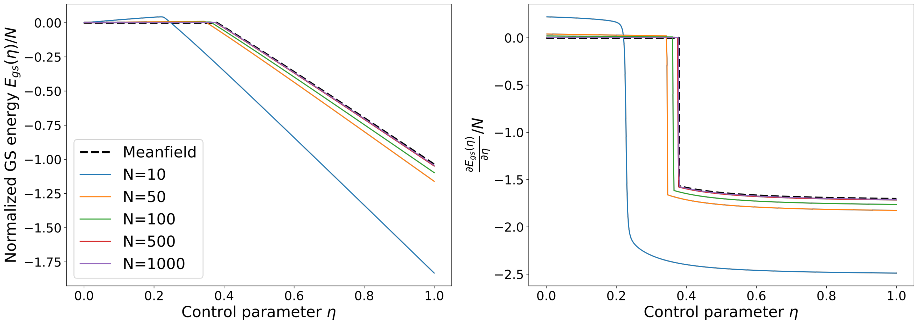
Doble pozo

$$\hat{\mathcal{H}} = (1-\eta)\hat{n} + \eta\left[\frac{\hat{n}^2+\hat{W}^2}{N-1} - 2\frac{\hat{n}\hat{W}^2+\hat{W}^2\hat{n}}{(N-1)(N-2)}\right]$$



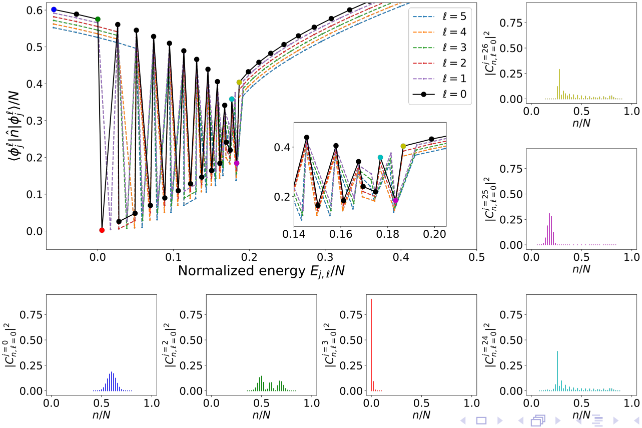
Doble pozo

$$\hat{\mathcal{H}} = (1-\eta)\hat{n} + \eta\left[\frac{\hat{n}^2+\hat{W}^2}{N-1} - 2\frac{\hat{n}\hat{W}^2+\hat{W}^2\hat{n}}{(N-1)(N-2)}\right]$$



Doble pozo

$$\hat{\mathcal{H}} = (1-\eta)\hat{n} + \eta\left[\frac{\hat{n}^2+\hat{W}^2}{N-1} - 2\frac{\hat{n}\hat{W}^2+\hat{W}^2\hat{n}}{(N-1)(N-2)}\right]$$



Desarrollos futuros

- Estudiar la fenomenología de $\hat{H}_{4b}$
- Caracterizar el espacio de las fases

Desarrollos futuros

- Estudiar la fenomenología de $\hat{H}_{4b}$
- Caracterizar el espacio de las fases

- Estudiar el sistema [H,C,N] con $U(3) \otimes U(3)$
- Extender el estudio al C_2H_2 cis-trans
- Mezcla de configuraciones

Desarrollos futuros

- Estudiar la fenomenología de $\hat{H}_{4b}$
- Caracterizar el espacio de las fases

- Estudiar el sistema [H,C,N] con $U(3) \otimes U(3)$
- Extender el estudio al C_2H_2 cis-trans
- Mezcla de configuraciones

- Encontrar sistema físico que presente un doble pozo con simetría rotacional

Desarrollos futuros

- Estudiar la fenomenología de $\hat{H}_{4b}$
- Caracterizar el espacio de las fases

- Estudiar el sistema [H,C,N] con $U(3) \otimes U(3)$
- Extender el estudio al C_2H_2 cis-trans
- Mezcla de configuraciones

- Encontrar sistema físico que presente un doble pozo con simetría rotacional

- Dinámica en el 2DVM
- OTOCs

¡Gracias por su atención!

[1] J.H. Baraban, P.B. Changala, G.Ch. Mellau, et al. *Science*, 350:1338–1342, 2015.

[2] F. Iachello. *Chem. Phys. Lett.*, 78:581, 1981.

[3] F. Iachello and S. Oss. *J. Chem. Phys.*, 104:6956–6963, 1996.

[4] F. Iachello, F. Pérez-Bernal, and P.H. Vaccaro. *Chem. Phys. Lett.*, 375:309 – 320, 2003.

[5] JKR, M. Carvajal, L. F. Santos, and F. Pérez-Bernal. *J. Phys. Chem. A*, 123:9544–9551, 2019.

[6] JKR, Francisco Pérez-Bernal, and Miguel Carvajal. *J. Quant. Spectrosc. and Rad. Transfer*, 216:107436, 2020.

[7] JKR, Francisco Pérez-Bernal, and Miguel Carvajal. *arXiv:2106.11044*, 2021.

[8] D. Larese and F. Iachello. *J. Mol. Struct.*, 1006:611 – 628, 2011.

[9] D. Larese, F. Pérez-Bernal, and F. Iachello. *J. Mol. Struct.*, 1051:310 – 327, 2013.

[10] F. Pérez-Bernal and O. Álvarez-Bajo. *Phys. Rev. A*, 81:050–101, 2010.

[11] F. Pérez-Bernal and F. Iachello. *Phys. Rev. A*, 77:032–115, 2008.

[12] F. Pérez-Bernal, L. F. Santos, P.H. Vaccaro, and F. Iachello. *Chem. Phys. Lett.*, 414:398 – 404, 2005.