QPTN-9 :: Phase transitions in atomic, molecular and other domains

An Overview of QPT and ESQPT in Molecular Systems

Facultad de Ciencias Experimentales
Centro de Estudios Avanzados en Física, Matemáticas y Computación
Universidad de Huelva

May 27, 2018

FÍSICA
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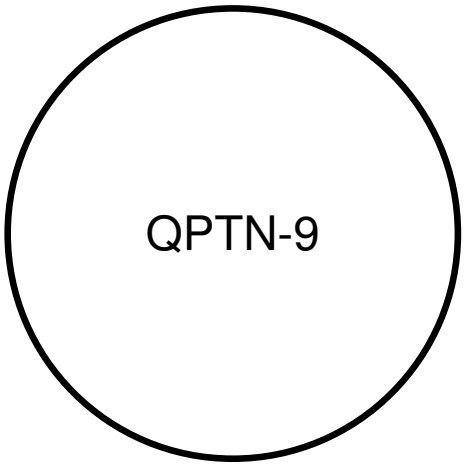
COMPUTACIÓN

Seminar Conspectus



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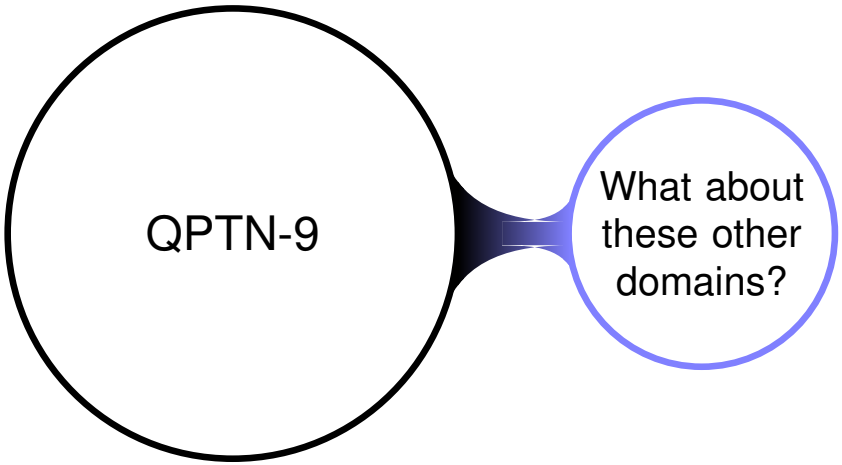

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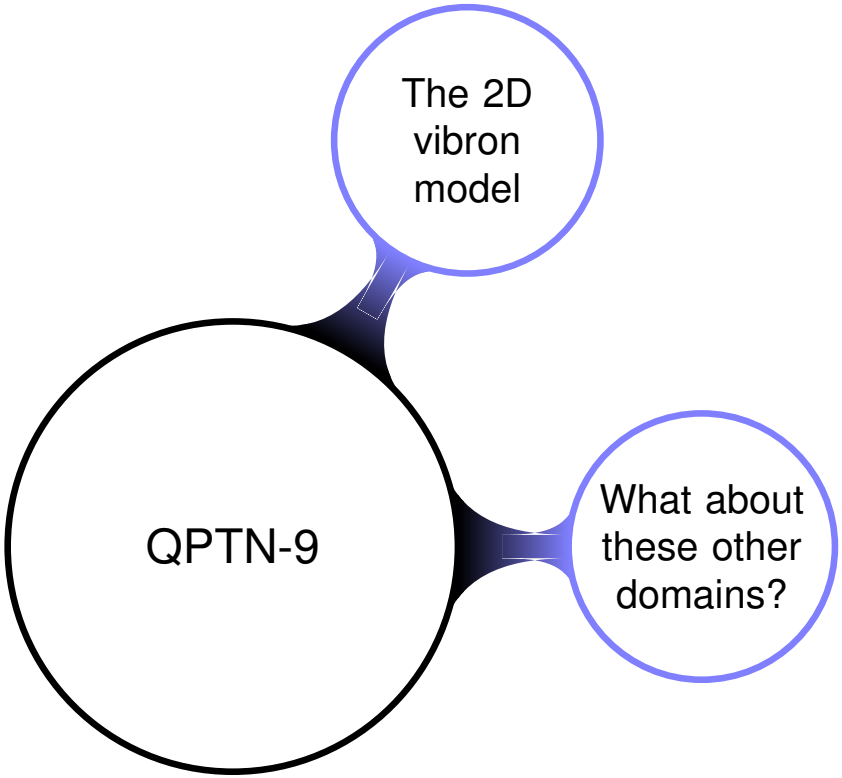

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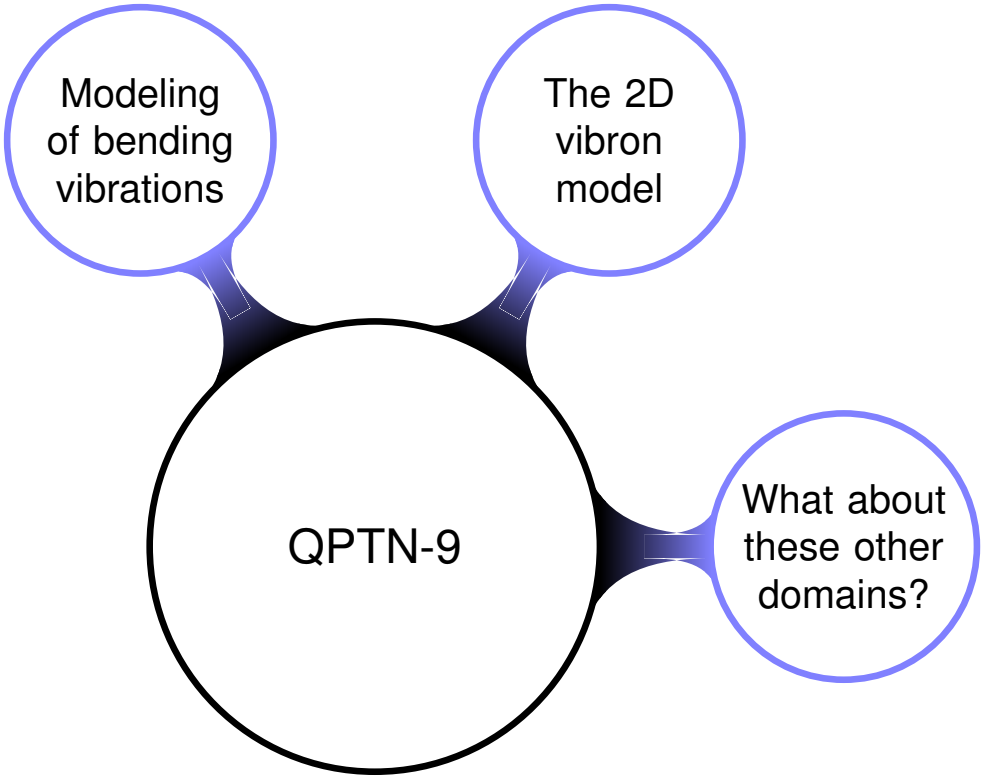

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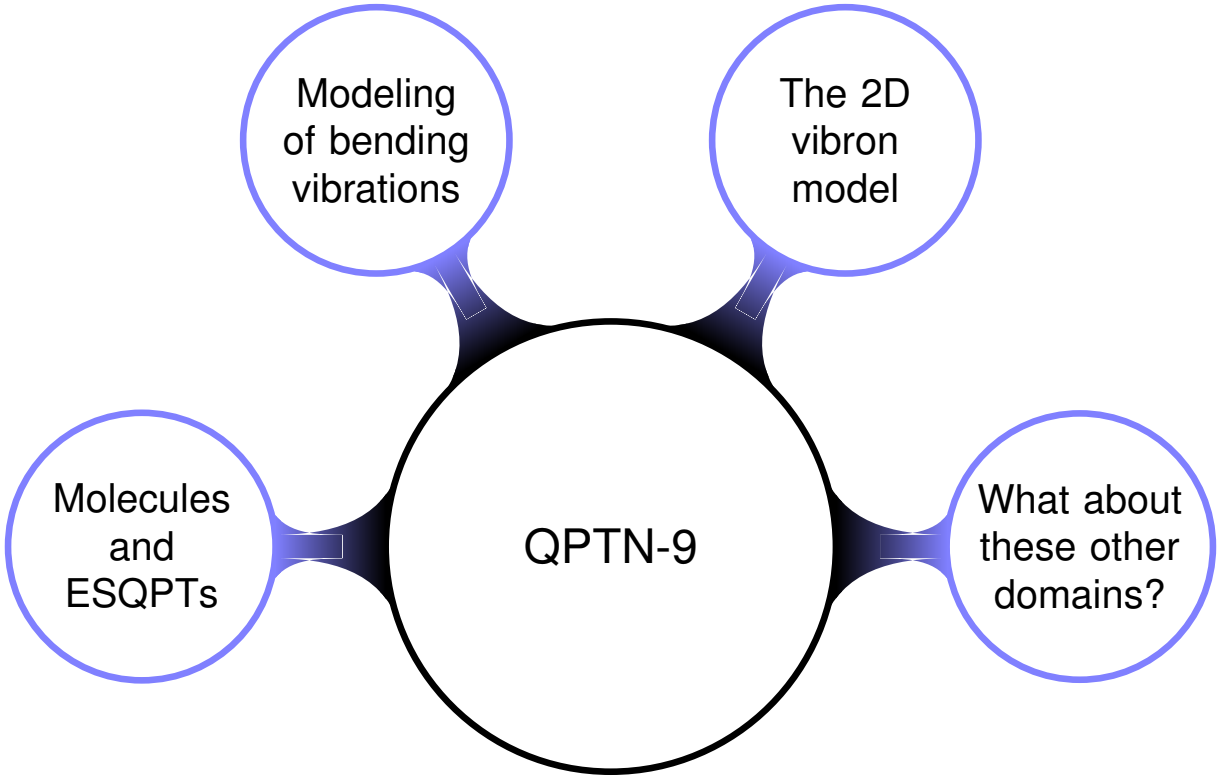

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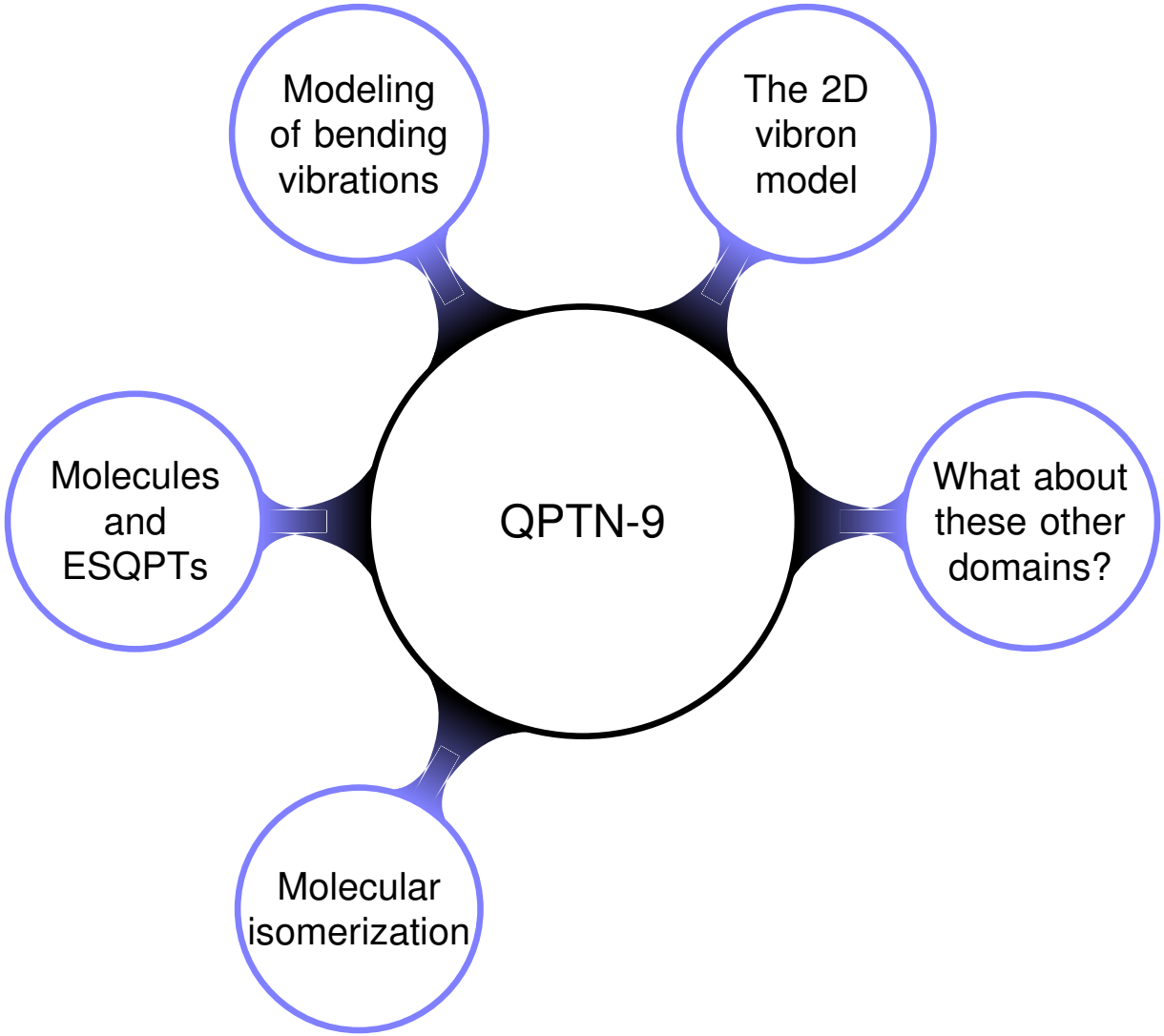

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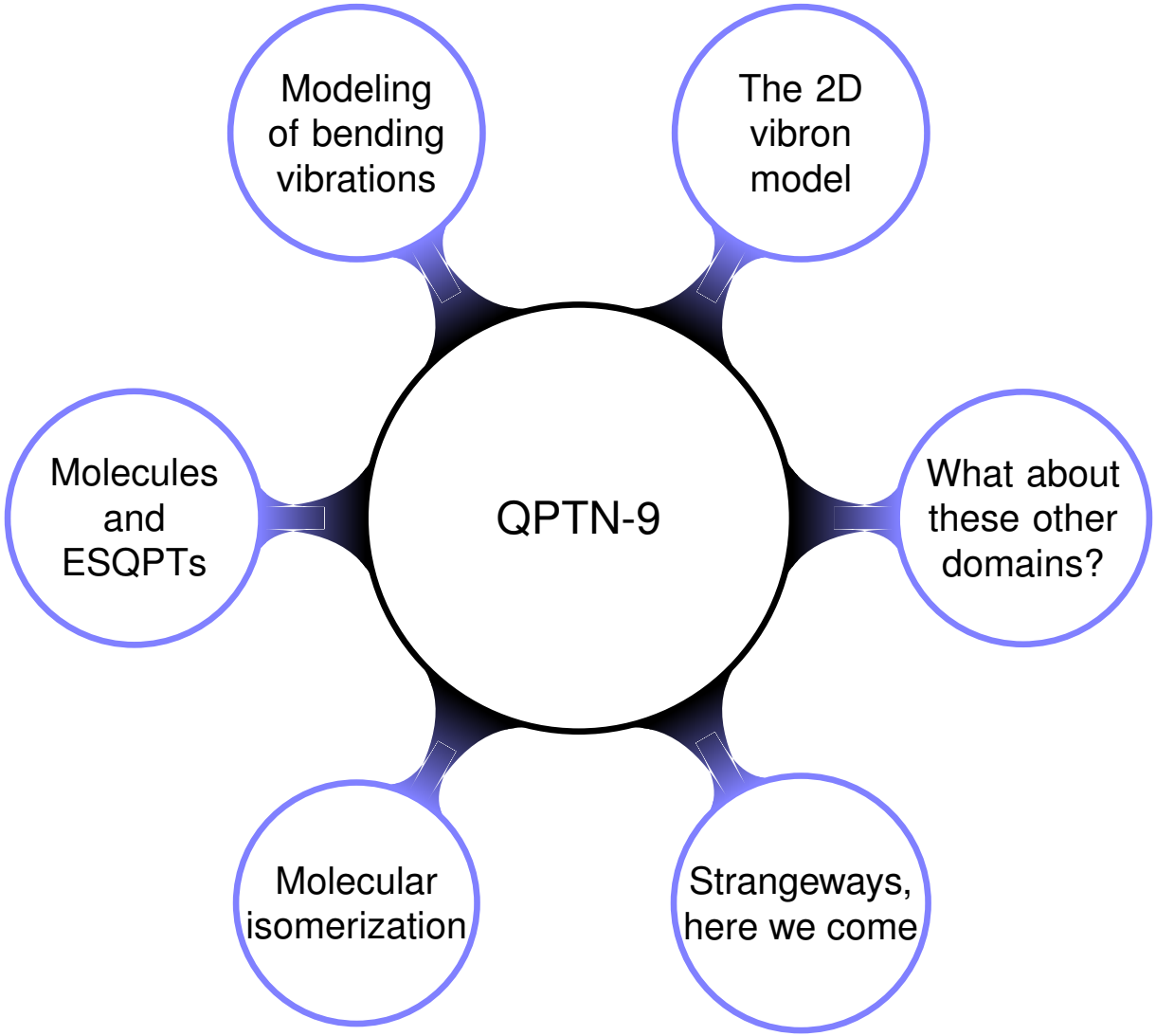
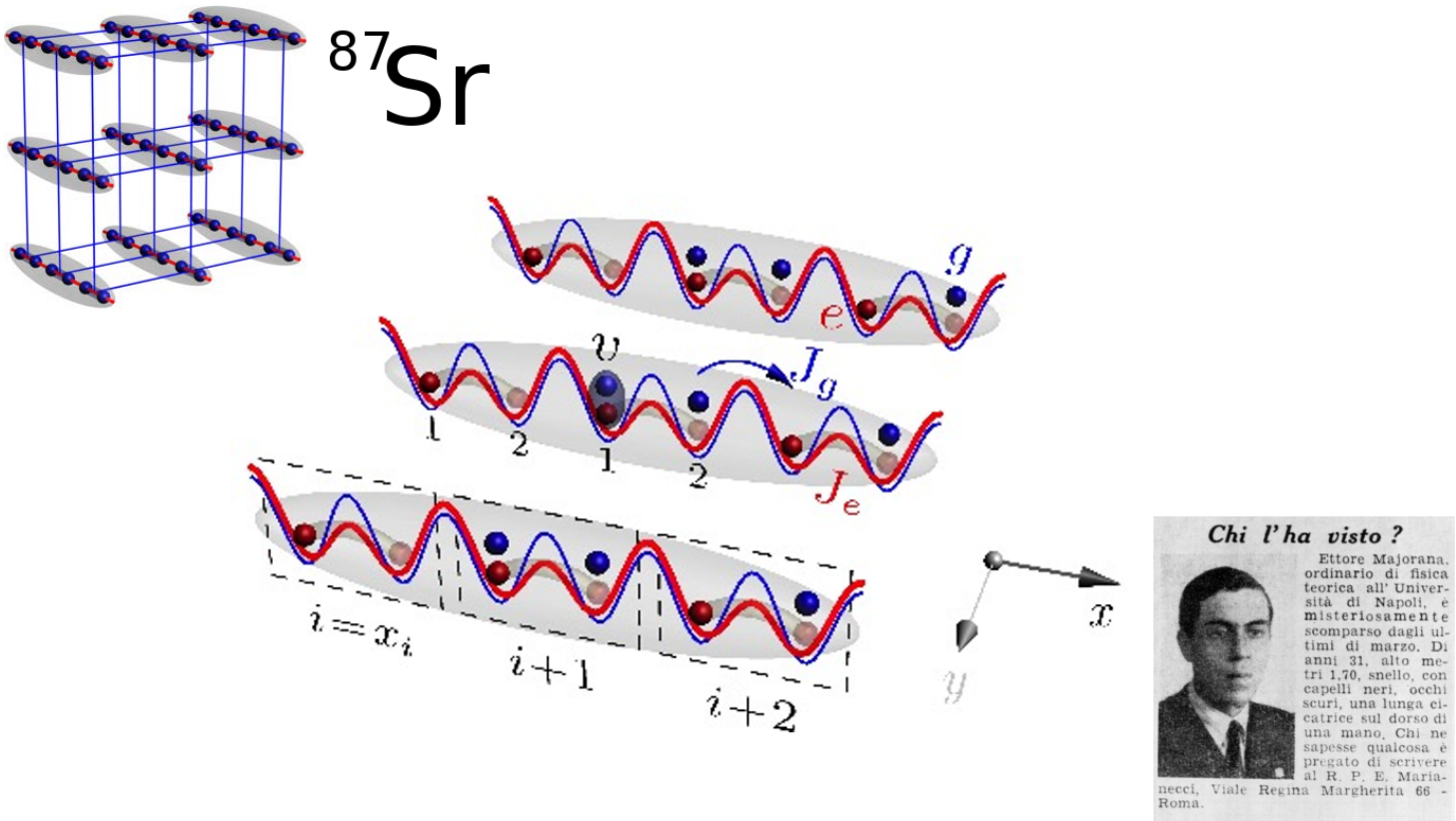


Topological superfluid phase with repulsive fermionic atoms

Gerardo Ortiz. Indiana University (USA)

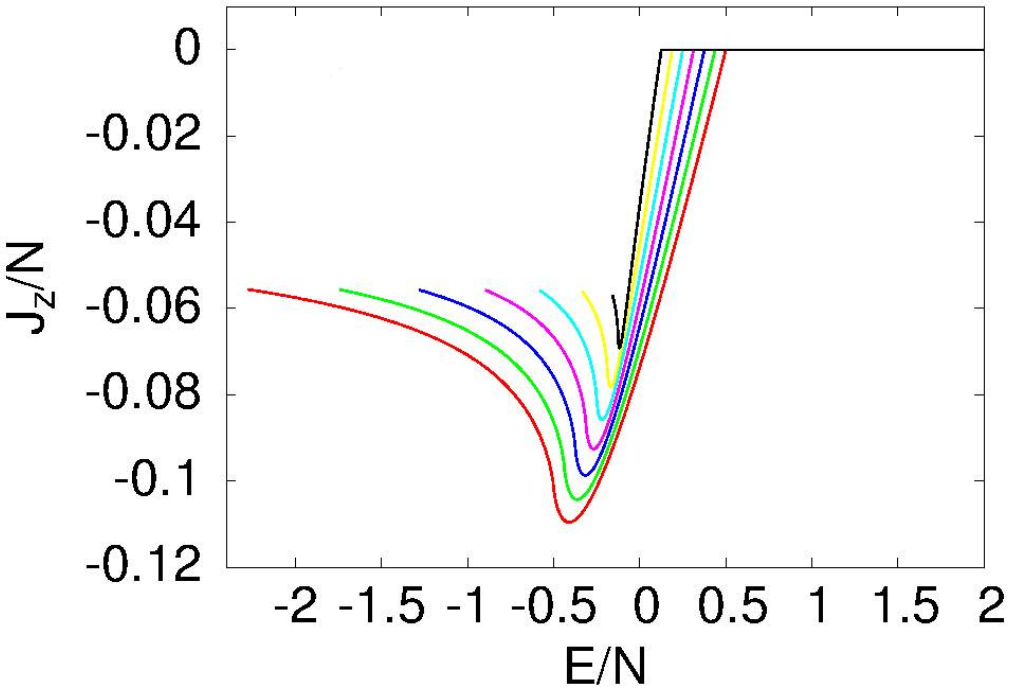


Chi l'ha visto ?

Ettore Majorana, ordinario di fisica teorica all' Università di Napoli, è misteriosamente scomparso dagli ultimi di marzo. Di anni 31, alto metri 1,70, snello, con capelli neri, occhi scuri, una lunga cicatrice sul dorso di una mano. Chi ne sapesse qualcosa è pregato di scrivere al R. P. E. Mariannecci, Viale Regina Margherita 66 - Roma.

Relationship between the ESPQT and the thermal phase transition in the Dicke model

Pedro Pérez Fernández, Universidad de Sevilla (SPAIN)



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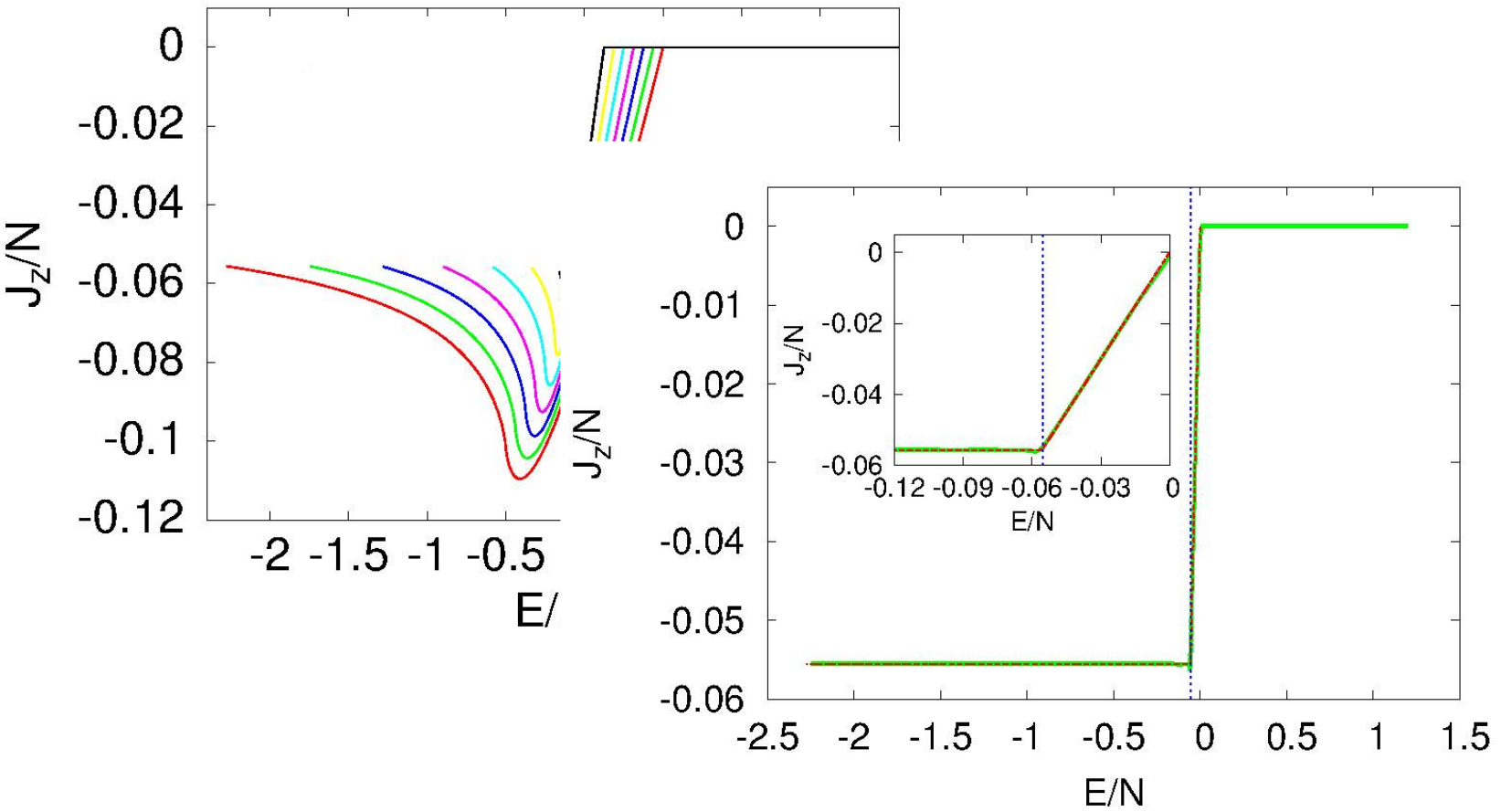
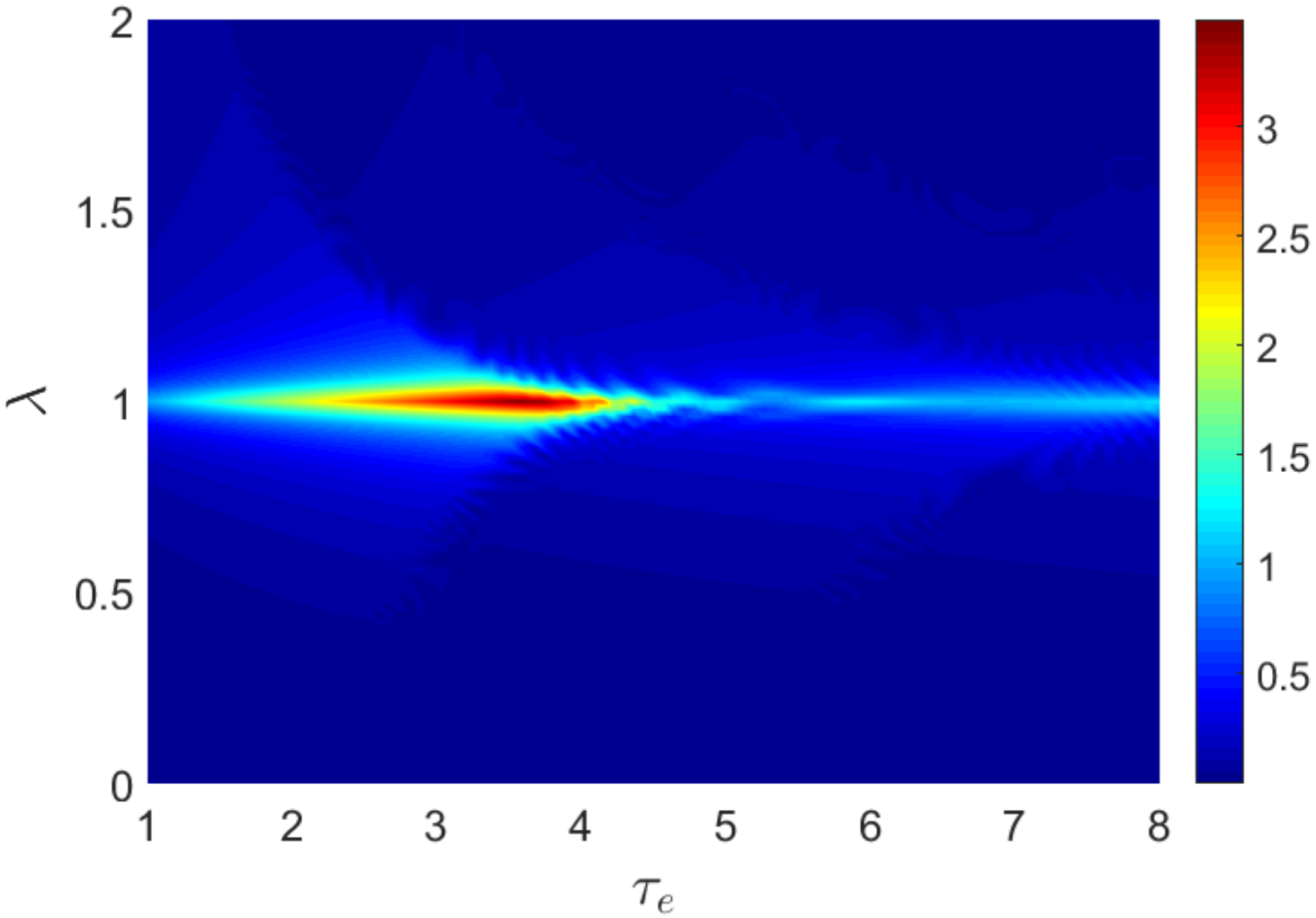


Excited-state quantum phase transition and quantum speed limit

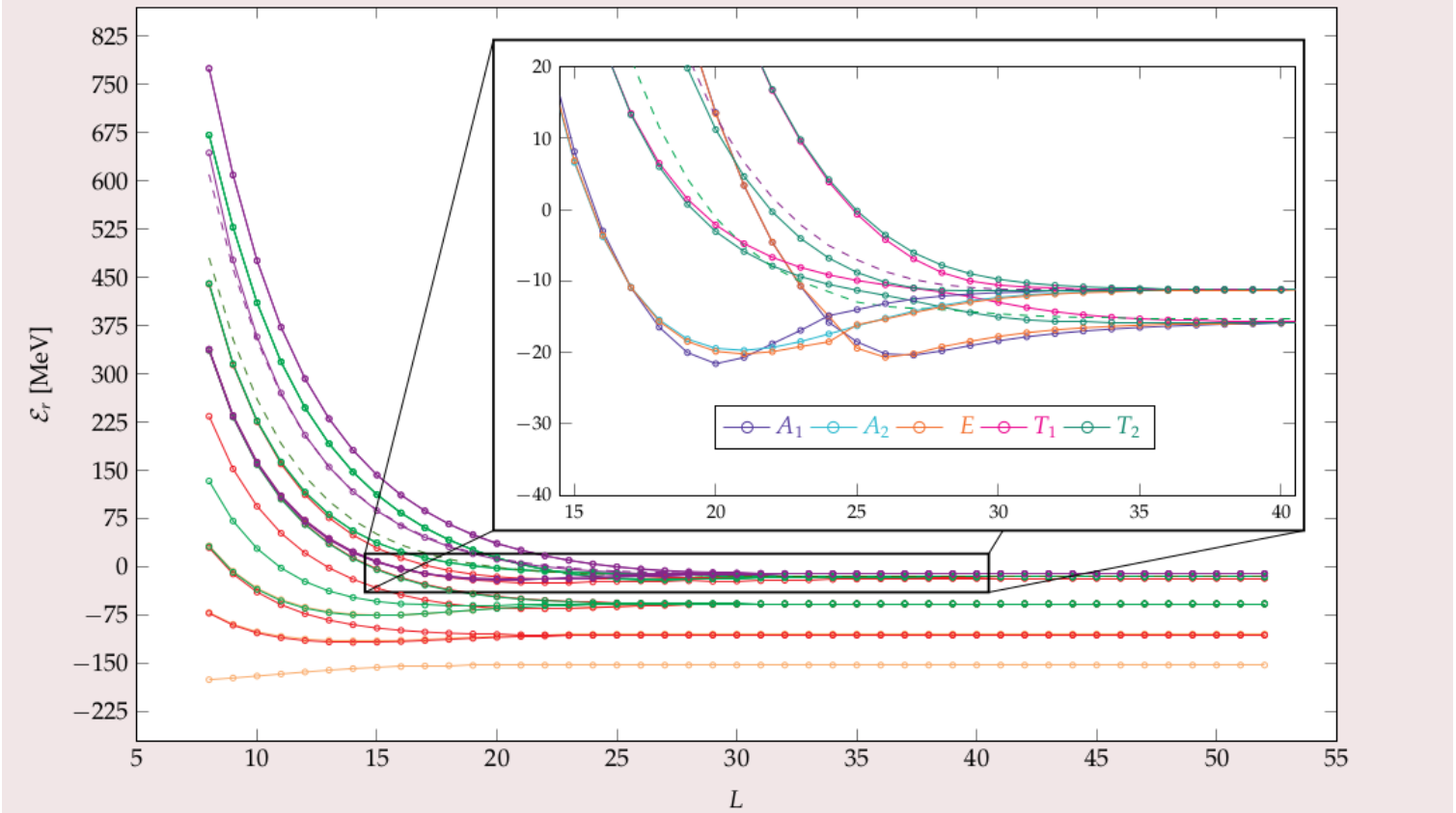
Quin Wang. Zheijang Normal University (CHINA)



Breaking and restoration of rotational symmetry in the low-energy spectrum of light alpha-conjugate nuclei on the lattice

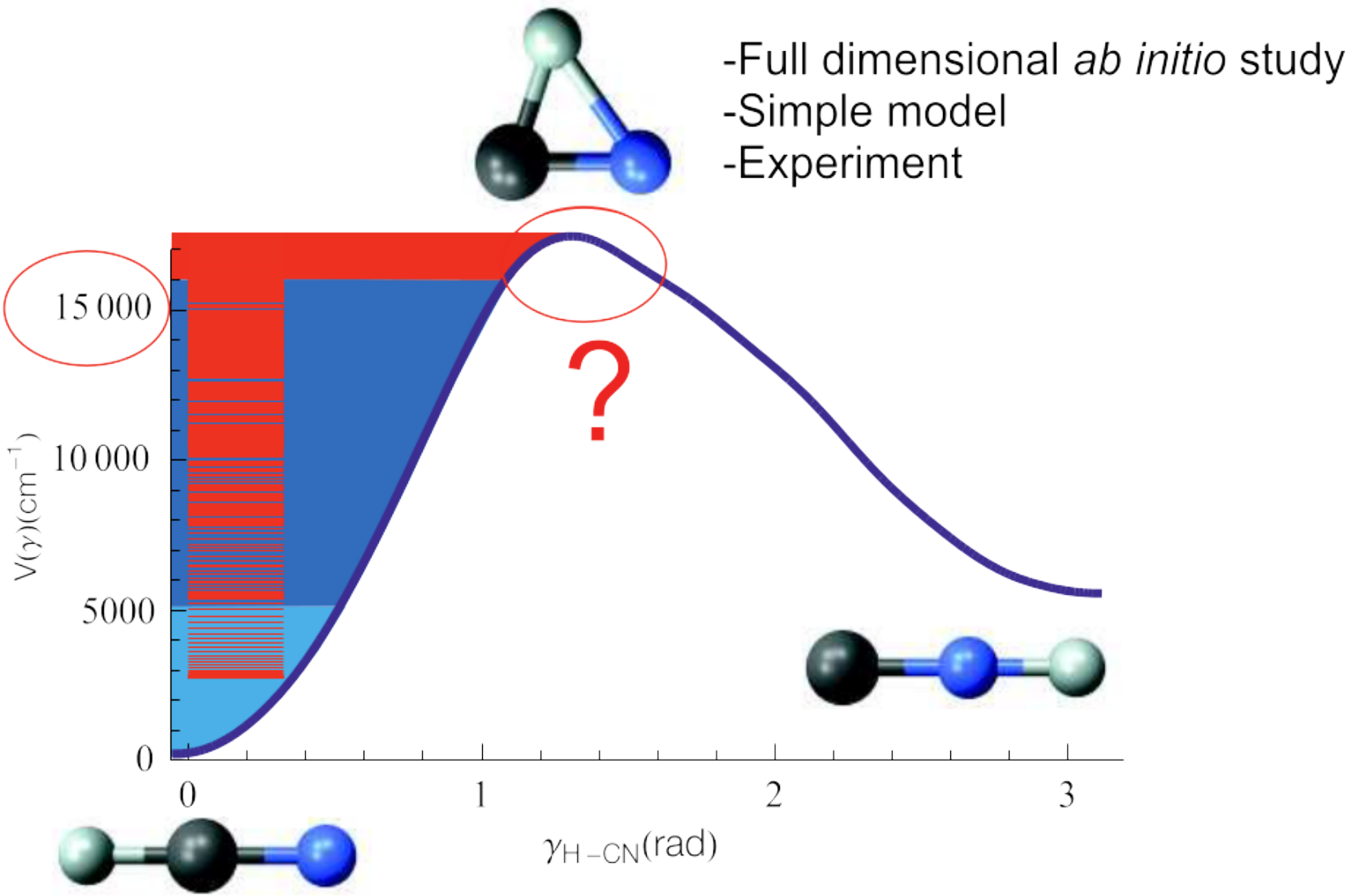
Gianluca Stellin, University of Bonn (GERMANY)

f=2.5, $a = 0.25$ fm



Saddle point localization of molecular wavefunctions

Georg Ch. Mellau, Justus-Liebig University Giessen (GERMANY)



F. Iachello, Contemp. Math. **160**, 151 (1994)
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The Vibron Model

An algebraic approach to molecular structure

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$$\left[\tau_i, \tau_j^\dagger\right] = \delta_{i,j} \; ; \quad i, j = x, y \qquad \left[\sigma, \sigma^\dagger\right] = 1$$

Circular Bosons:

$$\tau_\pm^\dagger = \mp \frac{\tau_x^\dagger \pm i\tau_y^\dagger}{\sqrt{2}} \quad , \quad \tau_\pm = \mp \frac{\tau_x \mp i\tau_y}{\sqrt{2}}$$

Generators of the $U(3)$ Dynamical Algebra:

$$\{\hat{n}, \hat{n}_s, \hat{\ell}, \hat{Q}_\pm, \hat{R}_\pm, \hat{D}_\pm\}$$

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2DVM Dynamical Symmetries

Branching rules and general Hamiltonian up to 2-body operators.

$$\begin{array}{ccccccc} U(3) & \supset & U(2) & \supset & SO(2) & \text{Dyn. Symmetry (I)} \\ N & & n & & \ell & \\ U(3) & \supset & SO(3) & \supset & SO(2) & \text{Dyn. Symmetry (II)} \\ N & & w & & \ell & \end{array}$$

$$\begin{array}{lll} U(2) & \hat{C}_1[U(2)] = \hat{n} & \hat{C}_2[U(2)] = \hat{n}(\hat{n}+1) \\ SO(3) & \hat{C}_2[SO(3)] = \hat{W}^2 = \frac{\hat{D}_+\hat{D}_- + \hat{D}_-\hat{D}_+}{2} + \hat{\ell}^2 & \\ SO(2) & \hat{C}_1[SO(2)] = \hat{\ell} & \hat{C}_2[SO(2)] = \hat{\ell}^2 \end{array}$$

General one- and two-body Hamiltonian operator:

$$\hat{H} = \varepsilon\,\hat{n} + \alpha\,\hat{n}(\hat{n}+1) + \beta\,\hat{\ell}^2 + A\hat{W}^2$$

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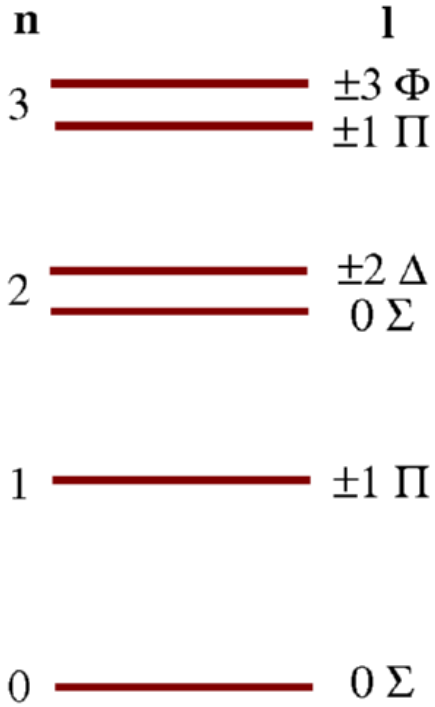
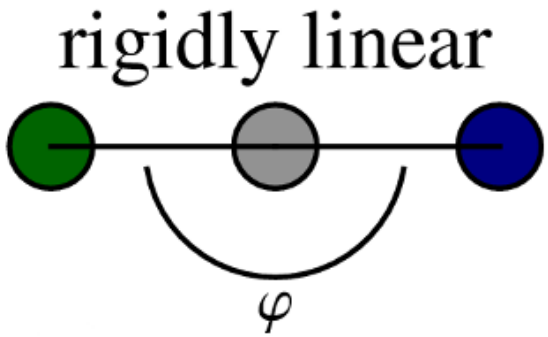
Cylindrical Oscillator Dynamical Symmetry

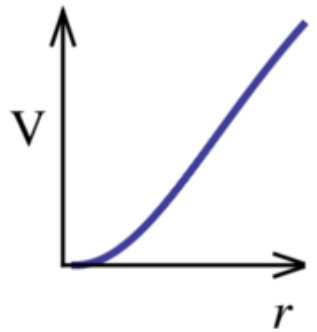
Chain I

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

$$\begin{aligned} n &= N, N-1, N-2, \ldots, 0 \\ \ell &= \pm n, \pm(n-2), \ldots, 1(\text{or } 0) \end{aligned}$$





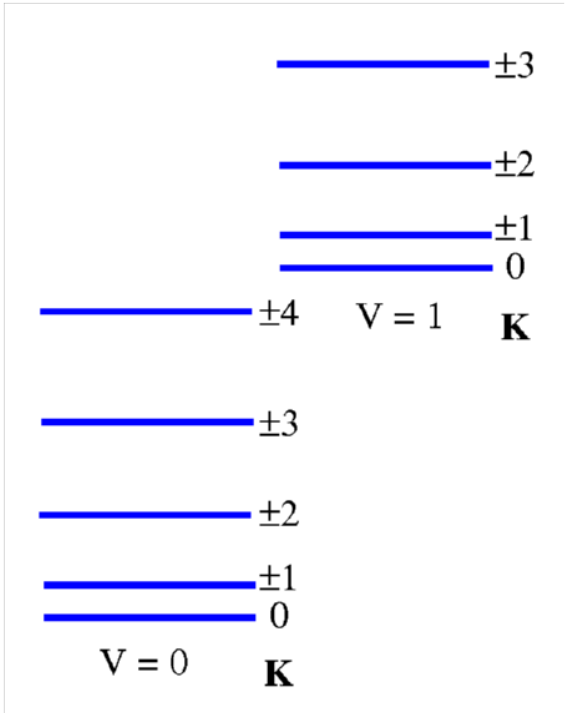


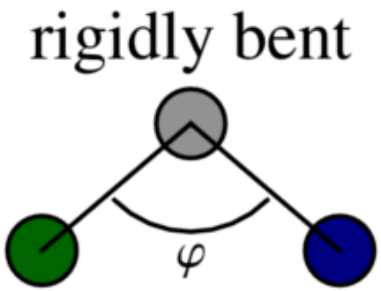
Displaced Oscillator Dynamical Symmetry

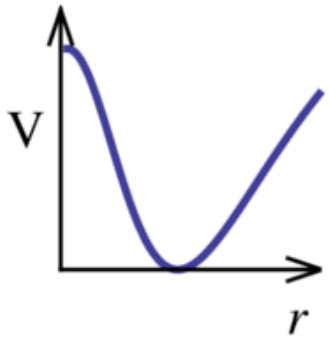
Chain II

$$\begin{array}{ccccc} U(3) & \supset & SO(3) & \supset & SO(2) \\ N & & \omega & & \ell \end{array}$$

$$\begin{aligned} \omega &= N, N-2, N-4, \ldots, 1(\text{or } 0) \\ \ell &= \pm\omega, \pm(\omega-1), \ldots, 0 \\ v &= \frac{N-\omega}{2} = 0, 1, \ldots, \frac{N-1}{2}(\text{or } \frac{N}{2}) \\ \ell &= 0, \pm 1, \pm 2, \ldots, \pm(N-2v) \end{aligned}$$







Shape Phase Transitions: QPTs *vs* ESQPTs

Ground State Quantum Phase Transitions

Singularities in the evolution of the system's ground state properties (shape phase transitions) as a control parameter is varied (aka zero-temperature phase transitions).

P. Cejnar and J. Jolie. *Prog. Part. Nucl. Phys.* 62 210 (2009)

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Shape phase transitions strictly take place at the thermodynamic limit (large N): importance of precursors for mesoscopic systems and the scaling behavior of the relevant quantities.

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Shape Phase Transitions: QPTs *vs* ESQPTs

Excited State Quantum Phase Transitions

Is this behavior extensible to states throughout the excitation spectrum? Yes

ESQPTs are universal to two-level pairing many-body models for both bosonic and fermionic constituents.

M.A. Caprio, P. Cejnar, F. Iachello. *Ann. Phys.* 323 1106 (2008).

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2DVM Phase Diagram

Single Bender Model Hamiltonian

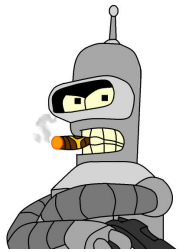
$$\begin{array}{ccccc} U(3) & \supset & U(2) & \supset & SO(2) \\ U(3) & \supset & SO(3) & \supset & SO(2) \end{array}$$

Dynamical Symmetry (I)

Dynamical Symmetry (II)

Single Bender Model Hamiltonian

$$\hat{\mathcal{H}} = \varepsilon \left[(1-\xi)\hat{n} + \frac{\xi}{N-1}\hat{P} \right]$$



- ε: energy scale
- ξ: control parameter: $\xi \in [0, 1]$
  - $\xi = 0.0$ rigidly-linear
  - $0.0 < \xi \leq 0.2$ quasilinear
  - $0.2 < \xi < 1.0$ non-rigid
  - $\xi = 1.0$ rigidly-bent

The system undergoes a second order QPT in $\xi_c = 0.2$.

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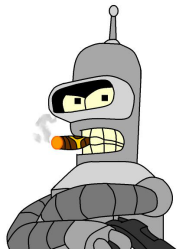

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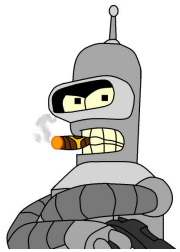

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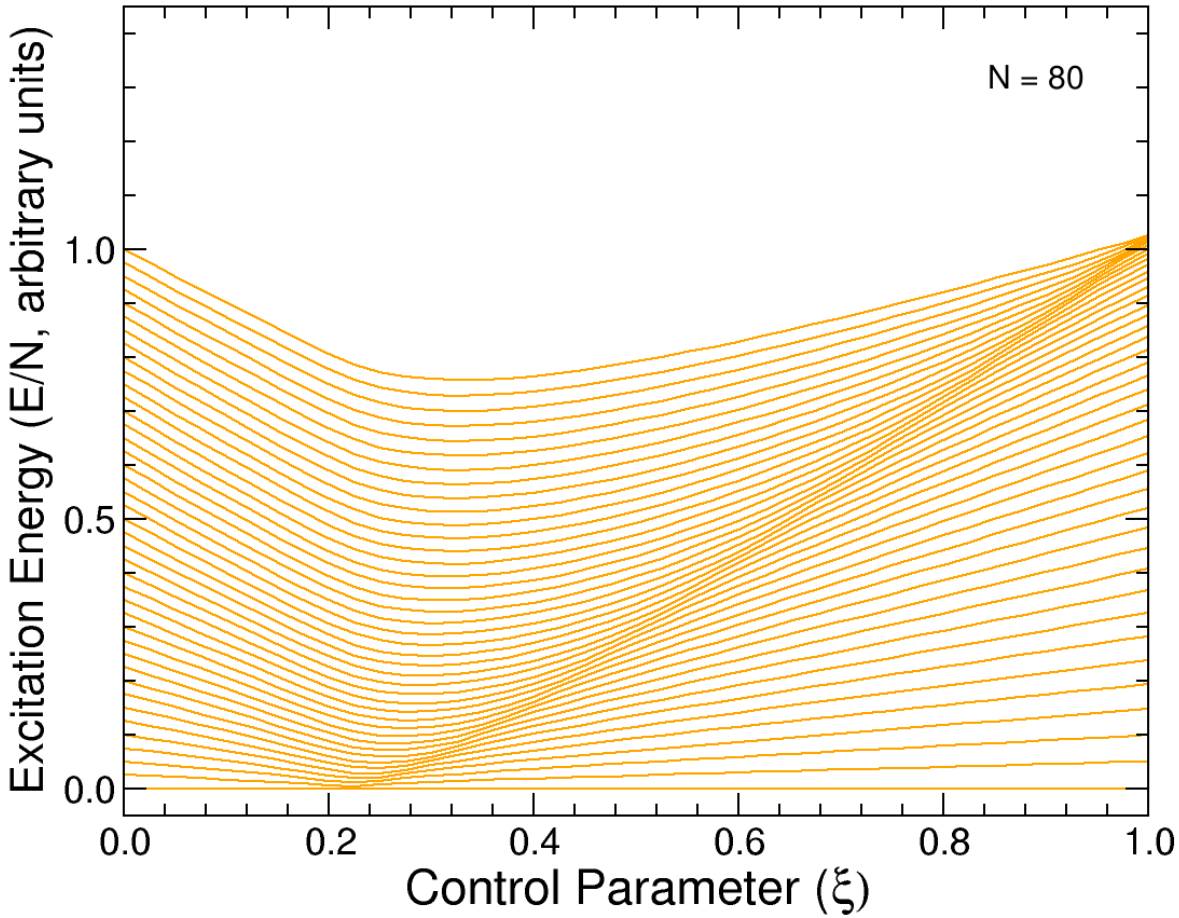
Possibility of crossing the ESQPT both horizontally and vertically.



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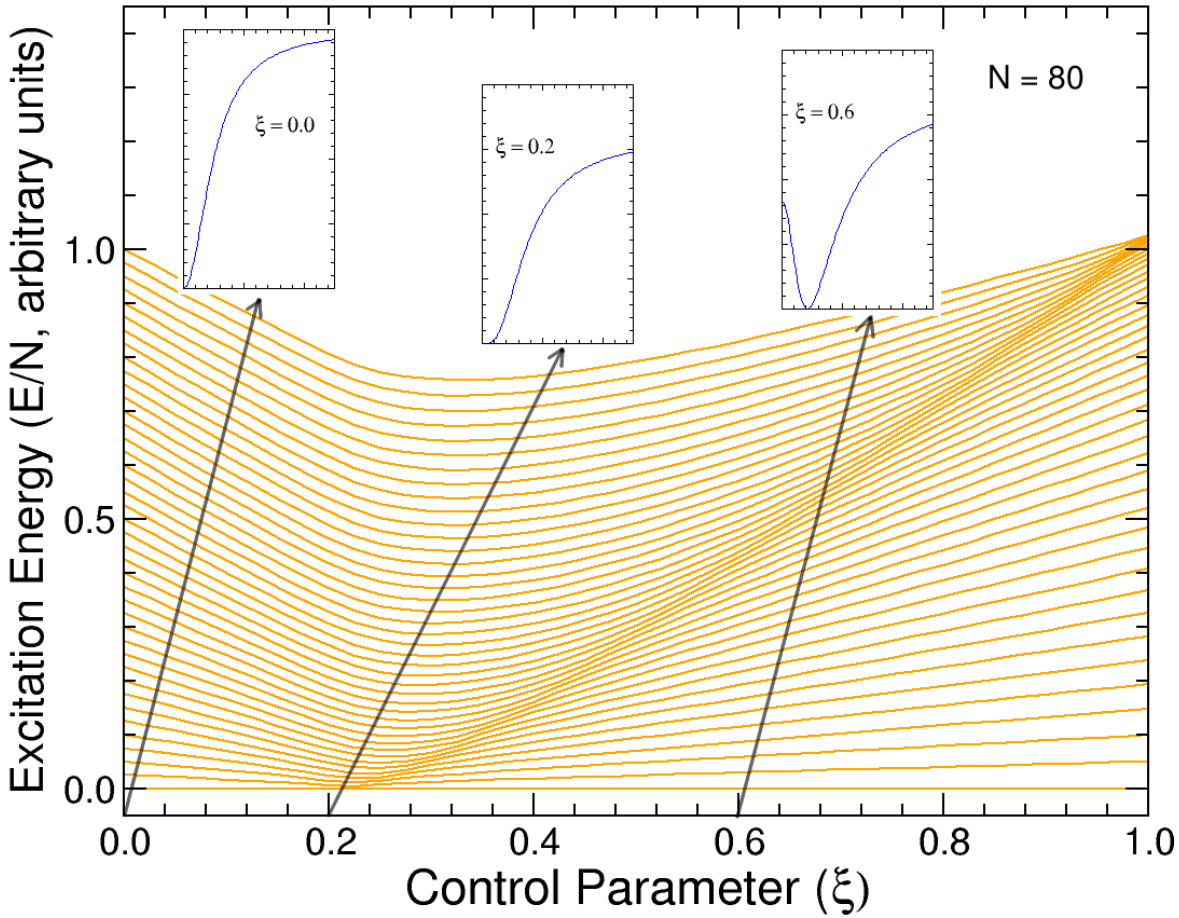

2DVM Excited State Quantum Phase Transition

M. A. Caprio, P. Cejnar, and F. Iachello. Ann. Phys. 323 1106 (2008).

Infinite local level density (in the thermodynamic limit) at the critical point propagates to higher excitation energies: SEPARATRIX.

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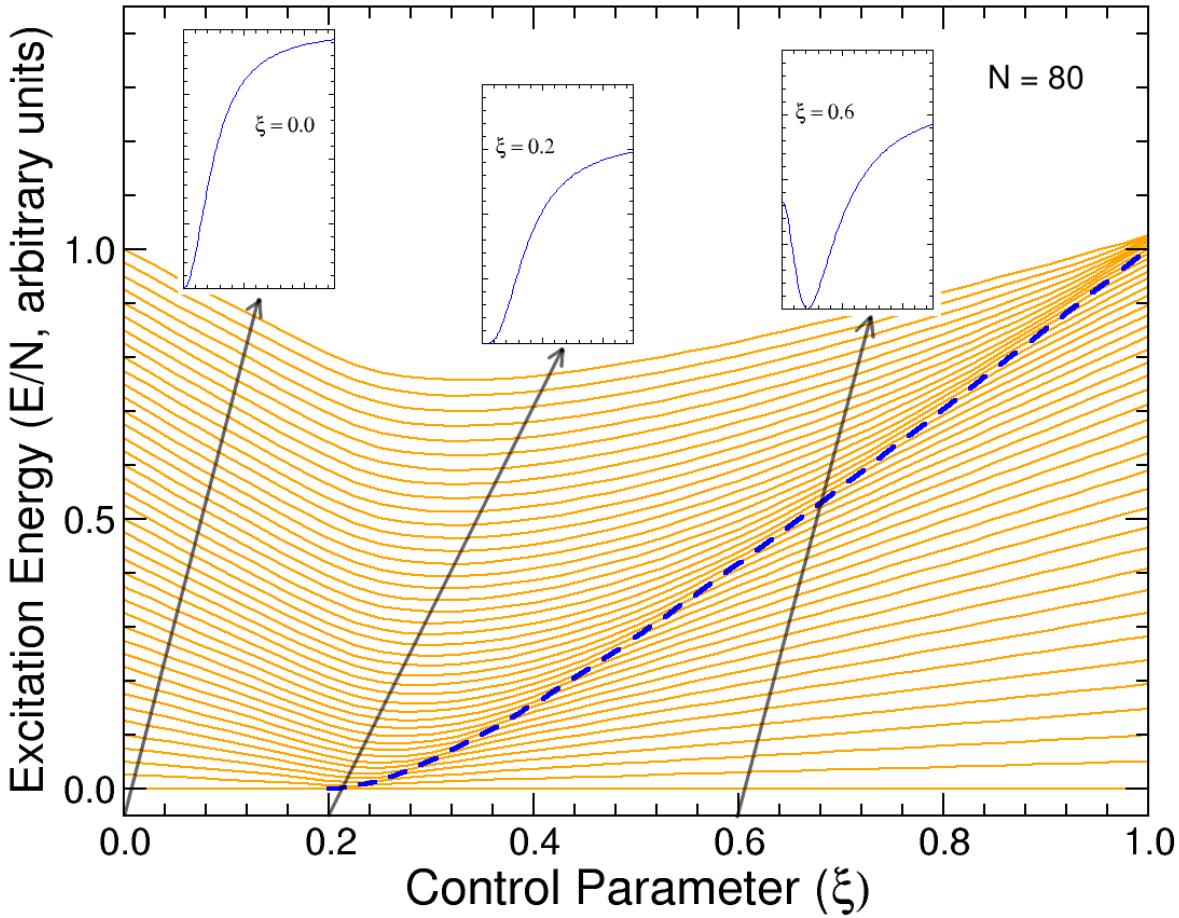
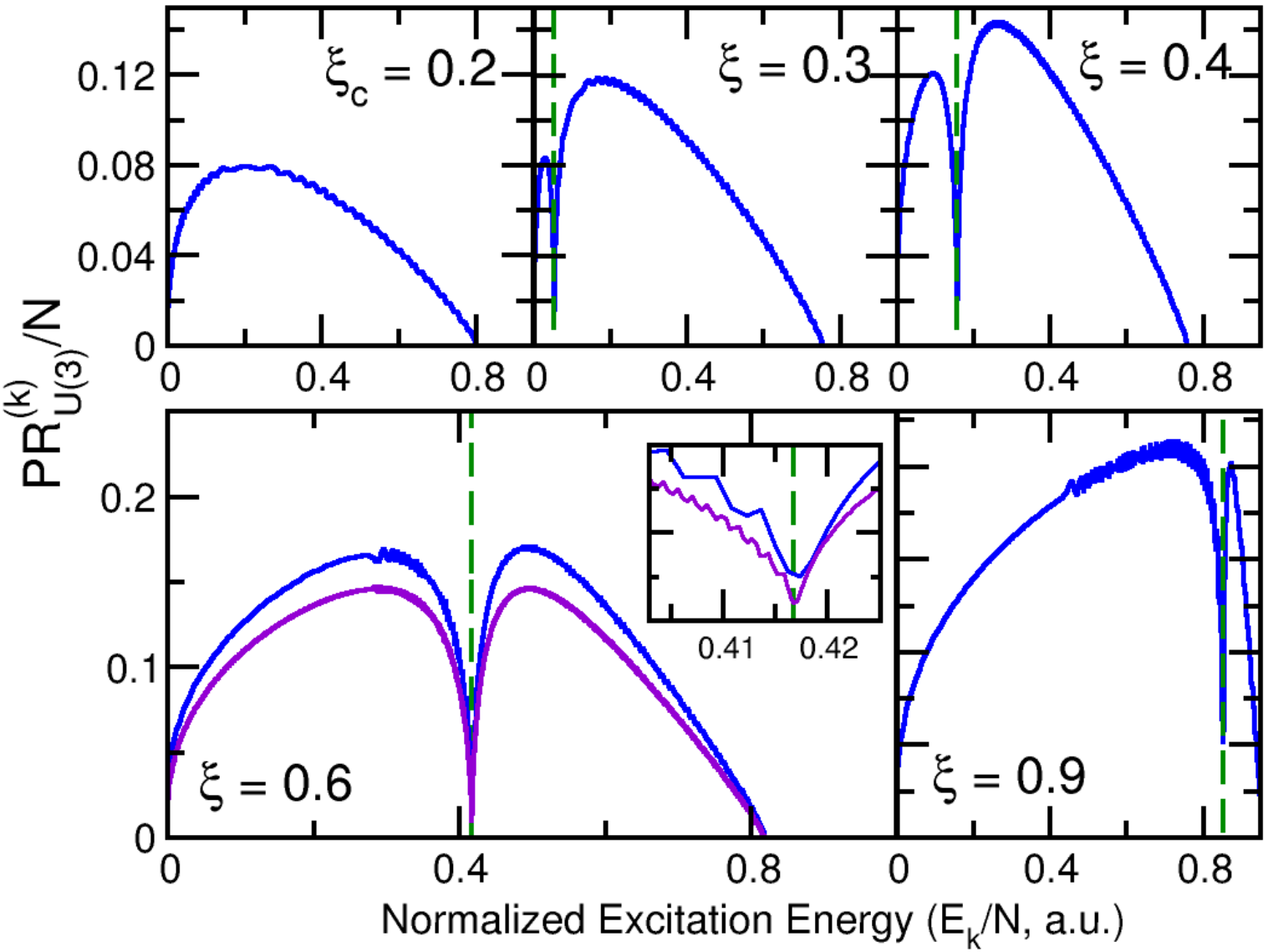


Eigenstate Structure: Participation Ratio in an ESQPT

Phys. Rev. A **92**, 050101 (2015), Phys. Rev. A **94**, 012113 (2016)

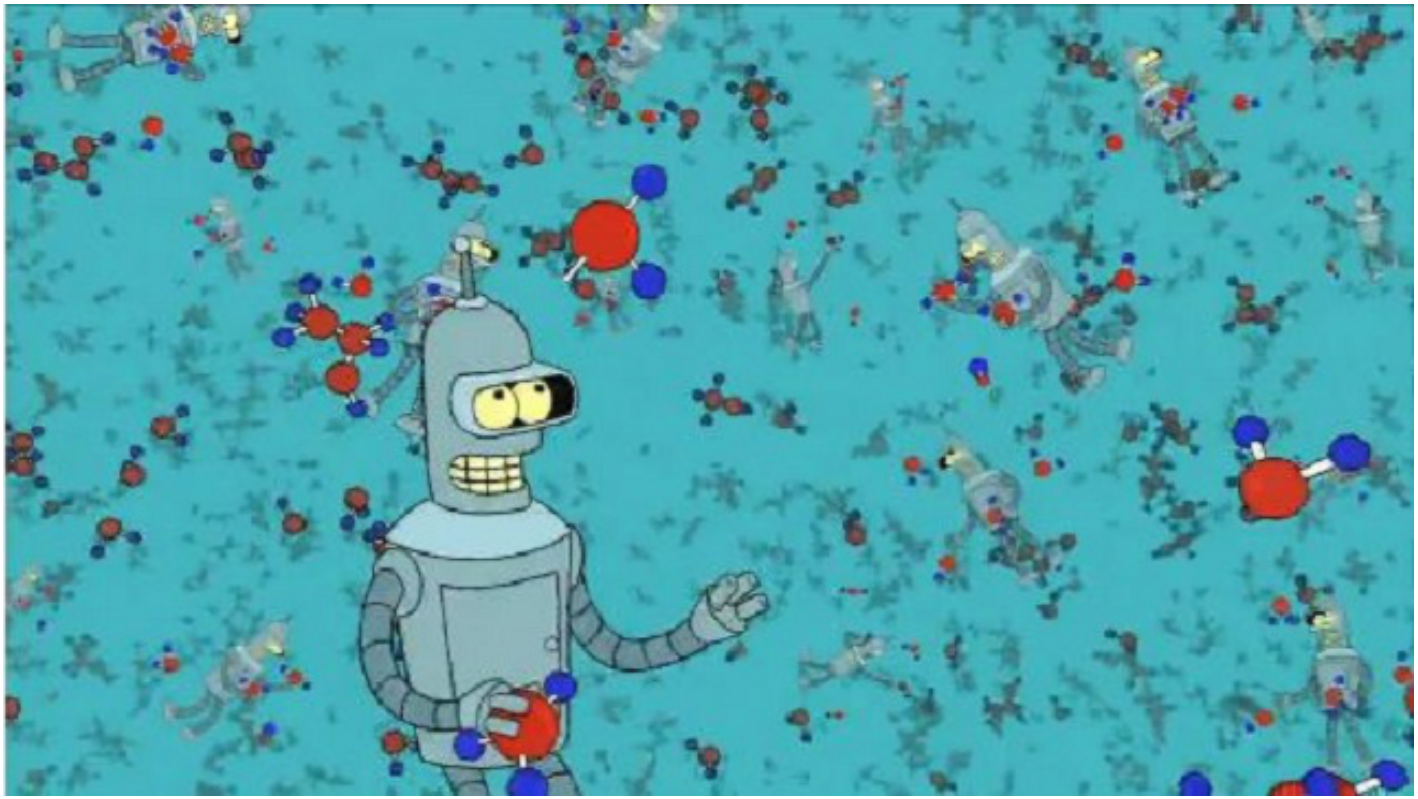
Chain I: Cylindrical oscillator case (N = 600, 2000)



Application to Single Bender Molecular Species

Vibrational bending excitation

- D. Larese and F. Iachello. J. Mol. Struct. **1006**, 611 (2011).
- D. Larese, FPB, and F. Iachello. J. Mol. Struct. **1051**, 310 (2013).



ESQPT/Quantum Monodromy in bending spectra

J. Mol. Struct. **1006**, 611 (2011), J. Mol. Struct. **1051**, 310 (2013)

Table 1
Best-fit values of Hamiltonian parameters. N (the integer vibron number) and ξ (control parameter value) are both dimensionless, while ε, α, β, A, and rms deviation are in cm^{-1}.

Molecule	N	ε	α	β	A	rms	ξ
HCNO	24	716.715	−13.0168	10.7685	7.4363	0.09	0.1927
DCNO	30	634.902	−12.5727	8.4958	5.2775	0.25	0.1942
BrCNO	96	642.047	−6.4154	3.1938	1.6980	0.57	0.2010
ClCNO	92	638.079	−6.4925	3.2283	1.7766	0.71	0.2025
CH_3NCS	73	523.947	−6.8652	7.8193	1.8524	0.48	0.2029
GeH_3NCO	90	385.319	−4.1902	4.6941	1.1172	0.38	0.2069
CH_3NCO	78	453.756	−5.5741	7.6712	1.6313	1.34	0.2168
OCCCS	30	77.5202	−0.13767	0.37183	0.0013568	0.05	0.0004
NCCNO	28	149.141	−1.8472	1.3019	0.97870	0.16	0.1507
NCNCS	70	203.572	−2.5766	1.4957	0.81344	2.18	0.2154

Molecule	N	ε	α	β	A	rms	ξ
HCN	50	749.88	−3.26	4.25	0.36	0.7	0.0227
HNC	40	853.65	−11.56	8.94	3.77	2.3	0.1471
NiCN	40	244	−2.8	4	0.1	5	0.0154
CaOH	20	363.5	−0.05	6.6	0.5	2.3	0.0261
CaOD [a]	27	273.7	−3.0	4.6	0.1	0.5	0.0097
MgOH[b]	20	397.4	−4.5		4.7	2.2	0.1833
MgOD[a,b]	27	299.4	−2.1		2.7	4.2	0.1886
OCS[b]	40	728.3	−5.1	1.4	2.2	0.2	0.1062
HNCS	25	810.1	−22.96	16.97	10.77	3.3	0.2419
H_2O[c]	143	4815.0	−32.15	15.44	8.7	9.1	0.2042
D_2O[c]	195	4163.0	−20.70	8.48	5.5	4.0	0.2031
H_2S[d]	140			12.10	2.12	5.9	1.0000
H_2Se[d]	170			9.29	1.53	5.9	1.0000

ESQPT/Quantum Monodromy in bending spectra

J. Mol. Struct. **1006**, 611 (2011), J. Mol. Struct. **1051**, 310 (2013)

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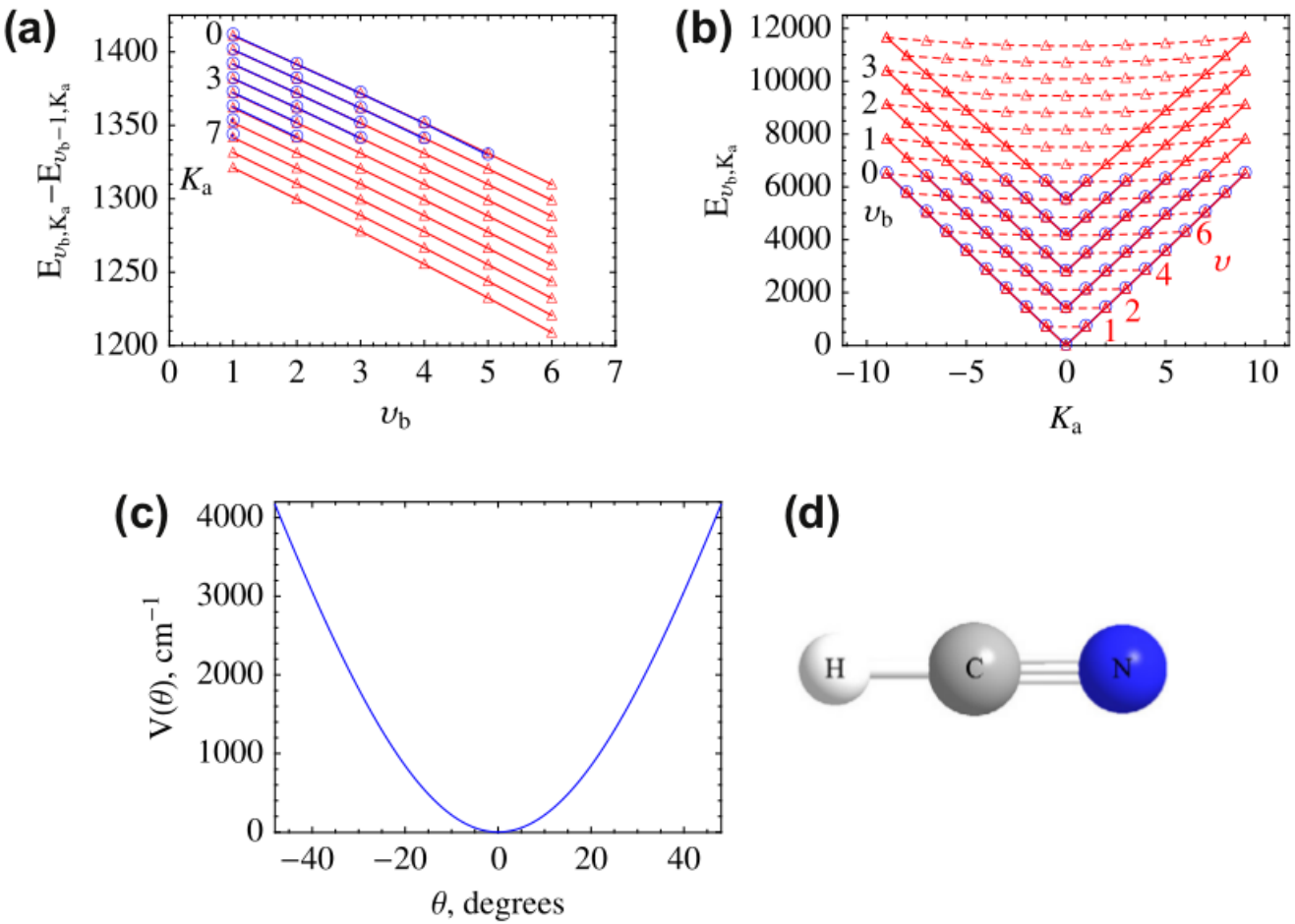
Dynamical Symmetry (I): HCN

J. Mol. Struct. **1051**, 310 (2013)



(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Bending Potential

(d) Molecule Model

$N = 40$

$\varepsilon = 794.88$

$\alpha = -3.96$

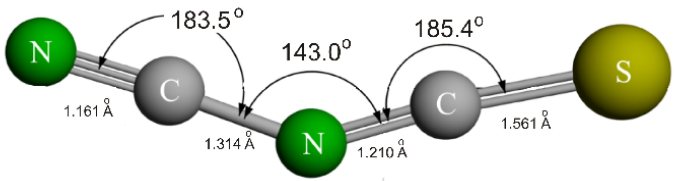
$\beta = 4.25$

$A = 0.36$

$rms = 0.7$ cm^{-1}

2DVM and the NCNCS bending spectrum

ESQPT in ν_7 normal mode of Cyanogen Isothiocyanate

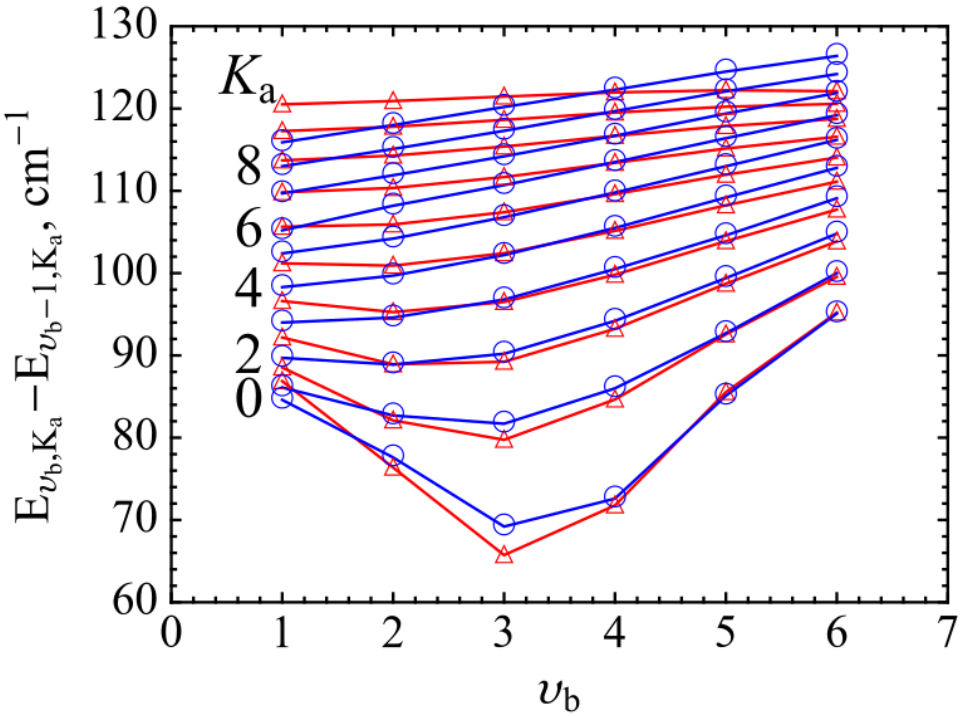


General Hamiltonian

$$\hat{H} = \varepsilon\,\hat{n} + \alpha\,\hat{n}(\hat{n}+1) + \beta\,\hat{\ell}^2 + A\hat{P}$$

N	rms (cm^{-1})
50	2.2
ϵ (cm^{-1})	α (cm^{-1})
203.57	-2.58
β (cm^{-1})	A (cm^{-1})
1.50	0.8134

J. Mol. Struct. **1006**, 611 (2011)



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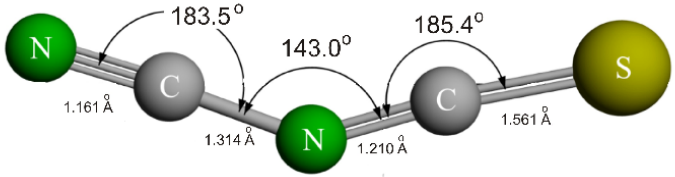

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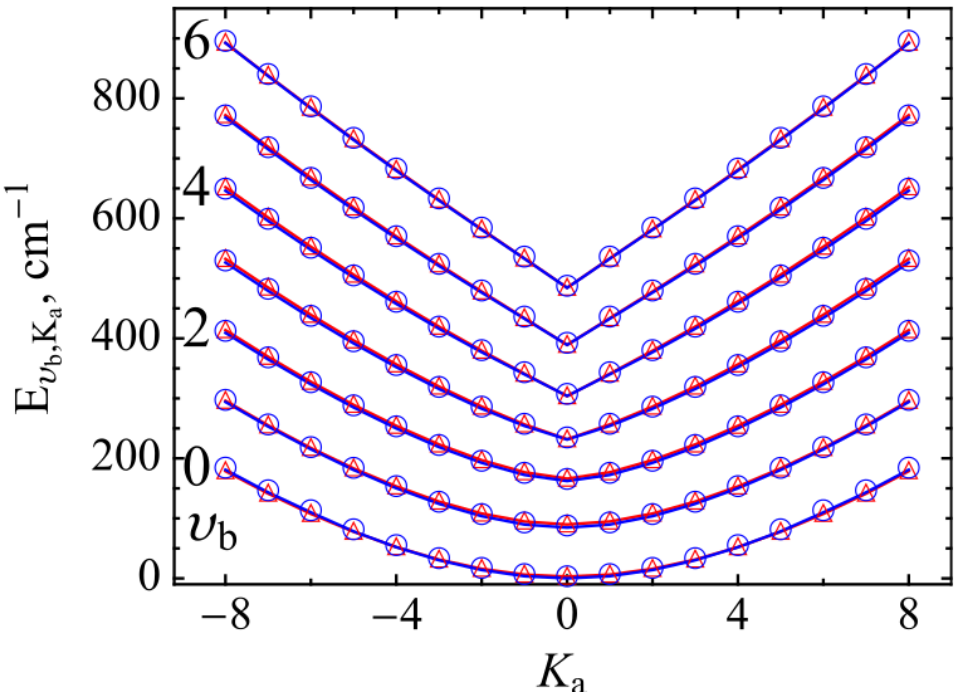
J. Mol. Struct. **1006**, 611 (2011)



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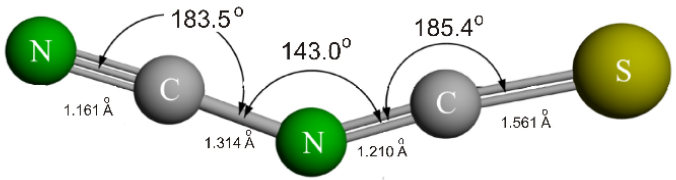

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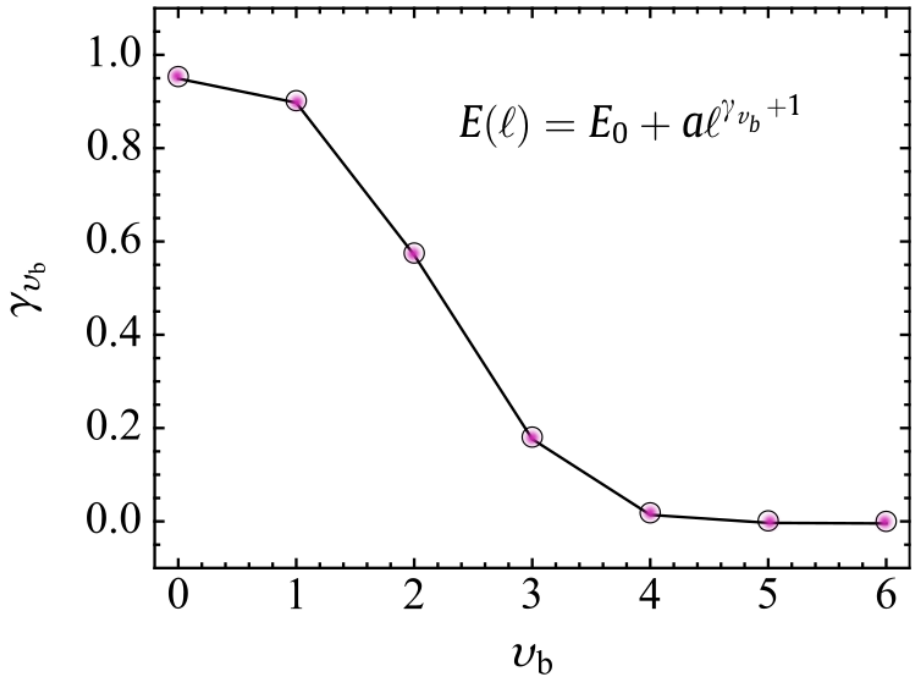

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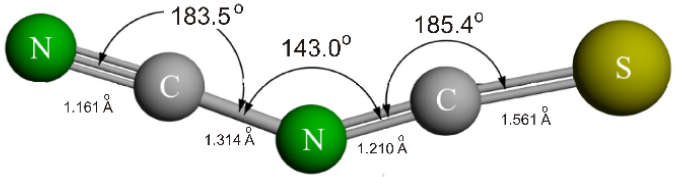

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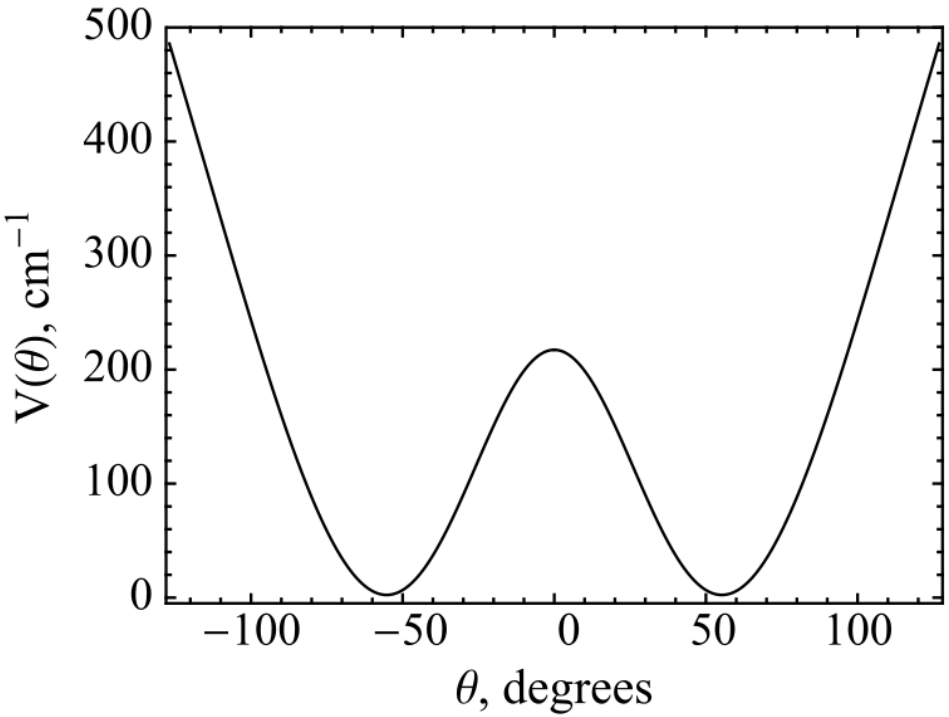

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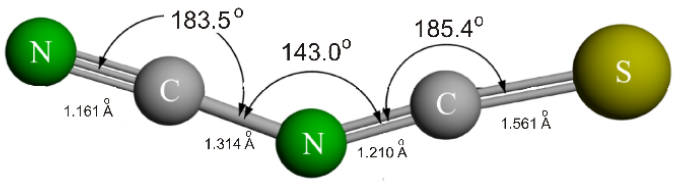

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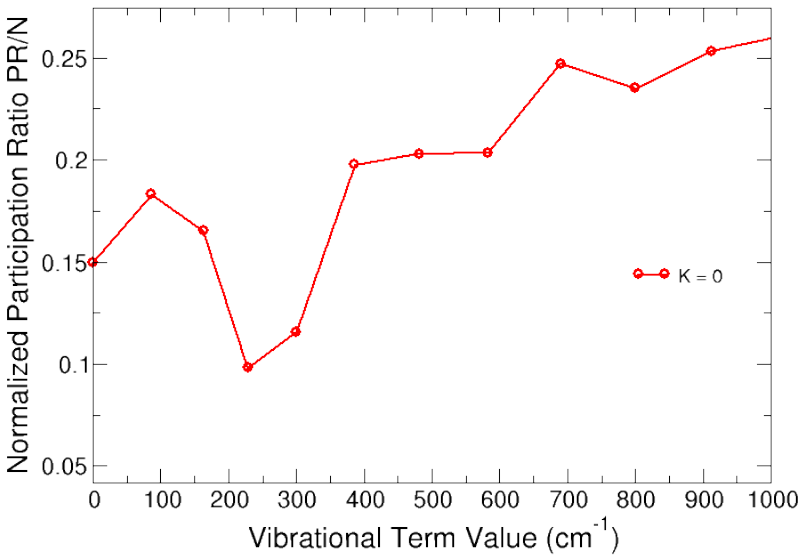

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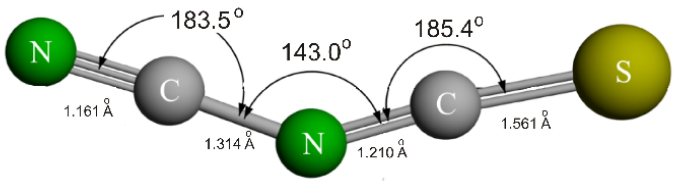

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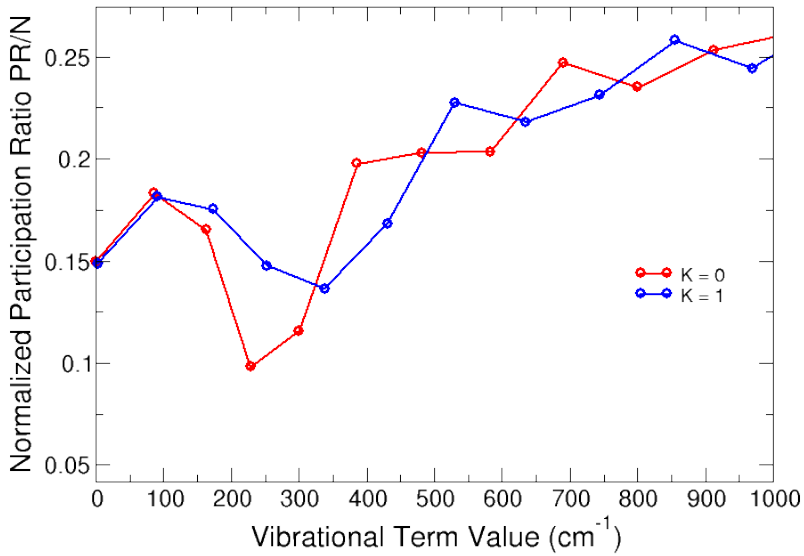

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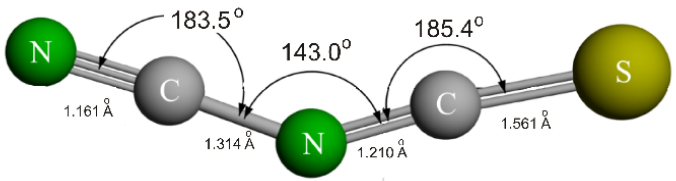

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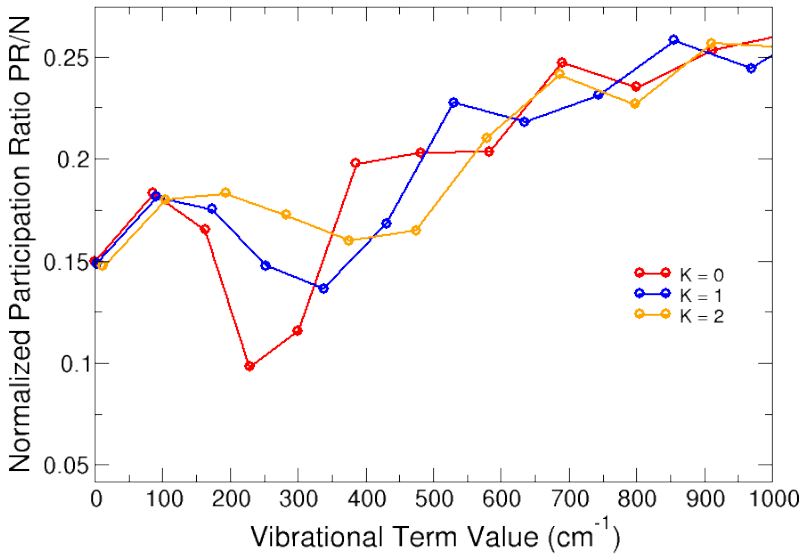

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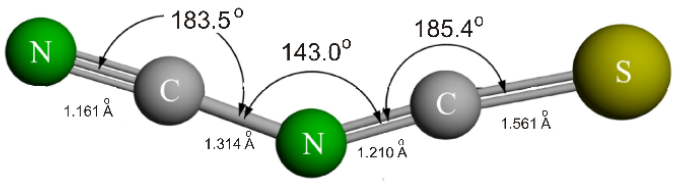

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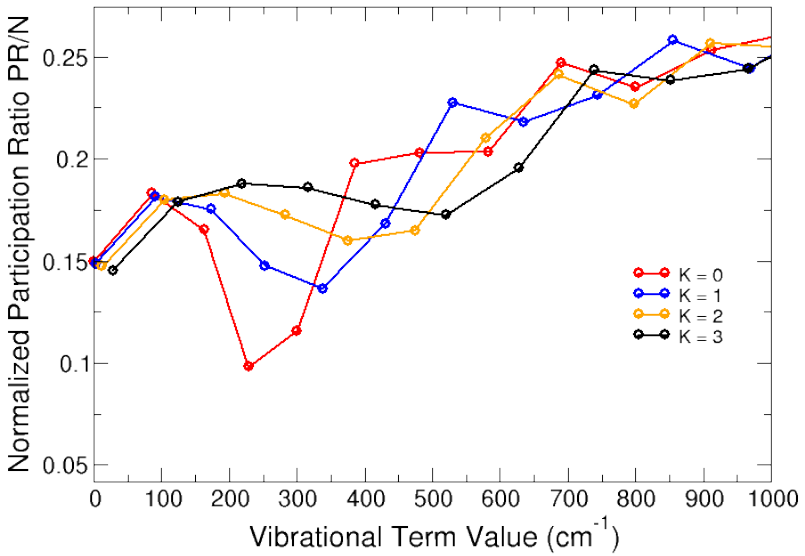

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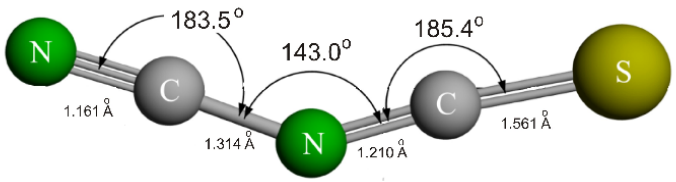

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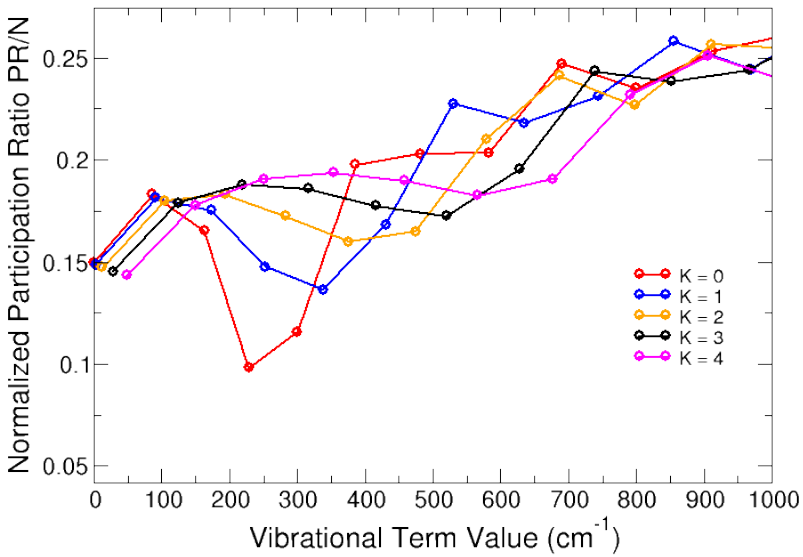
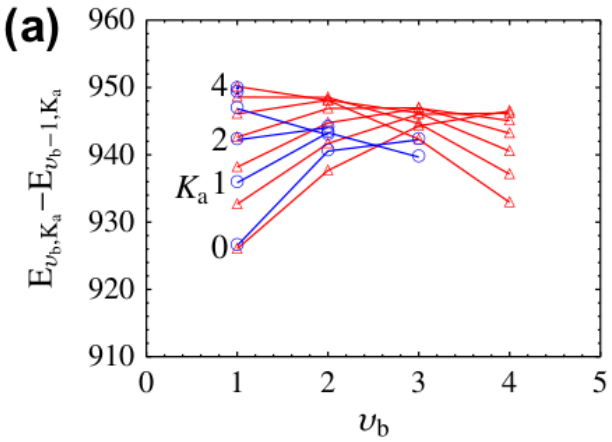
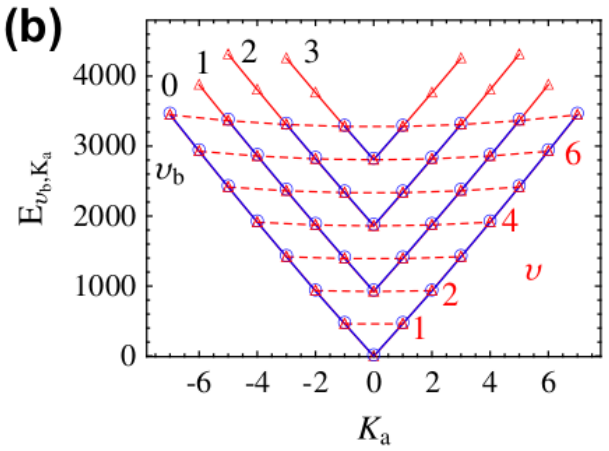
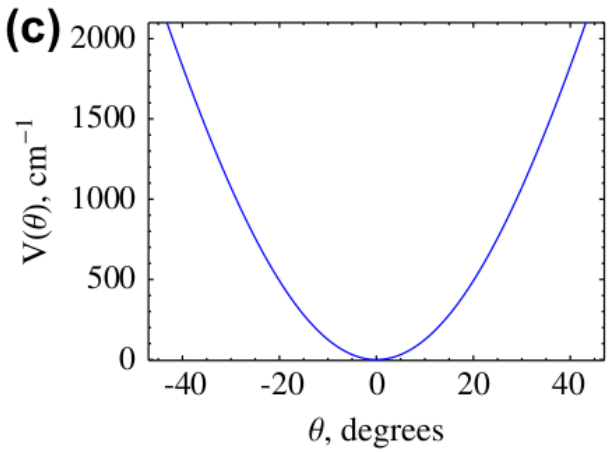


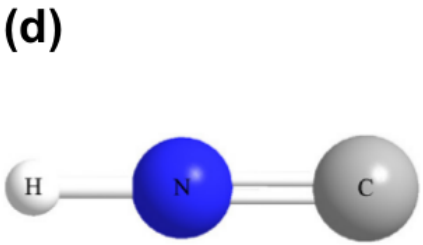
And... What's with HNC?

Figures from J. Mol. Struct. **1051**, 310 (2013)









(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Bending Potential

(d) Molecule Model

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$\alpha = -11.56$

$\beta = 8.94$

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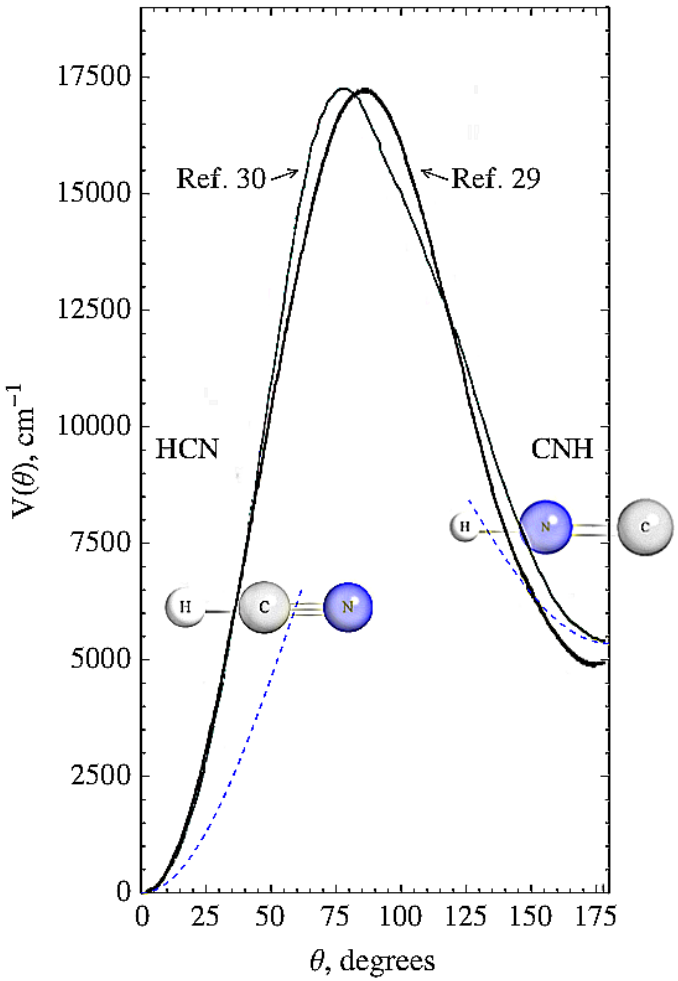
$rms = 2.3$ cm^{-1}

And... What's with HNC?

Figure and excerpt from J. Mol. Struct. **1051**, 310 (2013)



... Of particular interest is the comparison between hydrogen cyanide, HCN, and isocyanide, HNC. In a more complete description HCN and HNC are part of one potential surface. The qualitative and quantitative picture is well described in papers by Ross and Bunker [29] and Mellau, Winnewisser, and Winnewisser [30]...

Refs. J. Mol. Spectrosc. **101**, 199 (1983) and J. Mol. Spectrosc. **249**, 23 (2008).

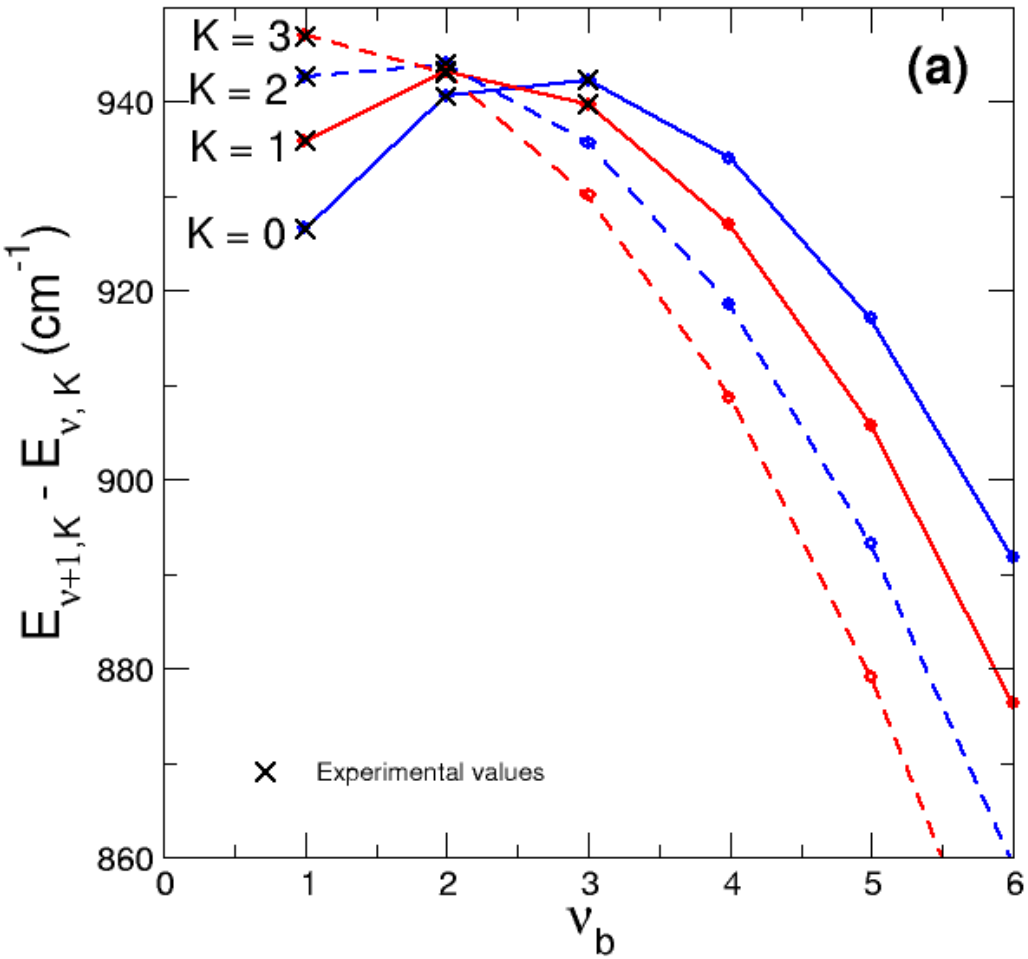
General Hamiltonian up to Four-Body Operators

Reanalysis of bending vibrational data in progress...

$$
\begin{aligned}
\hat{H} =& P_{11}\hat{n} \\
&+ P_{21}\hat{n}^2 + P_{22}\hat{\ell}^2 + P_{23}\hat{W}^2 \\
&+ P_{31}\hat{n}^3 + P_{32}\hat{n}\hat{\ell}^2 + P_{33}\left[\hat{n}\hat{W}^2 + \hat{W}^2\hat{n}\right] \\
&+ P_{41}\hat{n}^4 + P_{42}\hat{n}^2\hat{\ell}^2 + P_{43}\hat{\ell}^4 + P_{44}\hat{\ell}^2\hat{W}^2 \\
&+ P_{45}\left[\hat{n}^2\hat{W}^2 + \hat{W}^2\hat{n}^2\right] + P_{46}\hat{W}^4 + P_{47}\left[\hat{W}^2\hat{\overline{W}}^2 + \hat{\overline{W}}^2\hat{W}^2\right]/2
\end{aligned}
$$

HNC experimental data reanalysis

Warning: preliminary results!



(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Effective Frequency

(d) Participation Ratio

$N = 40$

$P_{11} = 1414(6)$

$P_{21} = -29.83(19)$

$P_{22} = 15.81(9)$

$P_{23} = -8.05(5)$

$P_{32} = 0.0487(14)$

$rms = 7 \times 10^{-2}$ cm^{-1}

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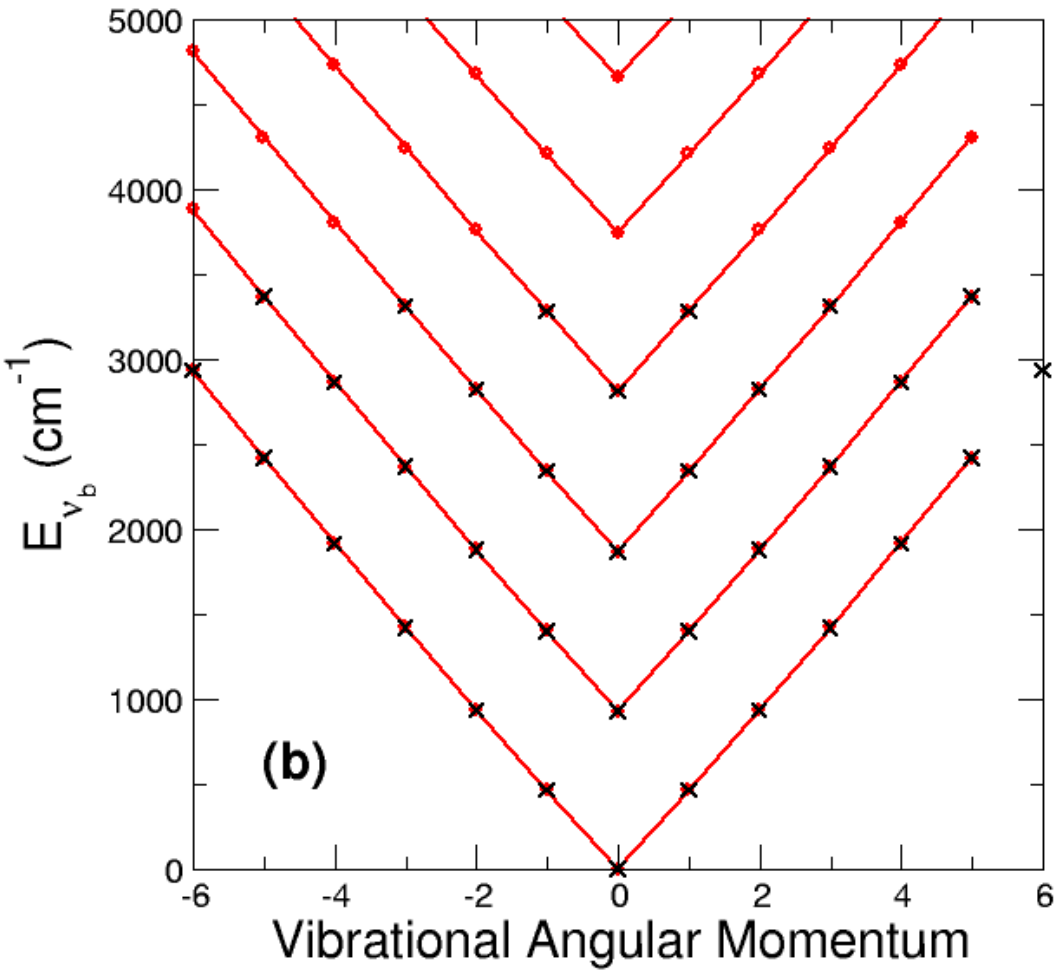

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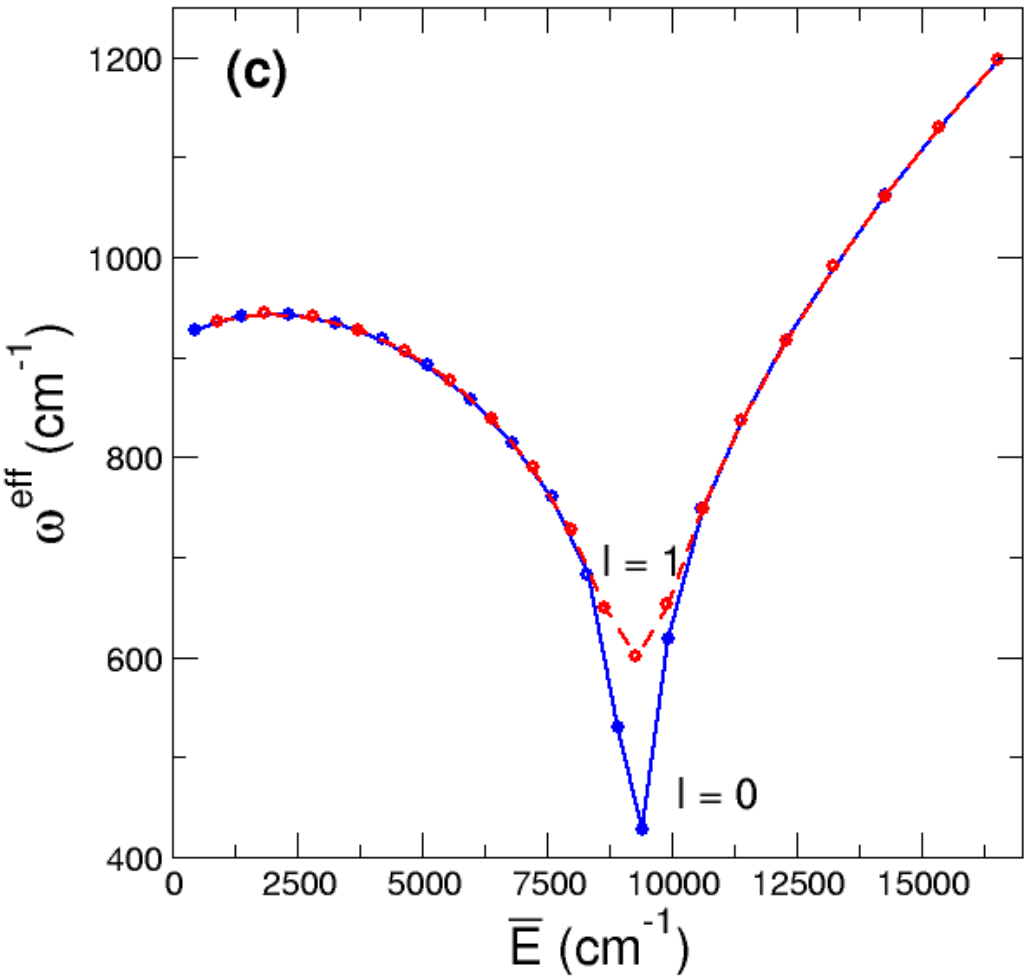

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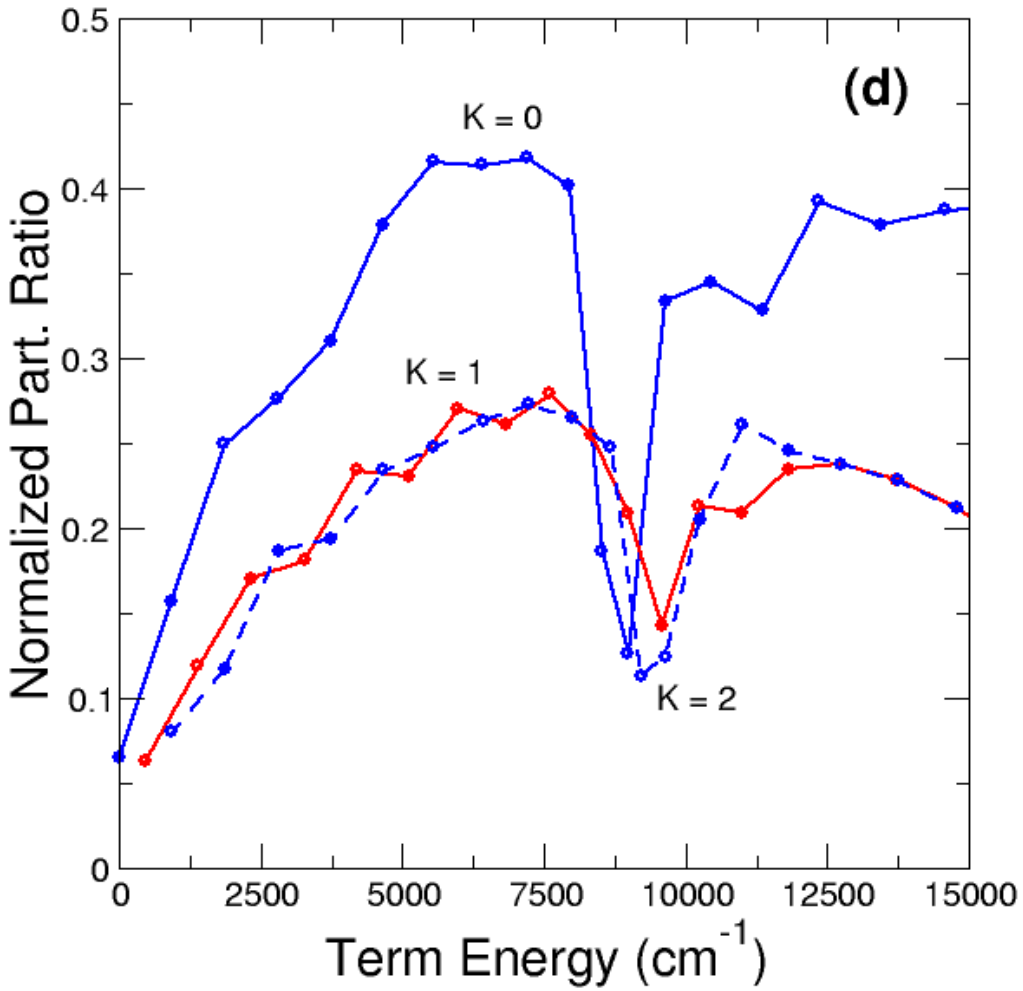

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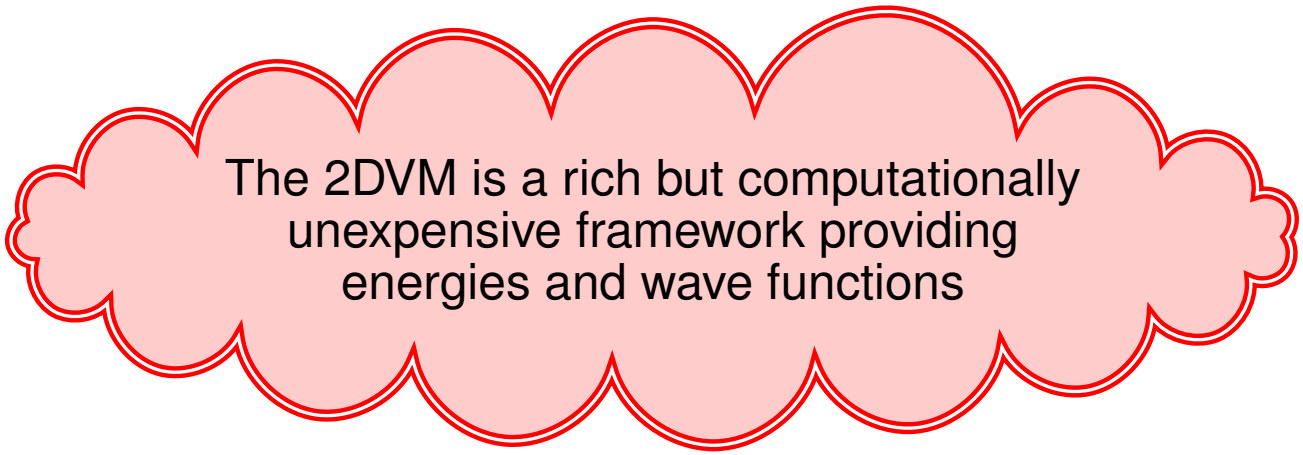
Where are we heading now?...



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Possibility of studying dynamics of the transition state

Many cool questions still open.
E.g. application to coupled systems (C_2H_2) and relationship with shape coexistence formalism

Collaborators and Suggested References

Work done in collaboration with:
Miguel Carvajal-Zaera (UHU, ES)
Jamil Khalouf (UHU, ES)
Lea Santos (YU, USA)
Franco Iachello (Yale, USA)

2D Vibron Model
Phys. Rev. A **77**, 032115 (2008)
Phys. Rev. A **81**, 050101(R) (2010)
J. Chem. Phys. **140**, 014304 (2014)

ESQPTs in Molecular Spectra
J. Mol. Struct. **1006**, 611 (2011)
J. Mol. Struct. **1051**, 310 (2013)

Molecular Isomerization
Science **350**, 1338 (2015)
Sci. Rep. **6**, 33068 (2016)

Thanks for your attention and
let's roll!