Coupled molecular benders modeling within the vibron model 2D limit

QPT (and ESQPT) in the 2D limit of the Vibron Model

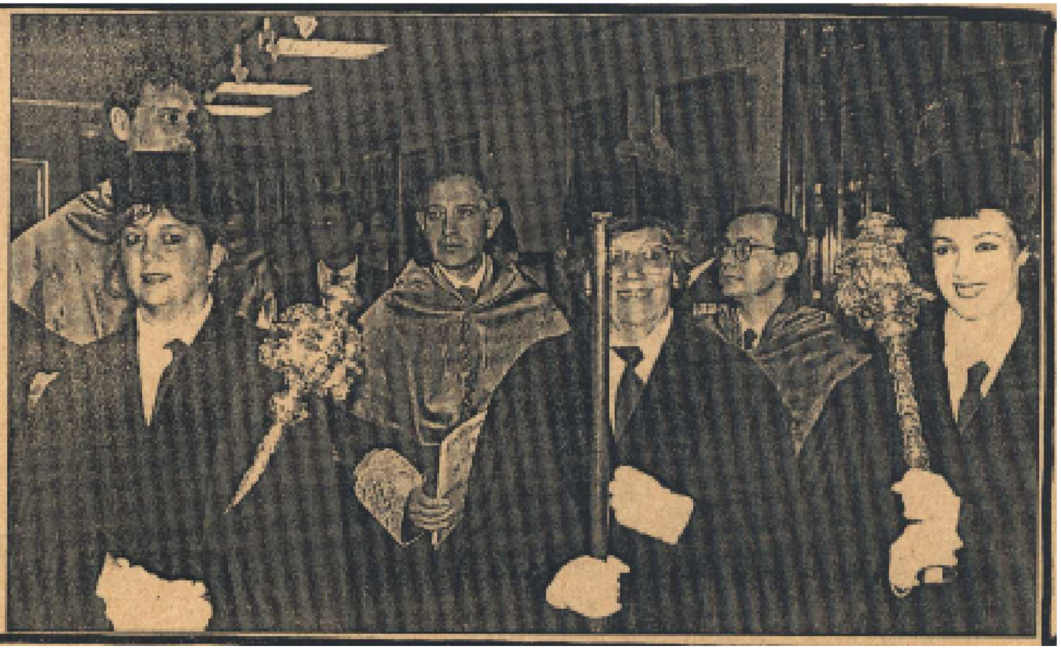
- Miguel Carvajal, José Enrique García-Ramos, **F. Pérez-Bernal** (University of Huelva)
- Francesco Iachello, Danielle Larese, Patrick H. Vaccaro (Yale University)
- Lorenzo Fortunato (Padova University)
- Osiris Álvarez-Bajo, Renato Lemus, Mariano Sánchez-Castellanos (ICN-UNAM)
- José Miguel Arias, Pedro Pérez-Fernández (University of Sevilla)

Doctor Honoris Causa Universitas Hispalensis

Doctor Honoris Causa Universitas Hispalensis

Francesco Iachello, Honoris Causa de la Universidad de Sevilla

El catedrático de Física Teórica de la Universidad estadounidense de Yale, Francesco Iachello, fue ayer investido Doctor Honoris Causa de la Hispalense. Iachello, que está considerado como uno de los físicos más destacados del último cuarto de siglo, ha sido galardonado con diferentes distinciones internacionales. En la imagen, Francesco Iachello, que ha colaborado con científicos de la Univerdidad de Sevilla, durante un momento de la solemne investidura.



De perfil

FRANCESCO IACHELLO

La Universidad de Sevilla acaba de conceder la distinción académica del doctorado honoris causa al catedrático de Física Teórica de la Universidad de Yale Francesco Iachello, considerado como una de las grandes figuras de la ciencia mundial del último cuarto de siglo. Nacido en Sicilia, está vinculado desde la infancia a la cultura española a través de su formación en un colegio de jesuitas y la lectura de poetas andaluces. Con él han colaborado algunos investigadores de la Hispalense desde principios de los ochenta.

– ¿Cree que los físicos teóricos están sustituyendo hoy a los filósofos?

– Así lo defienden algunos científi-

Doctor Honoris Causa Universitas Hispalensis

Nuevo doctor honoris causa El catedrático de Física Teórica de la Universidad de Yale (EE UU) Francesco Iachello recibió ayer de manos del rector Juan Ramón Medina Precioso el grado de doctor honoris causa por su destacada actividad investigadora que le ha valido las más altas distinciones del mundo científico internacional y los doctorados honoris causa por las universidades de Ferrara (Italia) y Chung-Yuan Christian de Taiwan, así como el Bonner Prize de la Sociedad Americana de Físicos en 1993.

Doctor Honoris Causa Universitas Hispalensis

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Outline of the presentation

- The 2D limit of the Vibron Model.
- Single bender: QPT and ESQPT.
- Single bender: beyond mean field results.
- Coupled benders: the $U(3) \otimes U(3)$ SGA.
- Coupled benders model Hamiltonian.
- Coupled benders phase diagram.
- Concluding remark.

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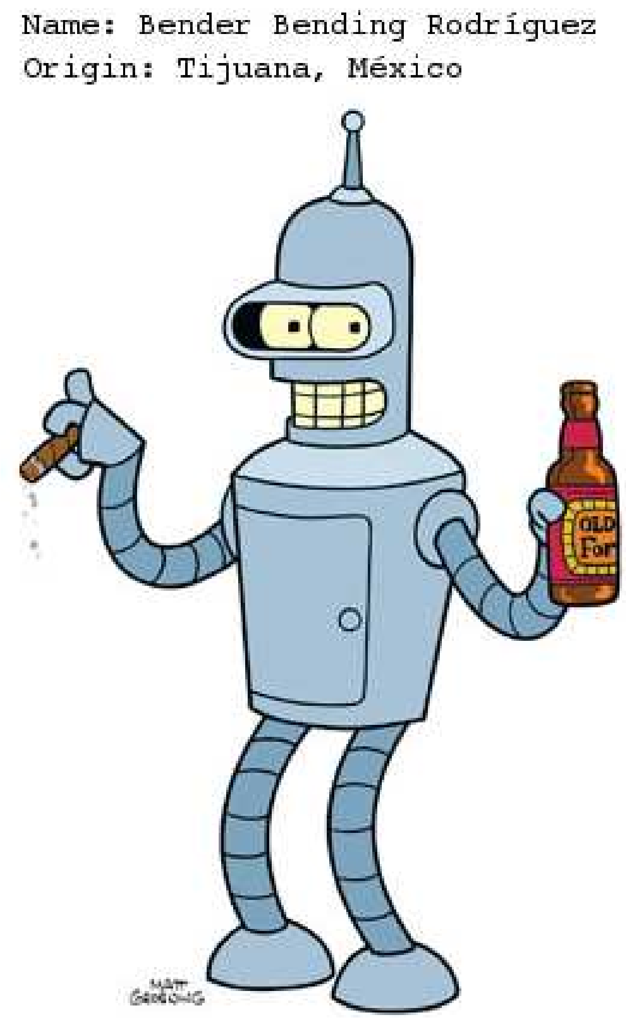

Study of N–dimensional systems $\Rightarrow U(N+1)$ Spectrum Generating Algebra.

F. Iachello, Contemp. Math. 160 151 (1994).

Algebraic Approach *alla Iachello*

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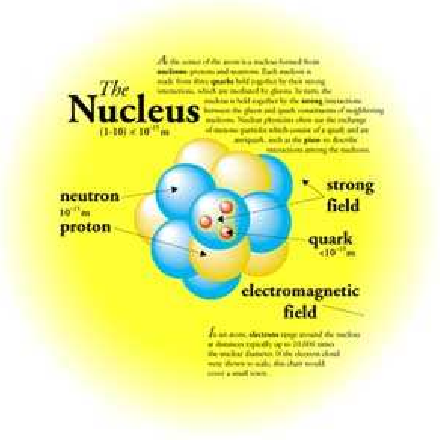
Nuclei



- Quadrupolar degree of freedom $\rightarrow N = 5$
- Spectrum Generating Algebra: $U(6)$
- Interacting Boson Model IBM
- A. Arima and F. Iachello. Phys. Rev. Lett. 35 1069 (1975)
- IBM-2, IBM-3, IBFM, SUSY in nuclei.

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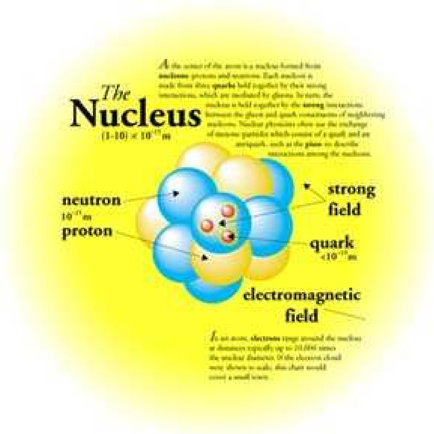

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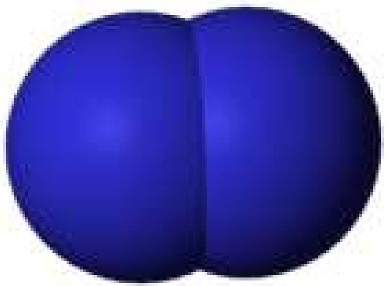
Molecules



- Dipolar interaction $\rightarrow N = 3$
- Spectrum Generating Algebra: $U(4)$
- Vibron Model
- F. Iachello. Chem. Phys. Lett. 78 581 (1981).

The Vibron Model: $U(4)$ dynamical algebra

The Vibron Model: the $U(4)$ Dynamical Algebra applied to the study of rovibrational molecular structure.

Modeling three-dimensional systems algebraically.

F. Iachello Chem. Phys. Lett. 78 581 (1981).

Volume 78, number 3 CHEMICAL PHYSICS LETTERS 15 March 1981

ALGEBRAIC METHODS FOR MOLECULAR ROTATION–VIBRATION SPECTRA

F. IACHELLO
Kernfysisch Versneller Instituut, University of Groningen, The Netherlands
and Physics Department, Yale University, New Haven, Connecticut 06520, USA

Received 10 December 1980

Algebraic techniques similar to those recently introduced in nuclear physics may be useful in the treatment of molecular spectra. A spectrum generating algebra appropriate to diatomic molecules is constructed. This algebra, U(4), is the simplest generalization to 3-D of the algebra of the 1-D Morse oscillator and a simplification of the U(6) algebra of nuclear rotation–vibration spectra.

The one-dimensional limit of the Vibron Model

The 1D limit of the Vibron Model: the $U(2)$ Dynamical Algebra applied to the study of vibrational molecular structure.

Modeling (coupled) one-dimensional systems algebraically.

O.S. van Roosmalen, I. Benjamin, and R.D. Levine.

J. Chem. Phys. 81 5986 (1984).

A unified algebraic model description for interacting vibrational modes in ABA molecules

O. S. van Roosmalen[a)]
Kellogg Radiation Laboratory, California Institute of Technology, Pasadena, California 91125

I. Benjamin and R. D. Levine
The Fritz Haber Molecular Dynamics Research Center, The Hebrew University, Jerusalem 91904, Israel

(Received 9 April 1984; accepted 6 July 1984)

A simple yet realistic model Hamiltonian which describes the essence of many aspects of the interaction of vibrational modes in polyatomics is discussed. The general form of the Hamiltonian is that of an intermediate case between the purely local mode and purely normal mode limits. Resonance interactions of the Fermi and Darling–Dennison types are shown to be special cases. The classical limit of the Hamiltonian is used to provide a geometrical content for the model and to illustrate the "phase-like" transition between local and collective (i.e., normal) mode behavior. Such transitions are evident as the coupling parameters in the Hamiltonian are changed and also for a given Hamiltonian as the energy is changed. Applications are provided to higher lying vibrational states of specific molecules (H_2O, O_3, SO_2, C_2H_2, and C_2D_2).

The one-dimensional limit of the Vibron Model

The 1D limit of the Vibron Model facilitates the incorporation of point symmetries and the application to the vibrational spectrum of polyatomic molecular species.

Building symmetry-adapted local basis.

R. Lemus.

Mol. Phys. 101 2511 (2003).

MOLECULAR PHYSICS, 20 AUGUST 2003, VOL. 101, NO. 16, 2511–2528

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A general method to obtain vibrational symmetry adapted bases in a local scheme

R. LEMUS*

Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, A.P. 70-543, Circuito Exterior, C.U., 04510 Mexico, D.F., Mexico

(Received 11 November 2002; revised version accepted 29 April 2003)

The 2D Vibron Model: modeling vibrational bending dynamics with a $U(3)$ Dynamical Algebra.

Modeling bidimensional systems algebraically.

F. Iachello and S. Oss. J. Chem. Phys. 104 6956 (1996).

Algebraic approach to molecular spectra: Two-dimensional problems

F. Iachello
Center for Theoretical Physics, Sloane Laboratory, Yale University, New Haven, Connecticut 06520-8120

S. Oss
Dipartimento di Fisica, Università di Trento and Istituto Nazionale di Fisica della Materia, 38050 Povo (TN), Italy

(Received 27 October 1995; accepted 7 February 1996)

The Lie algebraic approach is extended to two-dimensional problems (rotations and vibrations in a plane). Bending vibrations of linear polyatomic molecules are discussed. The algebraic approach is particularly well suited to treat coupled bending modes. The formalism needed to treat coupled benders is introduced and a sample case, acetylene, is analyzed in terms of two coupled local benders. [S0021-9606(96)01818-5]

The 2D Vibron Model: model-ling vibrational bending dynamics with an $U(3)$ Dynamical Algebra.

Modeling bidimensional systems algebraically.

F. Iachello and S. Oss. J. Chem. Phys. 104 6956 (1996).

Boson Operators $\{\tau_\alpha^\dagger, \tau_\alpha, \sigma^\dagger, \sigma\}; \alpha = x, y$.

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

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

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Generators of the algebra:

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

Dynamical Symmetries

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

Dynamical Symmetries

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

Dyn. Symmetry (I)

Dyn. Symmetry (II)

Dynamical Symmetries

$$U(3) \supset U(2) \supset SO(2) \quad \text{Dyn. Symmetry (I)}$$
$$N \qquad n \qquad \ell$$
$$U(3) \supset SO(3) \supset SO(2) \quad \text{Dyn. Symmetry (II)}$$
$$N \qquad w \qquad \ell$$

Dynamical Symmetries Generators

$U(2)$	$\{\hat{n}, \hat{l}, \hat{Q}_+, \hat{Q}_-\}$
$SO(3)$	$\{\hat{l}, \hat{D}_+, \hat{D}_-\}$
$SO(2)$	$\{\hat{l}\}$

Dynamical Symmetries

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

Dynamical Symmetries Generators

$$\begin{array}{ll} U(2) & \{\hat{n}, \hat{l}, \hat{Q}_+, \hat{Q}_-\} \\ SO(3) & \{\hat{l}, \hat{D}_+, \hat{D}_-\} \\ SO(2) & \{\hat{l}\} \end{array}$$

Casimir Operators

$$U(2) \quad \hat{C}_1[U(2)] = \hat{n} \quad \hat{C}_2[U(2)] = \hat{n}(\hat{n}+1)$$

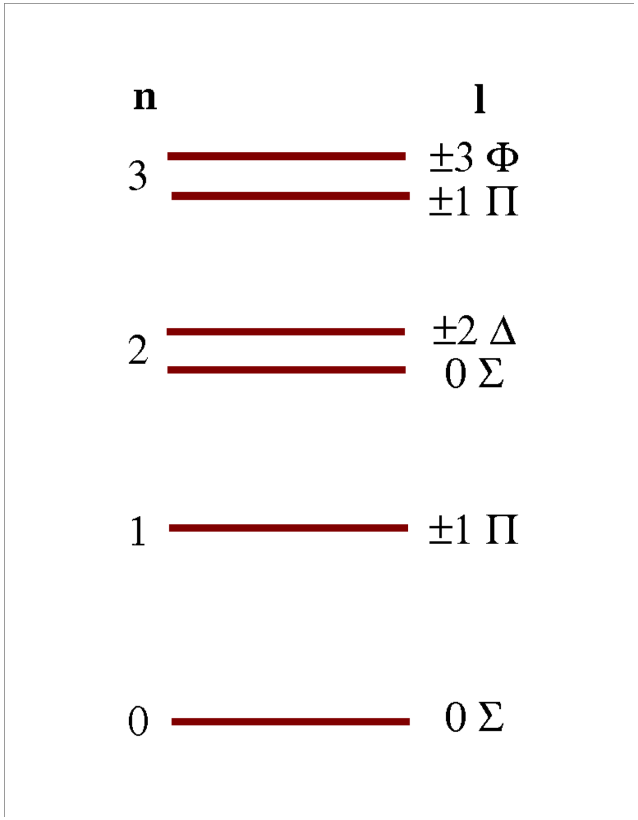
$$SO(3) \quad \hat{C}_2[SO(3)] = \hat{W}^2 = \frac{\hat{D}_+\hat{D}_- + \hat{D}_-\hat{D}_+}{2} + \hat{l}^2$$

$$SO(2) \quad \hat{C}_1[SO(2)] = \hat{l} \quad \hat{C}_2[SO(2)] = \hat{l}^2$$

Cylindrical Oscillator

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

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



Displaced Oscillator Chain

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

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

Displaced Oscillator Chain

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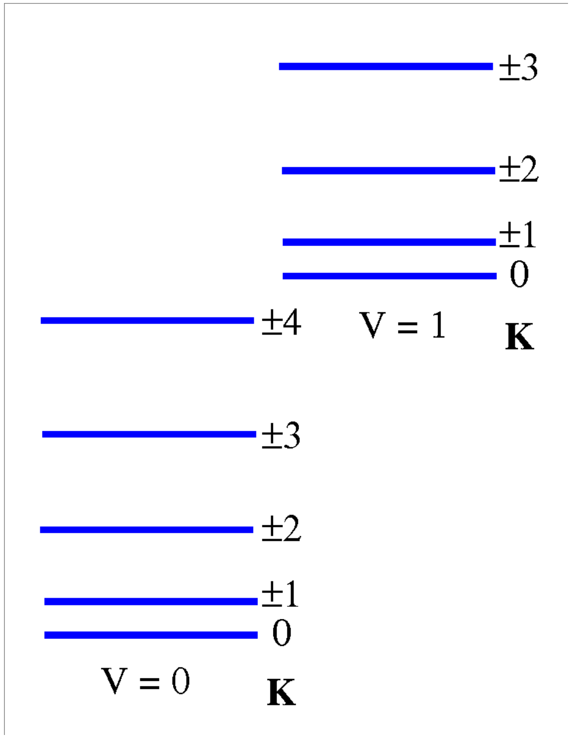

$U(3) \supset U(2) \supset SO(2)$ Dynamical Symmetry (I)

Single Bender Model Hamiltonian

$$U(3) \supset U(2) \supset SO(2) \quad \text{Dynamical Symmetry (I)}$$
$$U(3) \supset SO(3) \supset SO(2) \quad \text{Dynamical Symmetry (II)}$$

Single Bender Model Hamiltonian

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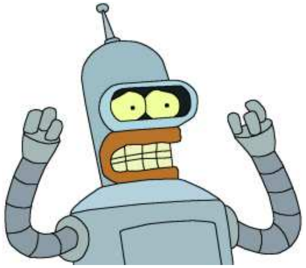

$$\hat{\mathcal{H}} = \varepsilon \left[(1-\xi)\hat{n} + \frac{\xi}{N-1}\hat{P} \right]$$

$$U(3) \supset U(2) \supset SO(2) \quad \text{Dynamical Symmetry (I)}$$
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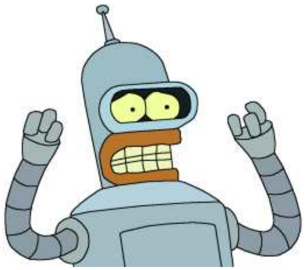
Single Bender Model Hamiltonian



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

- 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

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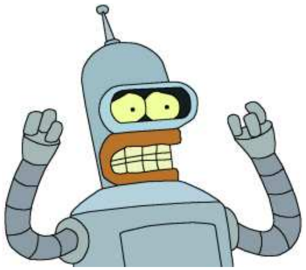

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The system undergoes a second order QPT in $\xi_c = 0.2$.

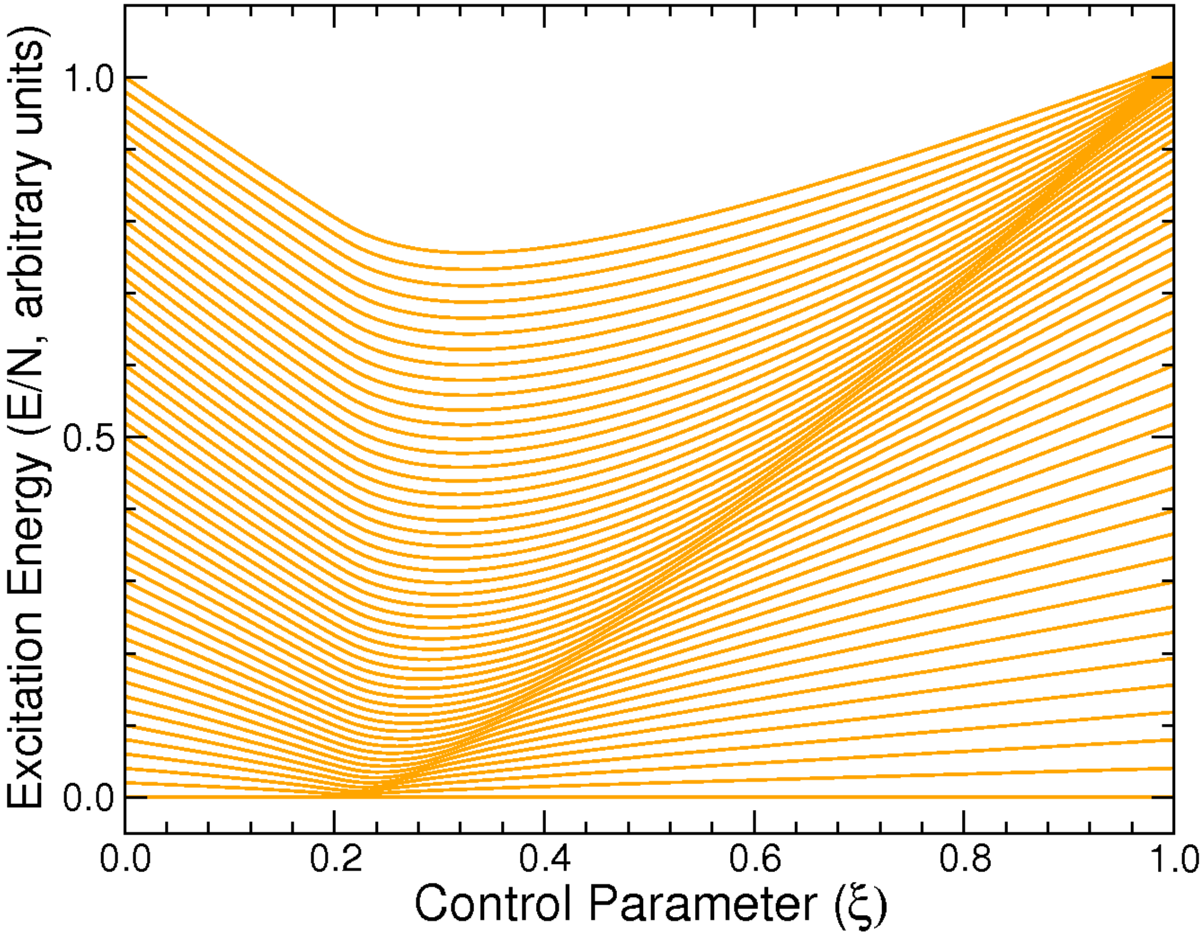
F. Pérez-Bernal and F. Iachello. Phys. Rev. A77 032115 (2008).

Excited State Quantum Phase Transition in 2DVM

Quantum Monodromy Diagram: Energy level density discontinuity

Excited State Quantum Phase Transition in 2DVM

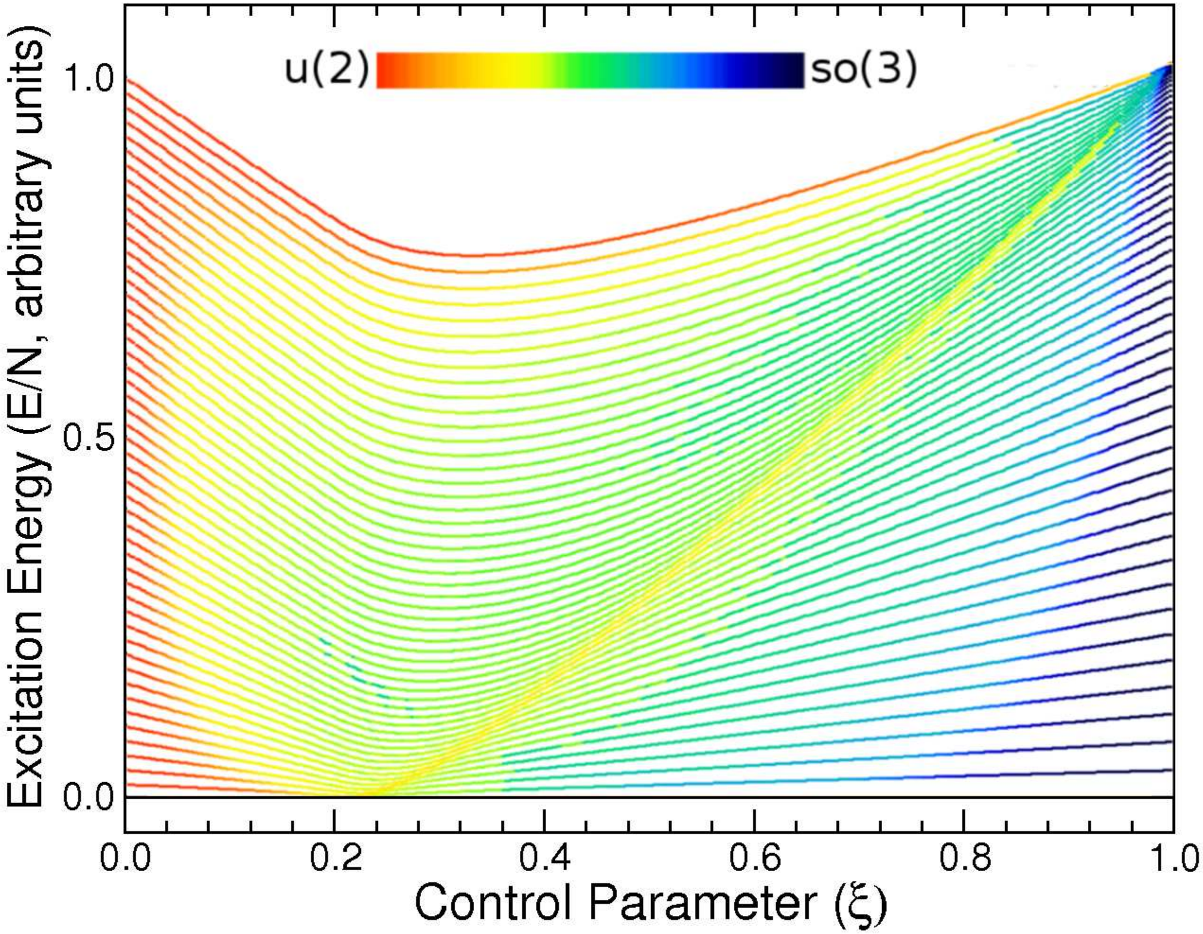
Quantum Monodromy Diagram: Energy level density discontinuity



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

Excited State Quantum Phase Transition in 2DVM

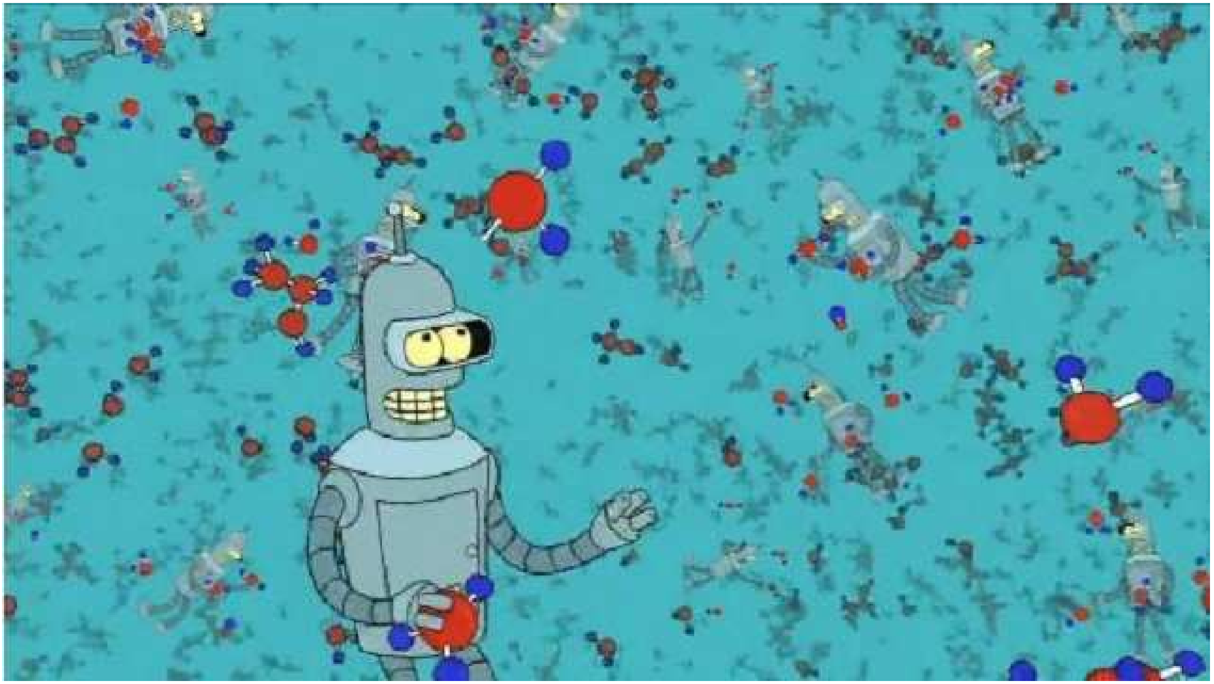
Quantum Monodromy Diagram: Energy level density discontinuity



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

Application to Single Bender Molecular Species

You will find a complete account of the application to single bender experimental data in Danielle Larese's seminar



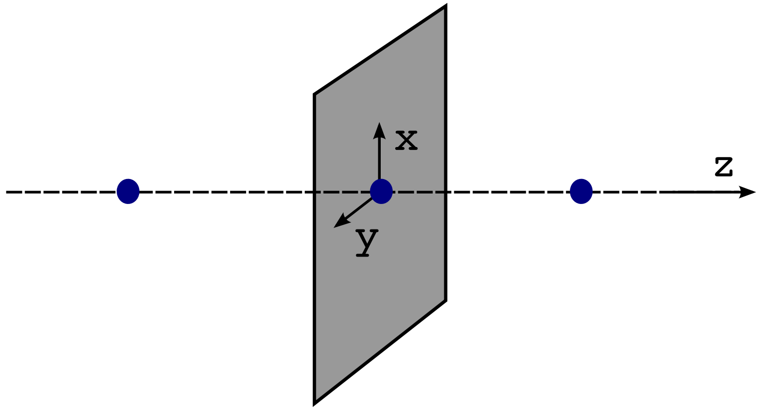
D. Larese and F. Iachello. J. Mol. Struct. 1006 611 (2011).

Coherent state approach

Projective coherent states define an intrinsic g.s. and a boson condensate

$$|i.s.\rangle = |[N]; r, \theta\rangle = \frac{1}{\sqrt{N!}} \left(b_c^\dagger\right)^N |0\rangle$$
$$b_c^\dagger = \frac{1}{\sqrt{1+r^2}} \left[\sigma^\dagger + x\tau_x^\dagger + y\tau_y^\dagger\right]$$

where (r, θ) are polar coordinates associated to Cartesian (x, y).



Algorithm proposed by Gilmore:

R. Gilmore J. Math. Phys. 20 891 (1979).

Observables of interest: ground state energy and $\langle \hat{n} \rangle$

Ground State Energy per Particle

$$\mathcal{E}_\xi(r) = \epsilon\left[(1-\xi)\frac{r^2}{1+r^2} + \xi\left(\frac{1-r^2}{1+r^2}\right)^2\right],$$

$$r_e = 0\,,\ \sqrt{\frac{5\xi-1}{3\xi+1}}\,,$$

$$\mathcal{E}_\xi(r_e) = \begin{cases} \xi & 0 \leq \xi \leq \xi_c \\ \frac{-9\xi^2+10\xi-1}{16\xi} & \xi_c < \xi \leq 1 \end{cases},$$

$$\frac{d^2\mathcal{E}_\xi(r_e)}{d\xi^2} = \begin{cases} 0 & 0 \leq \xi \leq \xi_c \\ -\frac{1}{8\xi^3} & \xi_c < \xi \leq 1 \end{cases}.$$

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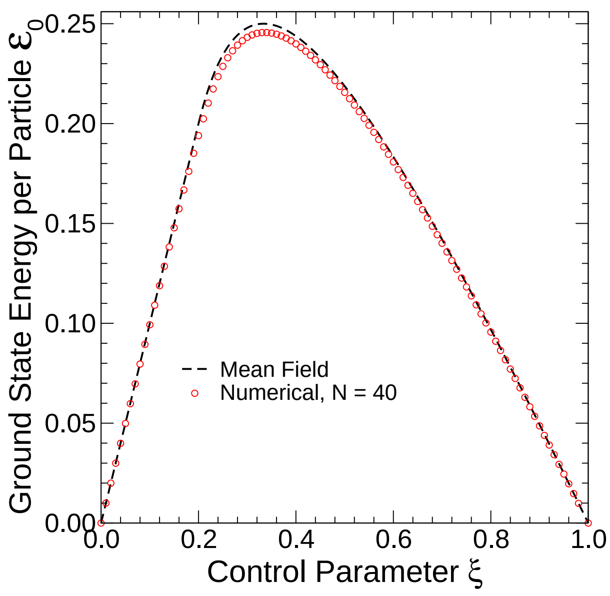

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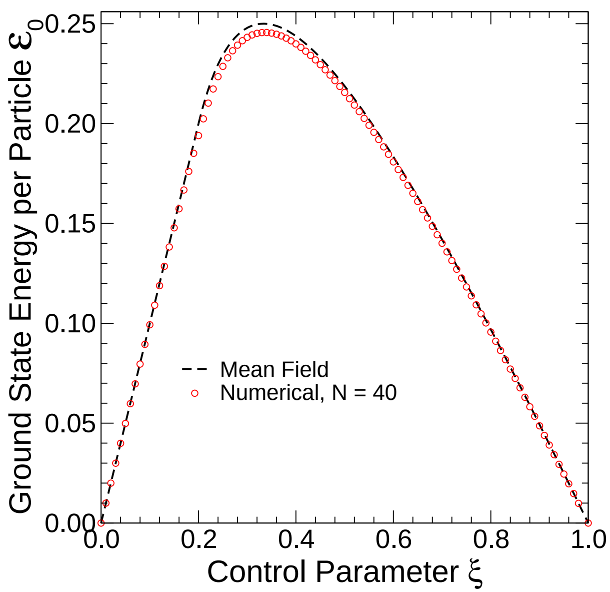

Expected value of the number of τ bosons

$$\langle\hat{n}\rangle = \langle[N];r,\theta|\hat{n}|[N];r,\theta\rangle\,,$$

$$\langle\hat{n}\rangle = N\frac{r_e^2}{1+r_e^2} = \begin{cases} 0 & 0\le\xi\le\xi_c \\ \frac{5\xi-1}{8\xi} & \xi_c<\xi\le 1 \end{cases}.$$

Observables of interest: ground state energy and $\langle \hat{n} \rangle$

Ground State Energy per Particle

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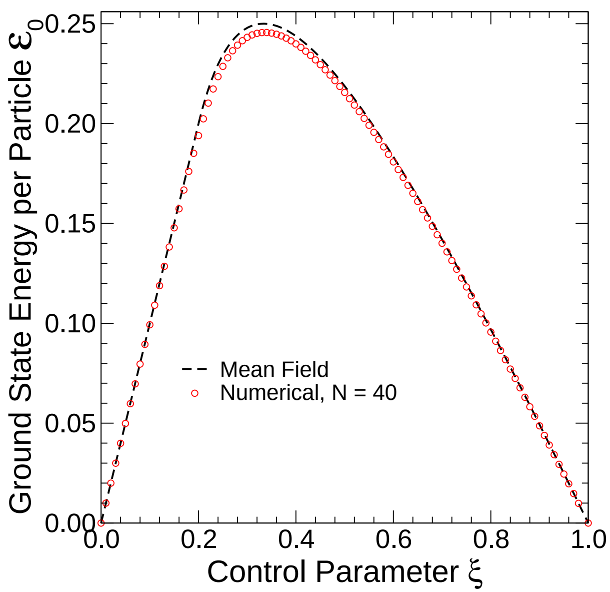
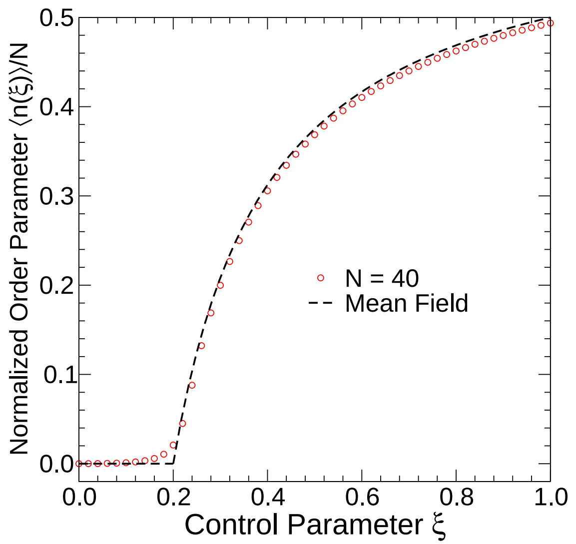


Expected value of the number of τ bosons

$$\langle \hat{n} \rangle = \langle [N]; r, \theta | \hat{n} | [N]; r, \theta \rangle\,,$$

$$\langle \hat{n} \rangle = N\frac{r_e^2}{1+r_e^2} = \begin{cases} 0 & 0 \le \xi \le \xi_c \\ \frac{5\xi-1}{8\xi} & \xi_c < \xi \le 1\,. \end{cases}$$



Finite-Size Corrections to the Mean Field Limit

Holstein-Primakoff expansion plus a Shift followed by a Bogoliubov Transformation.

$$
\begin{aligned}
\tau_i^\dagger \tau_j &= b_i^\dagger b_j \; ; \;\; i, j = x, y \, , \\
\tau_i^\dagger \sigma &= \sqrt{N}\, b_i^\dagger \sqrt{1 - \hat{n}_b / N} = \left(\sigma^\dagger \tau_i\right)^\dagger \; , \\
\hat{n}_\sigma &= \sigma^\dagger \sigma = N - \hat{n}_b \, ,
\end{aligned}
$$

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Symmetric Phase

$$\hat{H}_{sym} = \mathcal{E}_\xi(r_e)N + \left[3\xi - 1 + \Xi^{sym}(\xi)^{1/2}\right] + \Xi^{sym}(\xi)^{1/2}\hat{n}_a + \mathcal{O}(1/N) \,,$$

$$\Xi^{sym} = 5(\xi_c - \xi)(1-\xi) \,.$$

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Deformed Phase

$$\hat{H}_{def} = \mathcal{E}_\xi(r_e)N + \frac{1 - 6\xi - 27\xi^2 + 8\xi\Xi^{def}(\xi)^{1/2}}{16\xi} + \Xi^{def}(\xi)^{1/2}\hat{n}_a + \mathcal{O}(1/N) \,,$$
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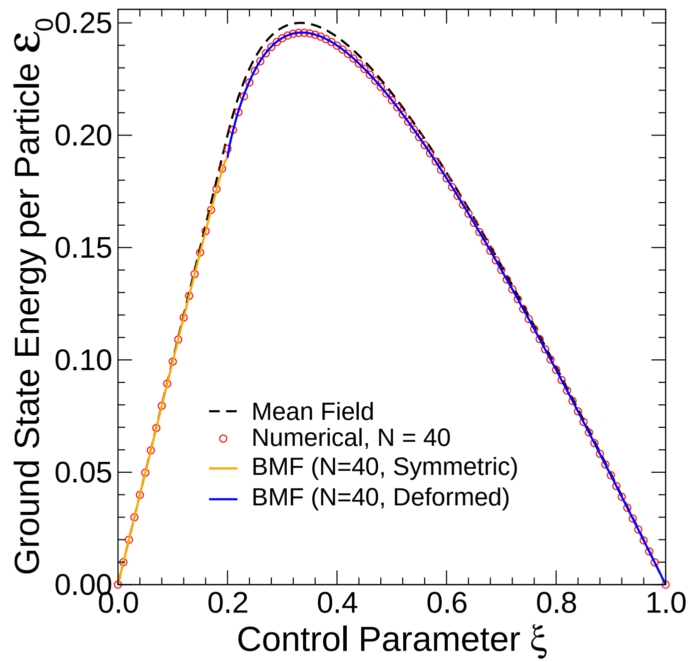
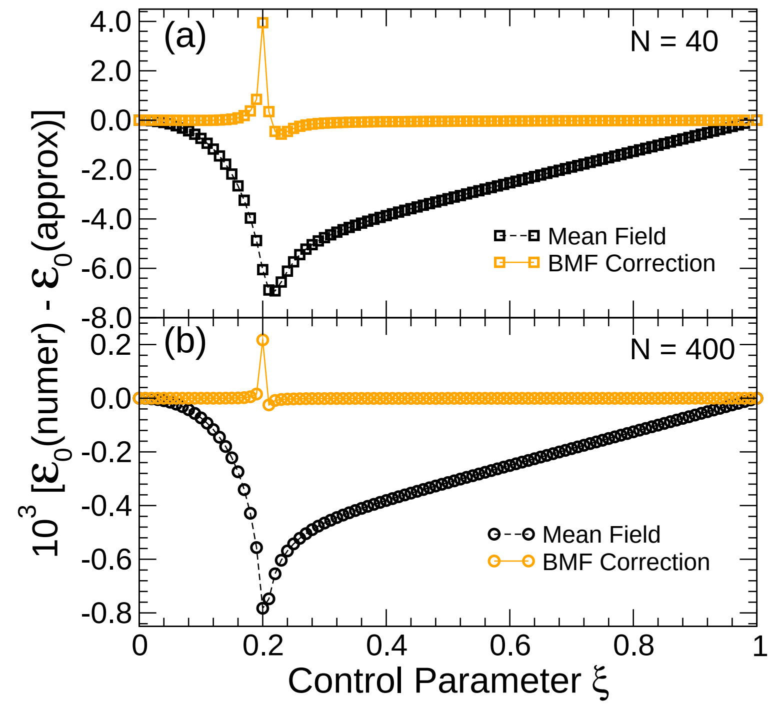
Application to two-level bosonic systems with $U(2L+2)$ SGA, for integer L.

S. Dusuel *et al*. Phys. Rev. C72 064332 (2005).

Finite-Size Correction to the Ground State Energy

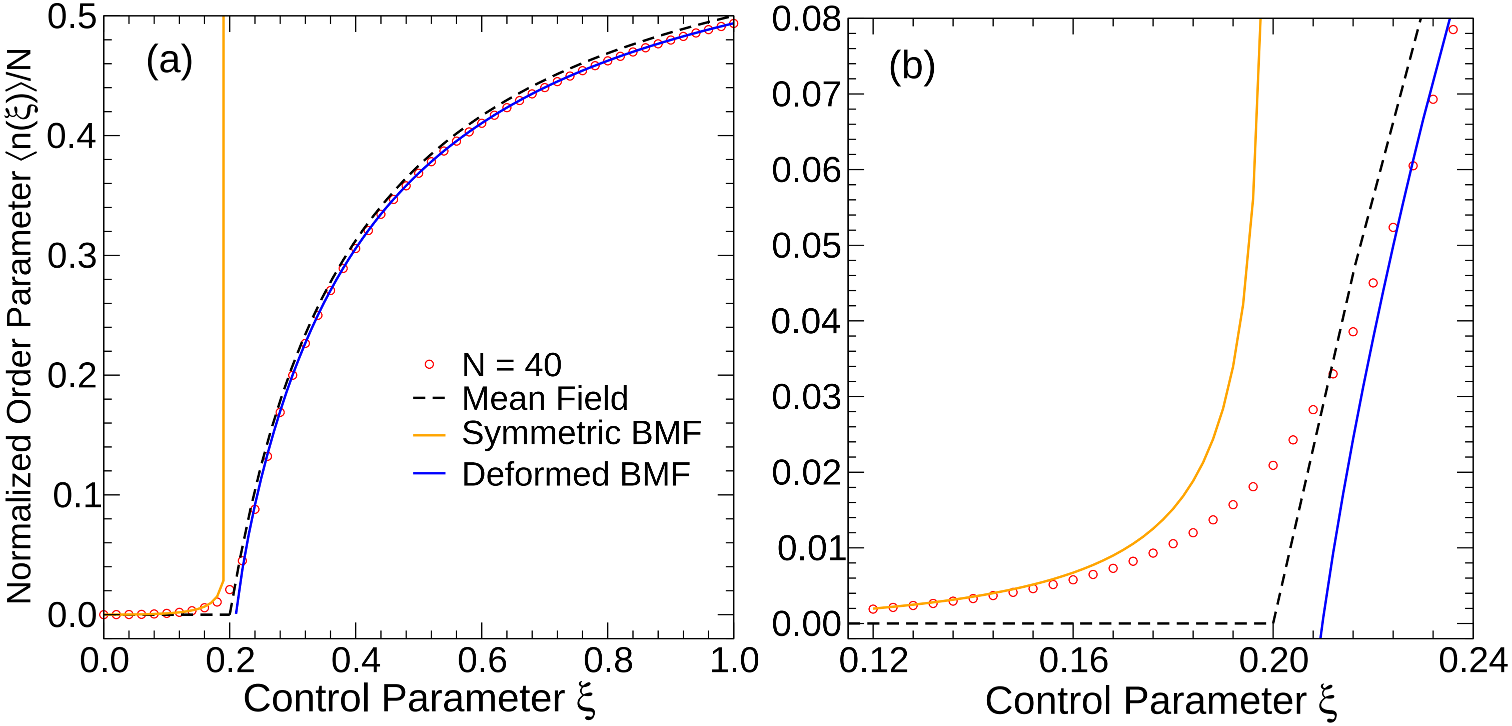




P. Pérez-Fernández, J.M. Arias, J.E. García-Ramos, and F. Pérez-Bernal,

Phys. Rev. A83 062125 (2011).

Finite-Size Correction to the Order Parameter



P. Pérez-Fernández, J.M. Arias, J.E. García-Ramos, and F. Pérez-Bernal,

Phys. Rev. A83 062125 (2011).

Finite-Size Scaling Exponents

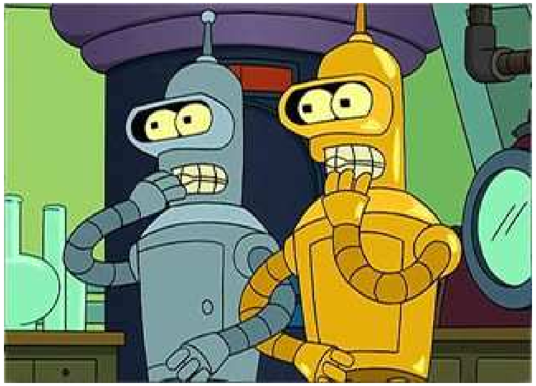
Φ	x_Φ	n_Φ	Scaling exponent	Numerical results [19]
$\mathcal{E}_0$	$+1/2$	$+1$	$-4/3$	$-A_{\epsilon 1} = -0.9564(5)$[a]
$\Delta_{1\text{ph}}$	$+1/2$	0	$-1/3$	$-A_{\Gamma_{1,\text{vib}}} = -0.337\,43(10)$
$\langle \hat{n} \rangle$	$-1/2$	0	$+1/3$	$-A_{n1} + 1 = 0.3770(5)$
T/N	$-1/2$	0	$+1/3$	$0.320\,26(13)$[b]

[19] Numerical Results: F. Pérez-Bernal and F. Iachello. Phys. Rev. A77 032115 (2008).

Dynamical symmetries for coupled benders

The $U_1(3) \times U_2(3)$ Lie algebra allows the description of coupled benders:

$$\sigma_j \ , \ \ \tau^\dagger_{j,\pm} = \mp \frac{\tau^\dagger_{j,x} \pm i\tau^\dagger_{j,y}}{\sqrt{2}} \ , \ \ j = 1, 2.$$



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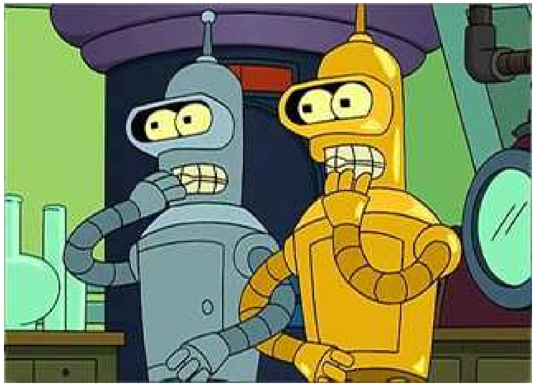

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$$\begin{array}{ccccccccc}
 & & & & SO_1(2) \otimes SO_2(2) & & & & \text{(Ia)} \\
 & & & / & & \backslash & & & \\
U_1(3) \otimes U_2(3) & \supset & U_1(2) \otimes U_2(2) & & & & SO_{12}(2), & & \\
 & & & \backslash & & / & & & \\
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 & & & & U_{12}(2) & & & & \text{(IIIa)} \\
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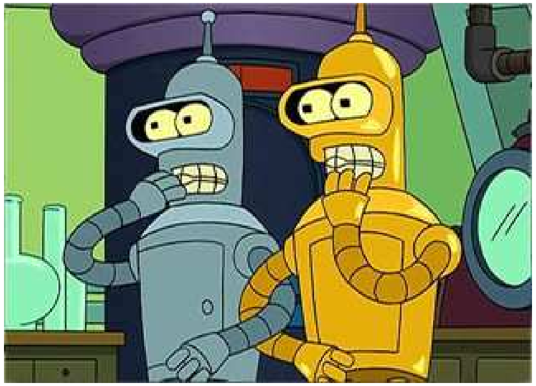

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F. Iachello and S. Oss, J. Chem. Phys. 104 6956 (1996).

Block Dimensions in the Coupled Benders Hamiltonian

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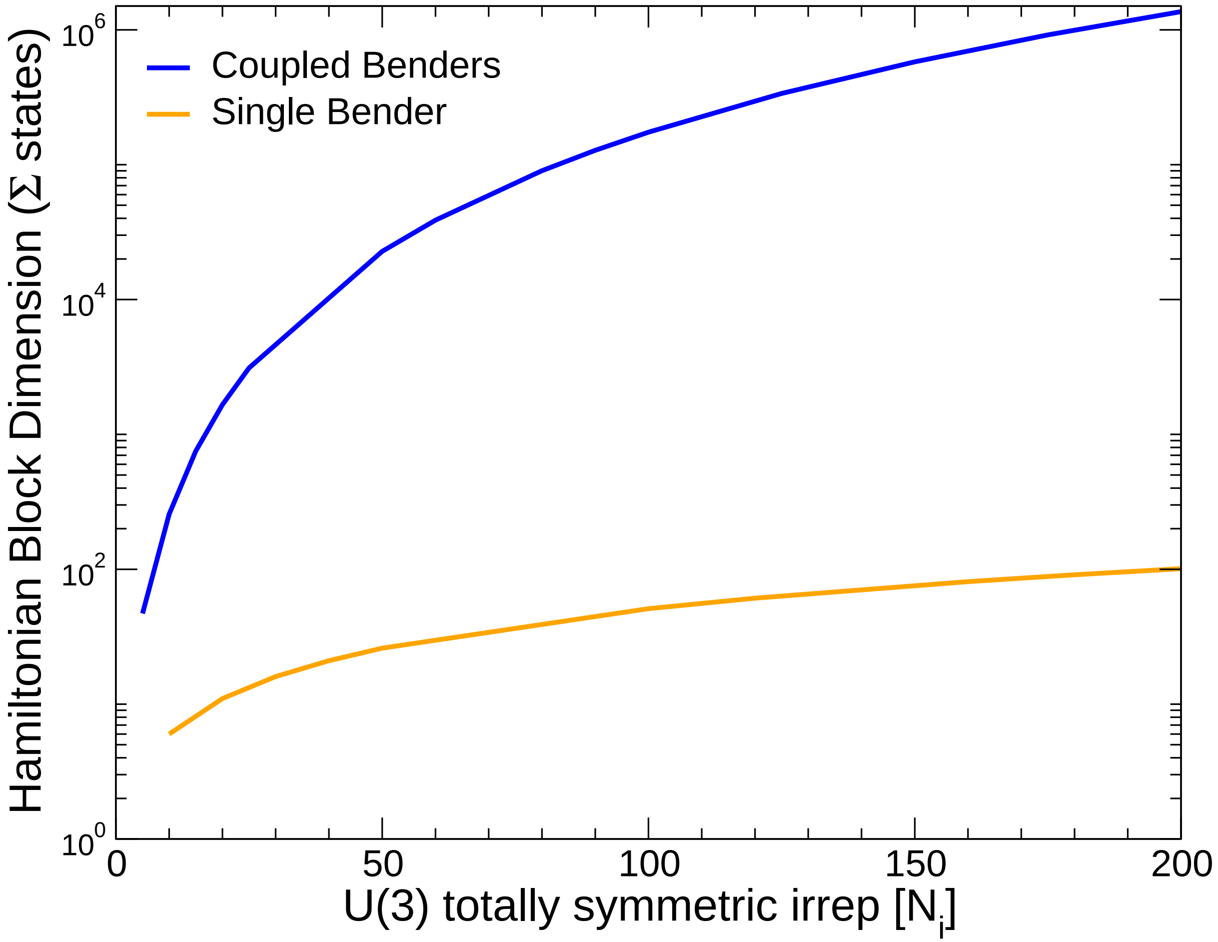

Coupled Benders: General and Model Hamiltonians

General Hamiltonian (9 parameters)

$$\begin{aligned}\hat{H} =& E_0' + \varepsilon\,(\hat{n}_1 + \hat{n}_2) + \alpha\,[\hat{n}_1(\hat{n}_1 + 1) + \hat{n}_2(\hat{n}_2 + 1)] + \alpha_{12}\hat{n}_1\hat{n}_2 \\ & + \lambda(\hat{D}_1 \cdot \hat{D}_2 + \hat{R}_1 \cdot \hat{R}_2) + B\,\hat{Q}_1 \cdot \hat{Q}_2 + A(\hat{W}_1^2 + W_2^2) + A_{12}\hat{W}_1 \cdot \hat{W}_2 \\ & + \beta(\hat{l}_1^2 + \hat{l}_2^2) + \beta_{12}\,\hat{l}_1\hat{l}_2\ .\end{aligned}$$

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Model Hamiltonian (3 control parameters: ξ, η_1, and η_2)

$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi)\left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N}\,\hat{Q}_1 \cdot \hat{Q}_2\right] + \frac{\xi}{N}\left[\hat{P}_1 + \hat{P}_2 + 2\eta_2\,\hat{W}_1 \cdot \hat{W}_2\right] \right\}$$

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F. Iachello and F. Pérez-Bernal, Mol. Phys. 106 223 (2008);
F. Iachello and F. Pérez-Bernal, J. Phys. Chem. A 113 13273 (2009).
F. Pérez-Bernal and L. Fortunato, Phys. Lett. A 376 236 (2012)

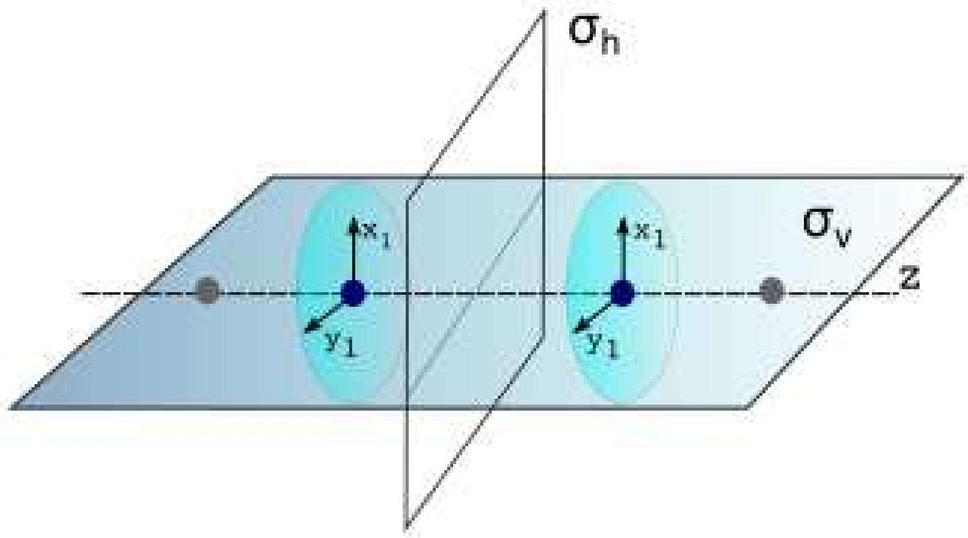
Coherent state approach

We define the intrinsic state and the boson condensate as

$$|i.s.\rangle = |[N_1][N_2]; r_1, \theta_1; r_2, \theta_2\rangle = \frac{1}{\sqrt{N_1! N_2!}} \left(b^{\dagger}_{c,1}\right)^{N_1} \left(b^{\dagger}_{c,2}\right)^{N_2} |0\rangle$$

$$b^{\dagger}_{c,i} = \frac{1}{\sqrt{1+r^2}} \left[\sigma^{\dagger}_i + \left(x_i \tau^{\dagger}_{i,x} + y_i \tau^{\dagger}_{i,y}\right)\right]$$

where (r_i, θ_i) are the polar coordinates associated to (x_i, y_i), $i = 1, 2$.



Coupled Benders Model Hamiltonian Energy Functional

$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

$$\begin{aligned} \mathcal{E}(r_1, r_2, \phi) =& (1-\xi) \left[\frac{1}{2} \sum_{i=1}^{2} \frac{r_i^2}{1+r_i^2} + \frac{\eta_1}{4} \left(\prod_{i=1}^{2} \frac{r_i^2}{1+r_i^2} \right) \cos(2\phi) \right] \\ & + \xi \left[\frac{1}{4} \sum_{i=1}^{2} \left(\frac{1-r_i^2}{1+r_i^2} \right)^2 + 2\,\eta_2 \left(\prod_{i=1}^{2} \frac{r_i}{1+r_i^2} \right) \cos(\phi) \right] \end{aligned}$$

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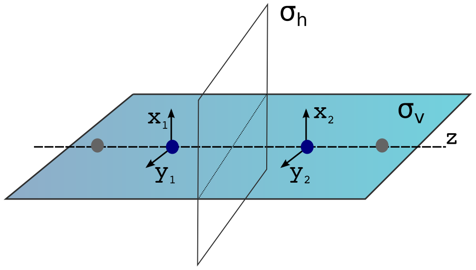
Linear, $\mathcal{D}_{\infty h}$

$r_1 = r_2 = 0$

(C_2H_2, $\tilde{X}$)



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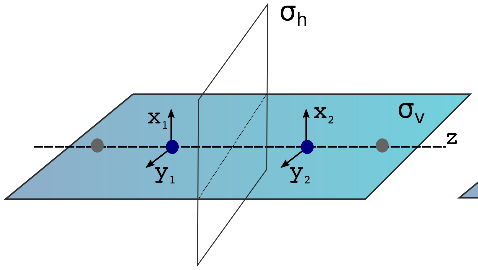
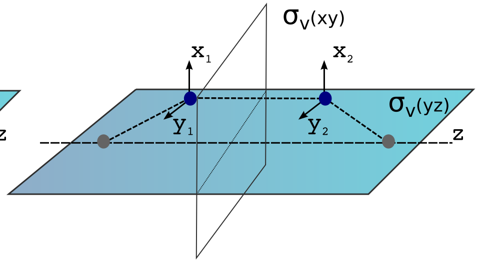


Cis, $\mathcal{C}_{2v}$

$r_1 = r_2 \neq 0, \phi = 0$

(2-butene)



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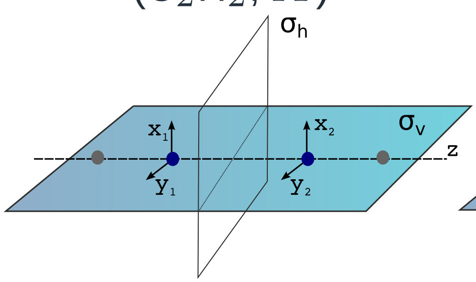

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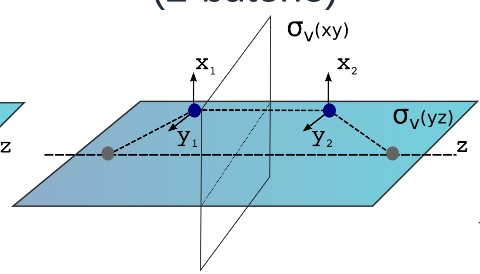
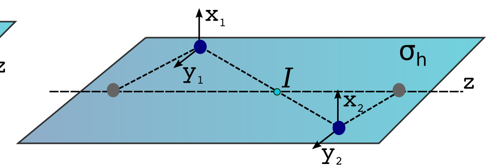
(2-butene)



Trans, $\mathcal{C}_{2h}$

$r_1 = r_2 \neq 0, \phi = \pi$

(C_2H_2, $\tilde{A}$)



Coupled Benders Model Hamiltonian Energy Functional

$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

$$\mathcal{E}(r_1, r_2, \phi) = (1-\xi) \left[\frac{1}{2} \sum_{i=1}^{2} \frac{r_i^2}{1+r_i^2} + \frac{\eta_1}{4} \left(\prod_{i=1}^{2} \frac{r_i^2}{1+r_i^2} \right) \cos(2\phi) \right] + \xi \left[\frac{1}{4} \sum_{i=1}^{2} \left(\frac{1-r_i^2}{1+r_i^2} \right)^2 + 2\,\eta_2 \left(\prod_{i=1}^{2} \frac{r_i}{1+r_i^2} \right) \cos(\phi) \right]$$

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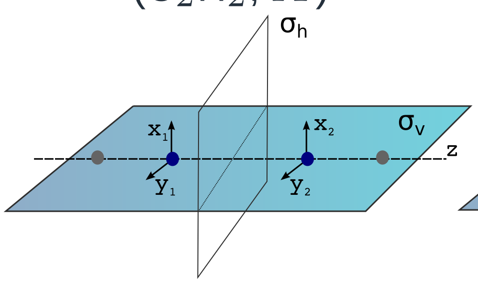
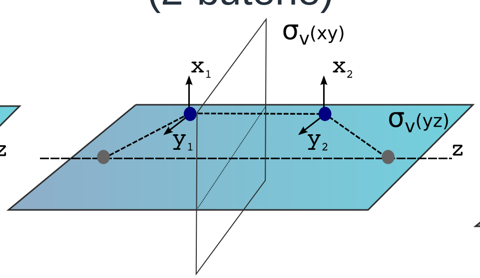
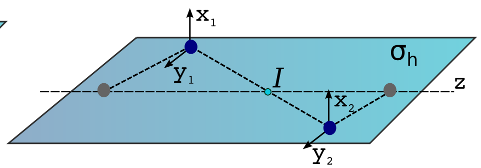
$r_1 = r_2 = 0$
(C_2H_2, $\tilde{X}$)



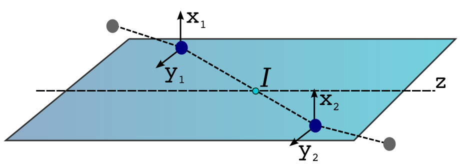
Cis, $\mathcal{C}_{2v}$
$r_1 = r_2 \neq 0, \phi = 0$
(2-butene)



Trans, $\mathcal{C}_{2h}$
$r_1 = r_2 \neq 0, \phi = \pi$
(C_2H_2, $\tilde{A}$)



Non-planar, $\mathcal{C}_2$
$r_1 = r_2 \neq 0 \phi \neq 0, \pi$
(H_2O_2)



Coupled Benders Model Hamiltonian Energy Functional

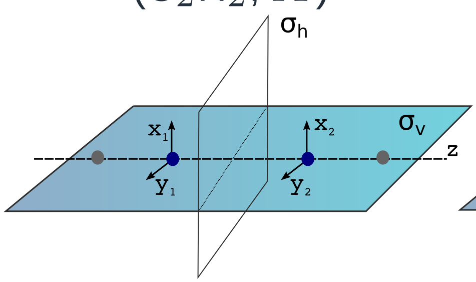
$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

$$\begin{aligned}\mathcal{E}(r_1, r_2, \phi) =& (1-\xi) \left[\frac{1}{2} \sum_{i=1}^{2} \frac{r_i^2}{1+r_i^2} + \frac{\eta_1}{4} \left(\prod_{i=1}^{2} \frac{r_i^2}{1+r_i^2} \right) \cos(2\phi) \right] \\ &+ \xi \left[\frac{1}{4} \sum_{i=1}^{2} \left(\frac{1-r_i^2}{1+r_i^2} \right)^2 + 2\,\eta_2 \left(\prod_{i=1}^{2} \frac{r_i}{1+r_i^2} \right) \cos(\phi) \right]\end{aligned}$$

Linear, $\mathcal{D}_{\infty h}$

$r_1 = r_2 = 0$

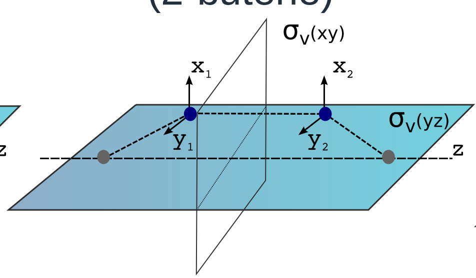
(C_2H_2, $\tilde{X}$)



Cis, $\mathcal{C}_{2v}$

$r_1 = r_2 \neq 0, \phi = 0$

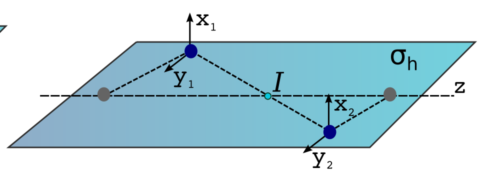
(2-butene)



Trans, $\mathcal{C}_{2h}$

$r_1 = r_2 \neq 0, \phi = \pi$

(C_2H_2, $\tilde{A}$)



Non-planar, $\mathcal{C}_2$

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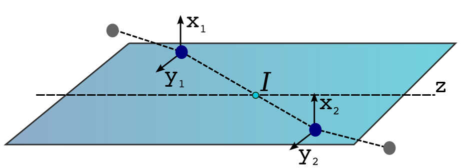
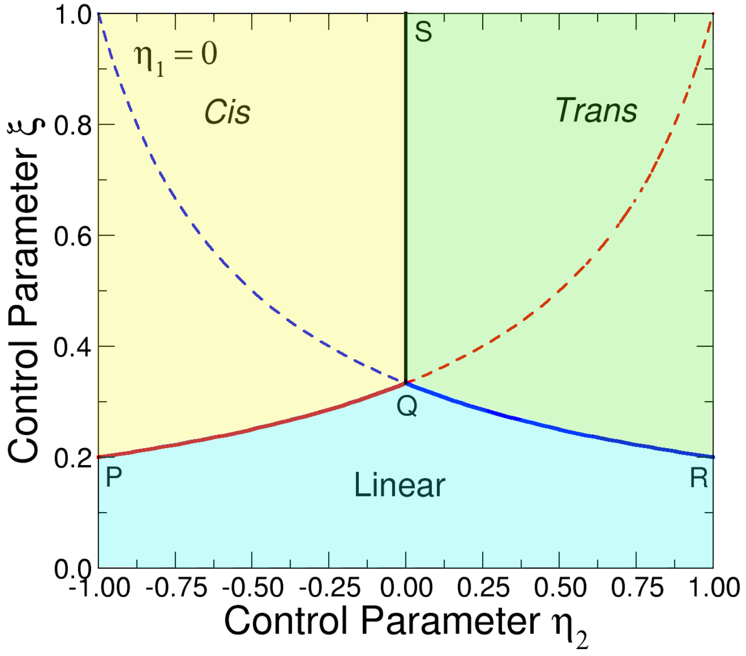
(H_2O_2)



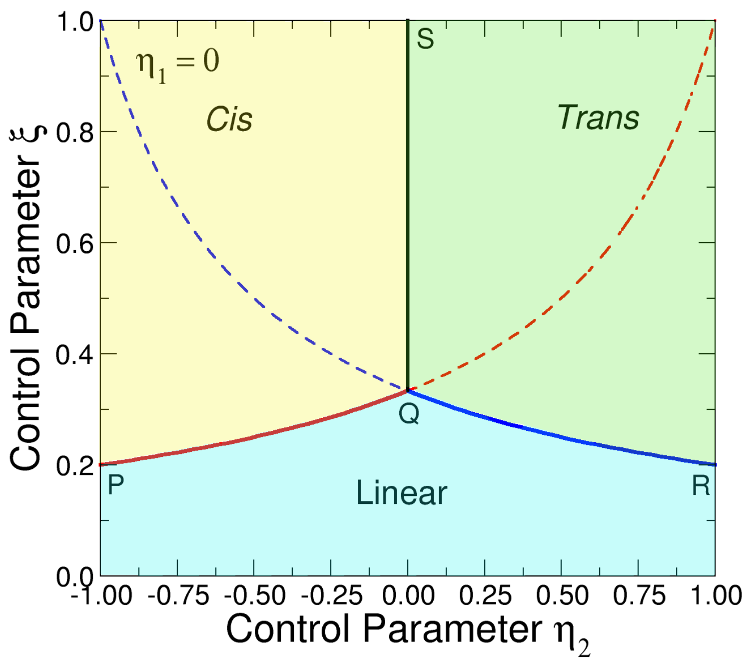
F. Iachello and F. Pérez-Bernal, Mol. Phys. 106 223 (2008); J. Phys. Chem. A 113 13273 (2009).

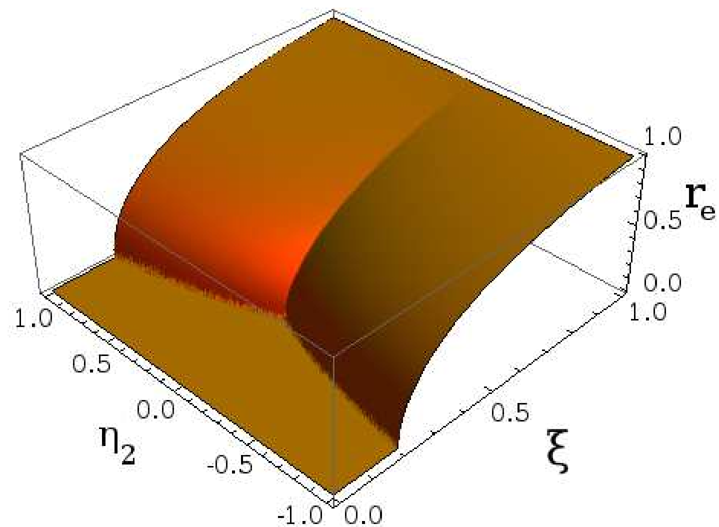
Phase Diagram in the $\eta_1 = 0$ case

Phase Diagram and Order parameter r_e in the $\eta_1 = 0$ case.



Phase Diagram and Order parameter r_e in the $\eta_1 = 0$ case.

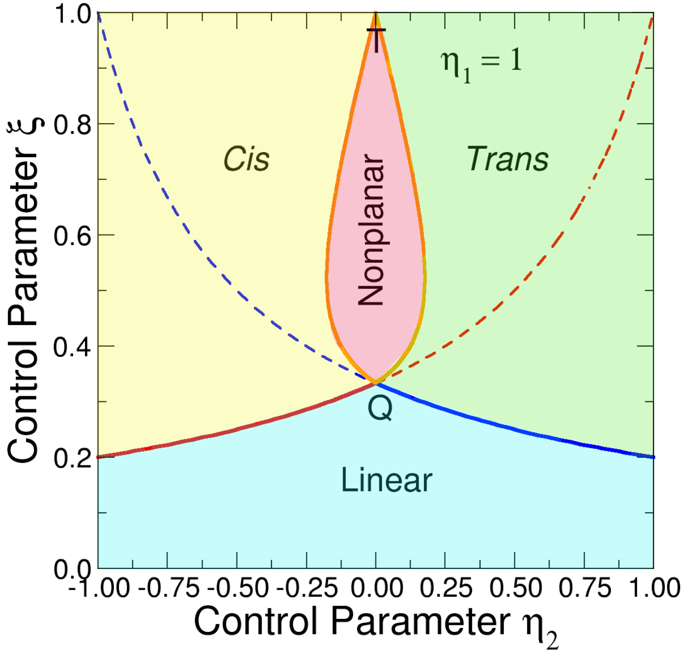




Agrees with results in F. Iachello and F. Pérez-Bernal, Mol. Phys. 106 223 (2008).

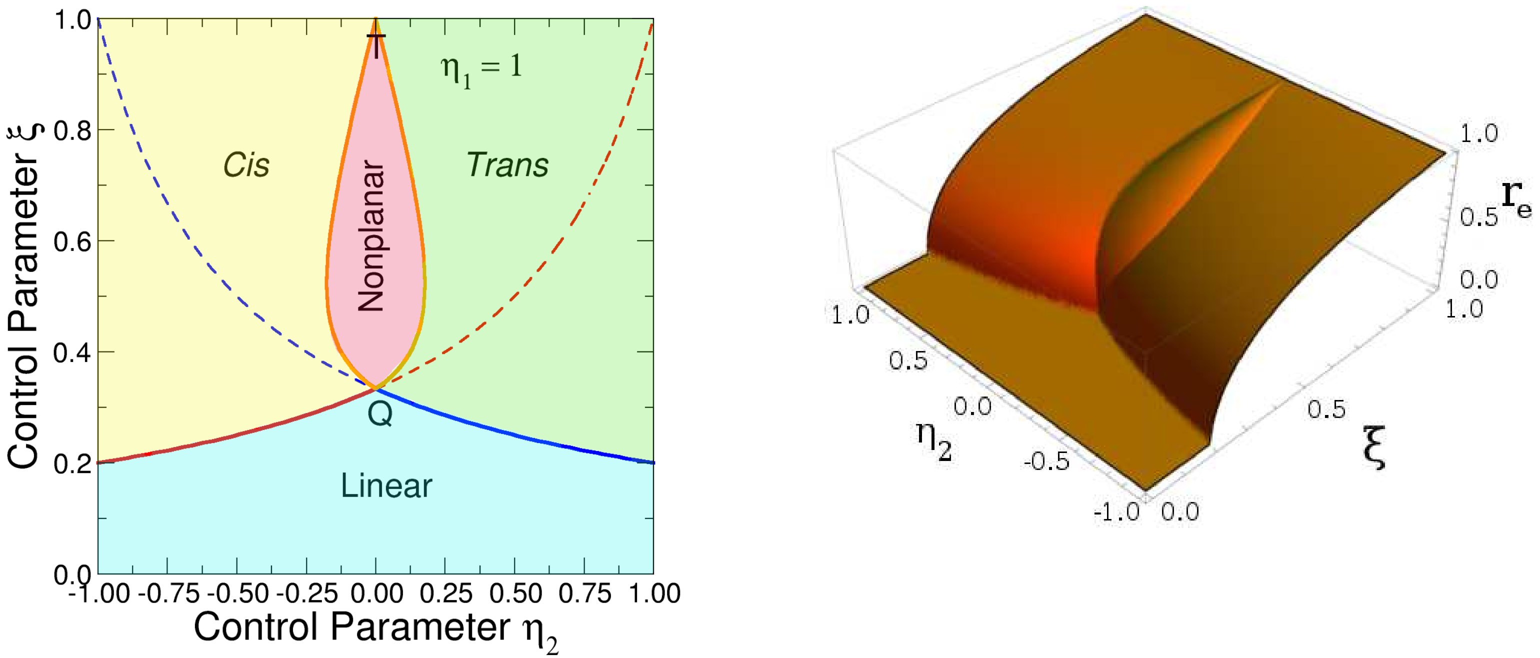
F. Pérez-Bernal and L. Fortunato, Phys. Lett. A 376 236 (2012).

Phase Diagram and Order parameter r_e in the $\eta_1 = 1$ case.



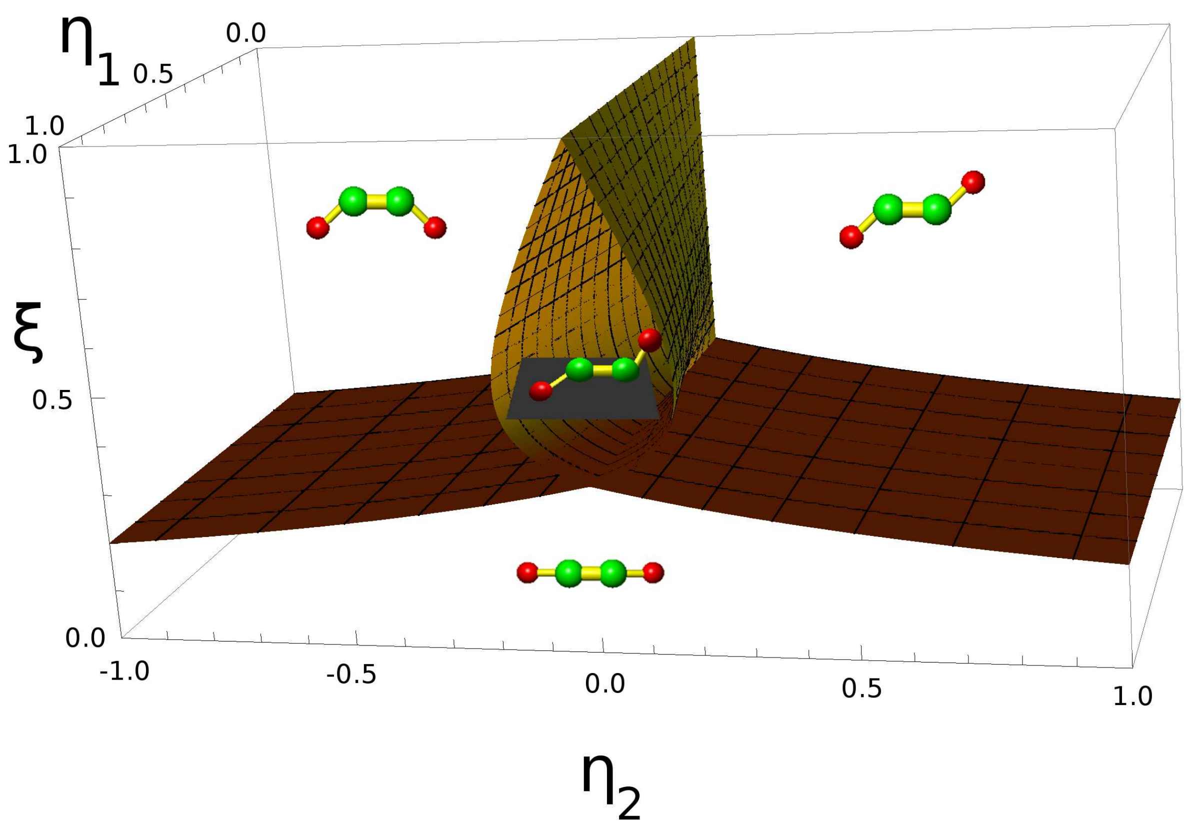
Phase Diagram in the $\eta_1 = 1$ case

Phase Diagram and Order parameter r_e in the $\eta_1 = 1$ case.



F. Pérez-Bernal and L. Fortunato, Phys. Lett. A 376 236 (2012)

Coupled Benders Phase Diagram



F. Pérez-Bernal and L. Fortunato, Phys. Lett. A 376 236 (2012)

Concluding Remark

Only one concluding remark:

Franco, thanks for all the good moments spent together and your inspiring help.
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