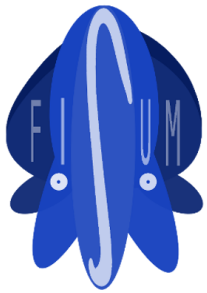
An Algebraic Approach to Molecular Structure: The Vibron Model

Curro Pérez Bernal

Huelva University

curropb@uhu.es

July 7, 2015



Overview

Outline

1993: 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.

1993: Doctor Honoris Causa Universitas Hispalensis

1993: Doctor Honoris Causa Universitas Hispalensis

Algebraic Approach Basic Steps

- Definition of the Spectrum Generating Algebra (SGA), aka Dynamical Algebra, for the system under study.

Algebraic Approach Basic Steps

- Definition of the Spectrum Generating Algebra (SGA), aka Dynamical Algebra, for the system under study.
- Every operator is expressed in terms of the SGA generators.

Algebraic Approach Basic Steps

- Definition of the Spectrum Generating Algebra (SGA), aka Dynamical Algebra, for the system under study.
- Every operator is expressed in terms of the SGA generators.
- Consideration of the possible Dynamical Symmetries.

Algebraic Approach Basic Steps

- Definition of the Spectrum Generating Algebra (SGA), aka Dynamical Algebra, for the system under study.
- Every operator is expressed in terms of the SGA generators.
- Consideration of the possible Dynamical Symmetries.
- Dynamical symmetries' branching rules and Casimir operators eigenvalues.

Algebraic Approach Basic Steps

- Definition of the Spectrum Generating Algebra (SGA), aka Dynamical Algebra, for the system under study.
- Every operator is expressed in terms of the SGA generators.
- Consideration of the possible Dynamical Symmetries.
- Dynamical symmetries' branching rules and Casimir operators eigenvalues.
- Phenomenological Approach: find parameter values that optimize the agreement with experimental data.

Definitions: Spectrum Generating Algebra (SGA)

Definition

The Spectrum Generating Algebra (SGA) is such that its generators allow to connect the eigenstates of the system's Hamiltonian. Thus, the system's Hilbert space carries an irreducible representation (irrep) of the SGA. The Hamiltonian and every other operator of interest are written in terms of the SGA generators.

Definitions: Symmetry Algebra & Dynamical Symmetry

Definition

The Symmetry Algebra (SA) is a subalgebra of the SGA containing the SGA generators that commute with the Hamiltonian operator. Degenerate eigenstates carry SA irreps.

Definitions: Symmetry Algebra & Dynamical Symmetry

Definition

The Symmetry Algebra (SA) is a subalgebra of the SGA containing the SGA generators that commute with the Hamiltonian operator. Degenerate eigenstates carry SA irreps.

Definition

Dynamical Symmetries (DS) are subalgebra chains starting in the SGA and ending in the SA. They represent limiting physical situations that are analytically solvable. Each DS provides a basis to carry out the calculations.

Outline

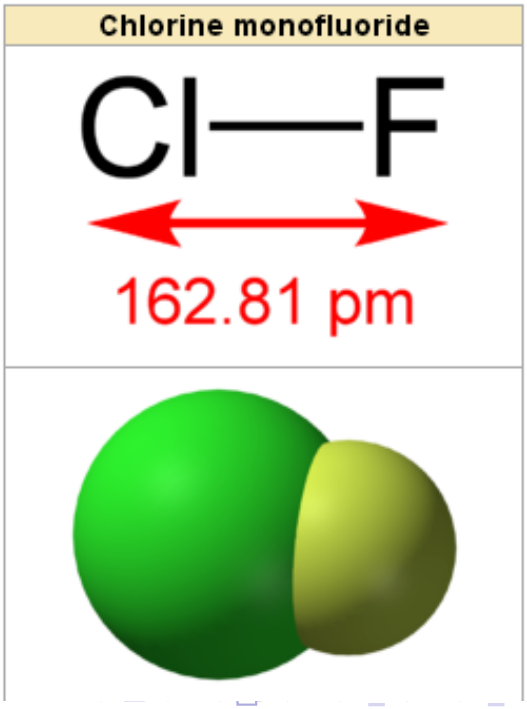
Algebraic approach to molecular spectroscopy: the Vibron Model

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

Study of N–dimensional systems $\Rightarrow$ $U(N+1)$ SGA

Molecules

- Dipolar interaction: $N = 3$
- SGA: $U(4)$
- Vibron Model (VM)
- F. Iachello
  Chem. Phys. Lett. 78 581 (1981)
- 1D and 2D limits of the Vibron Model



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

$U(4)$ Lie Algebra applied to rovibrational molecular structure. Modeling 3D systems algebraically.

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 Vibron Model main ingredients

Boson Operators: $\{p_\alpha^\dagger, p_\alpha, s^\dagger, s\}$; $\alpha = \pm 1, 0$

$$\left[\tilde{p}_\alpha, p_\beta^\dagger\right] = \delta_{\alpha,\beta} \; ; \quad \alpha, \beta = -1, 0, 1 \qquad \left[\tilde{s}, s^\dagger\right] = 1$$

Spherical Bosons: $\left\{p_\pm^\dagger, p_0^\dagger, s^\dagger, \tilde{p}_\pm = p_\mp, \tilde{p}_0 = -p_0, \tilde{s} = s\right\}$

The Vibron Model main ingredients

Boson Operators: $\{p^\dagger_\alpha, p_\alpha, s^\dagger, s\}$; $\alpha = \pm 1, 0$

$$\left[\tilde{p}_\alpha, p^\dagger_\beta\right] = \delta_{\alpha,\beta} \; ; \quad \alpha, \beta = -1, 0, 1 \qquad \left[\tilde{s}, s^\dagger\right] = 1$$

Spherical Bosons: $\left\{p^\dagger_\pm, p^\dagger_0, s^\dagger, \tilde{p}_\pm = p_\mp, \tilde{p}_0 = -p_0, \tilde{s} = s\right\}$

Generators of the $U(4)$ SGA

$$\hat{n}_p = \sqrt{3}[p^\dagger \times \tilde{p}]^{(0)} \; ; \; \hat{n}_s = s^\dagger \tilde{s}$$
$$\hat{L}_\mu = \sqrt{2}[p^\dagger \times \tilde{p}]^{(1)}_\mu \; ; \; \hat{Q}_\nu = [p^\dagger \times \tilde{p}]^{(2)}_\nu$$
$$\hat{R}_\mu = [p^\dagger \times \tilde{s} - s^\dagger \times \tilde{p}]^{(1)}_\mu \; ; \; \hat{D}_\mu = i[p^\dagger \times \tilde{s} + s^\dagger \times \tilde{p}]^{(1)}_\mu$$
$$\mu = \pm 1, 0; \nu = \pm 2, \pm 1, 0$$

2DVM Dynamical Symmetries and Hamiltonian

Dynamical Symmetries

$$\begin{array}{ccccccc} U(4) & \supset & U(3) & \supset & SO(3) & \text{Dyn. Symmetry (I)} \\ N & & n_p & & L & \\ U(4) & \supset & SO(4) & \supset & SO(3) & \text{Dyn. Symmetry (II)} \\ N & & w & & L & \end{array}$$

2DVM Dynamical Symmetries and Hamiltonian

Dynamical Symmetries

$$\begin{array}{ccccccc} U(4) & \supset & U(3) & \supset & SO(3) & \text{Dyn. Symmetry (I)} \\ N & & n_p & & L & \\ U(4) & \supset & SO(4) & \supset & SO(3) & \text{Dyn. Symmetry (II)} \\ N & & w & & L & \end{array}$$

Dynamical Symmetries Generators

$$\begin{array}{cc} U(3) & \{\hat{n}_p, \hat{L}_\mu, \hat{Q}_\nu\} \\ SO(4) & \{\hat{L}_\mu, \hat{D}_\mu\} \\ SO(3) & \{\hat{L}\} \end{array}$$

$$\begin{array}{cc} U(3) & \hat{C}_1[U(3)] = \hat{n}_p \quad \hat{C}_2[U(3)] = \hat{n}_p(\hat{n}_p+2) \\ SO(4) & \hat{C}_2[SO(4)] = \hat{L}^2 + \hat{D}^2 \\ SO(3) & \hat{C}_2[SO(3)] = \hat{L}^2 \end{array}$$

2DVM Dynamical Symmetries and Hamiltonian

Dynamical Symmetries

$$\begin{array}{ccccccc} U(4) & \supset & U(3) & \supset & SO(3) & \text{Dyn. Symmetry (I)} \\ N & & n_p & & L & \\ U(4) & \supset & SO(4) & \supset & SO(3) & \text{Dyn. Symmetry (II)} \\ N & & w & & L & \end{array}$$

$$\begin{array}{cc} U(3) & \hat{C}_1[U(3)] = \hat{n}_p \quad \hat{C}_2[U(3)] = \hat{n}_p(\hat{n}_p+2) \\ SO(4) & \hat{C}_2[SO(4)] = \hat{L}^2 + \hat{D}^2 \\ SO(3) & \hat{C}_2[SO(3)] = \hat{L}^2 \end{array}$$

General one- and two-body Hamiltonian operator

$$\hat{H} = E_0 + \varepsilon\,\hat{n}_p + \alpha\,\hat{n}_p(\hat{n}_p+2) + A\,(\hat{L}^2 + \hat{D}^2) + B\,\hat{L}^2$$

Dynamical symmetry II: SO(4) limit spectrum

F. Iachello. *Chem. Phys. Lett.* 78 581 (1980).

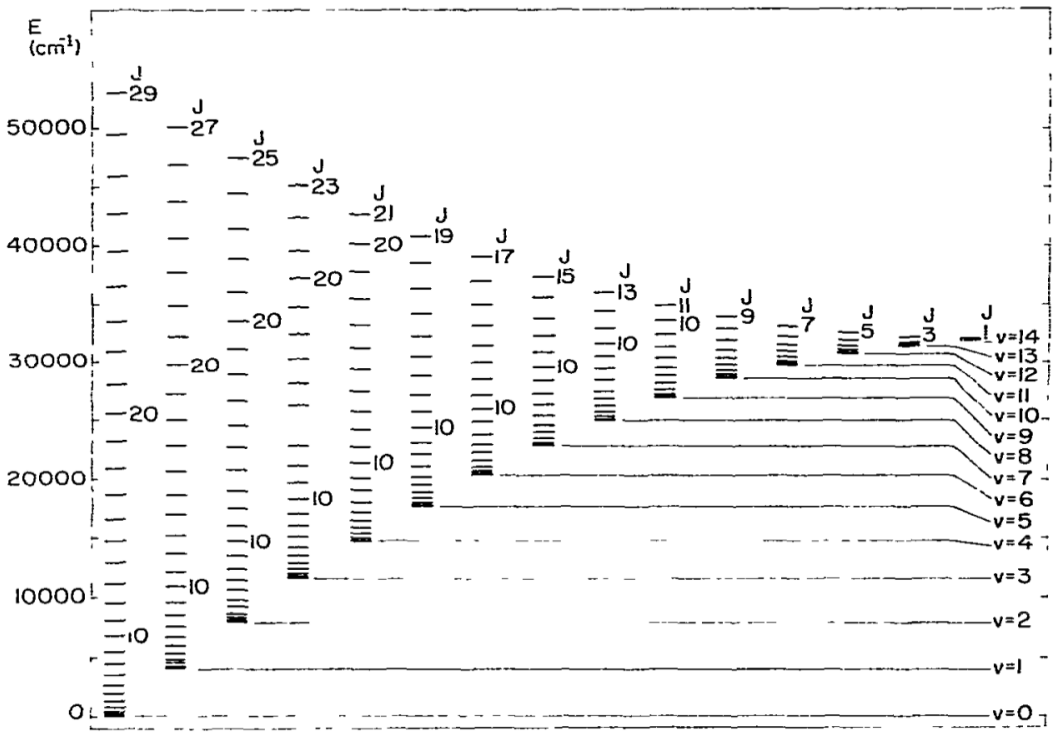


Fig. 1. A typical spectrum with O(4) symmetry and $N = 29$. The energy levels are given by (19) with $-A(8 + 4N) = 4395.24$ cm^{-1}, $B = 60.809$ cm^{-1} and are counted from the lowest level $v = 0, J = 0$. The quantum numbers J and $v = (N - \omega)/2$ are given next to the levels.

The 1D limit of the Vibron Model

The $U(2)$ Lie algebra applied to the study of vibrational molecular structure modeling (coupled) 1D 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 1D limit of the Vibron Model

Incorporation of molecular point group symmetries and application to vibrational spectrum of polyatomic molecular species.
R. Lemus. *Mol. Phys.* 101 2511 (2003).

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*)

A general approach to obtain symmetry adapted bases from a local set of states is presented. The approach is based on the identification of the invariant subspaces which, when projected by means of the eigenfunction method developed by Chen (1989, Group Representation Theory for Physicists Singapore, World Scientific), allow the generation of a symmetry adapted basis. The symmetrized functions so obtained are further taken as a basis to diagonalize simultaneously a set of normal number operators, which provides a set of normal states expanded in terms of the symmetry adapted local basis. In this approach the normal number operators are generated implicitly from the one quantum space through a tensorial formalism. Although the normal operators are defined in a harmonic basis, the locality of the basis allows the approach to be extended to anharmonic functions. This approach has the additional advantage of allowing the elimination of the spurious states, a common problem in a local coordinate representation. An important advantage of this symmetrization method is that it allows generation of a code to analyse any molecular system with a minimum set of input data.

The 2D limit of the Vibron Model: bending vibrations

The $U(3)$ Lie algebra applied to the study of 2D systems (benders).

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. © *1996 American Institute of Physics.* [S0021-9606(96)01818-5]

Outline

Molecular Spectroscopy: Water

Example: H_2O, $\tilde{X}$ electronic state, $\mathcal{C}_{2v}$ symmetry

Modern spectroscopy techniques allow the precise measurement of highly-excited rovibrational molecular states (approx. 10^5 experimental term energies).

Molecular Spectroscopy: Water

Example: H_2O, $\tilde{X}$ electronic state, $\mathcal{C}_{2v}$ symmetry

Modern spectroscopy techniques allow the precise measurement of highly-excited rovibrational molecular states (approx. 10^5 experimental term energies).

Rotational excitation: asymmetric rotor

H_2O: $J_{K_A K_C}$, $1_{01} = 23.79\ \text{cm}^{-1}$, $1_{10} = 42.37\ \text{cm}^{-1}$
$\rightarrow E_{rot} \simeq 10\ \text{cm}^{-1} \simeq 0.0012\ \text{eV}$

Molecular Spectroscopy: Water

Example: H_2O, $\tilde{X}$ electronic state, $\mathcal{C}_{2v}$ symmetry

Modern spectroscopy techniques allow the precise measurement of highly-excited rovibrational molecular states (approx. 10^5 experimental term energies).

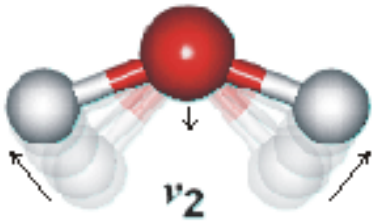
Rotational excitation: asymmetric rotor

H_2O: $J_{K_A K_C}$, $1_{01} = 23.79\ \text{cm}^{-1}$, $1_{10} = 42.37\ \text{cm}^{-1}$
$\rightarrow E_{rot} \simeq 10\ \text{cm}^{-1} \simeq 0.0012\ \text{eV}$

Vibrational excitation, water normal modes

H_2O, stretching: A symm. $\nu_1 = 3657.053\ \text{cm}^{-1}$;
B symm. $\nu_3 = 3755.029\ \text{cm}^{-1} \rightarrow E_{str} \simeq 0.4\ \text{eV}$
H_2O, bending: A symm. $\nu_2 = 1594.746\ \text{cm}^{-1} \rightarrow E_{bend} \simeq 0.1\ \text{eV}$

Molecular bending vibrations

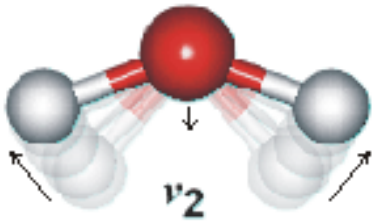


www1.lsbu.ac.uk/water

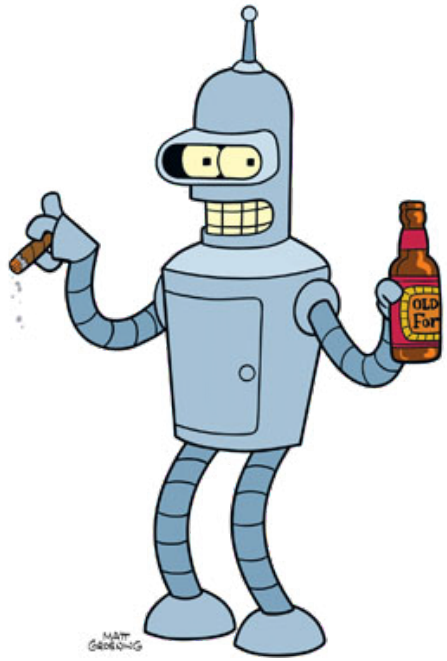
Bending Vibrations

- Different experimental techniques to access different energy scales involved.
- Many experimental energy levels.
- Experimental errors $\leq 1/1000$.
- Highly-excited bending overtones at reach.

Molecular bending vibrations



www1.lsbu.ac.uk/water



Bending Vibrations

- Different experimental techniques to access different energy scales involved.
- Many experimental energy levels.
- Experimental errors $\leq 1/1000$.
- Highly-excited bending overtones at reach.

Outline

The 2D Limit of the Vibron Model (2DVM)

The 2D limit of the vibron model is the simplest two-level model which still retains a non-trivial angular momentum quantum number.

It has been successfully applied to the modeling of the bending vibrational dynamics of several molecular species.

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

The 2D limit of the vibron model (2DVM)

Boson Operators: $\{\tau_i^\dagger, \tau_i, \sigma^\dagger, \sigma\}$; $i = x, y$

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

The 2D limit of the vibron model (2DVM)

Boson Operators: $\{\tau_i^\dagger, \tau_i, \sigma^\dagger, \sigma\}$; $i = x, y$

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

Circular Bosons

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

The 2D limit of the vibron model (2DVM)

Boson Operators: $\{\tau_i^\dagger, \tau_i, \sigma^\dagger, \sigma\}$; $i = x, y$

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

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 $U(3)$ SGA

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

FPB and F. Iachello. *Phys. Rev.* A77 032115 (2008)

2DVM Dynamical Symmetries and Hamiltonian

Dynamical Symmetries

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

2DVM Dynamical Symmetries and Hamiltonian

Dynamical Symmetries

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

$$\begin{array}{ll} U(2) & \{\hat{n}=\tau_+^\dagger\tau_+ + \tau_-^\dagger\tau_-; \hat{\ell}; \hat{Q}_+ = \sqrt{2}\tau_+^\dagger\tau_-; \hat{Q}_- = \sqrt{2}\tau_-^\dagger\tau_+\} \\ SO(3) & \{\hat{\ell}; \hat{D}_+ = \sqrt{2}(\tau_+^\dagger\sigma - \sigma^\dagger\tau_-); \hat{D}_- = \sqrt{2}(-\tau_-^\dagger\sigma + \sigma^\dagger\tau_+)\} \\ SO(2) & \{\hat{\ell} = \tau_+^\dagger\tau_+ - \tau_-^\dagger\tau_-\} \end{array}$$

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

2DVM Dynamical Symmetries and Hamiltonian

Dynamical Symmetries

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

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

General one- and two-body Hamiltonian operator

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

2DVM Casimir Operator Matrix Elements: Chain I

$$\begin{aligned}
\langle [N]; n_2^l | \hat{n} | [N]; n_1^l \rangle =& n_1 \, \delta_{n_2,n_1} \\
\langle [N]; n_2^l | \hat{\ell}^2 | [N]; n_1^l \rangle =& l^2 \, \delta_{n_2,n_1} \\
\langle [N]; n_2^l | \hat{W}^2 | [N]; n_1^l \rangle =& \left[(N-n_1)(n_1+2) + (N-n_1+1)n_1 + l^2 \right] \delta_{n_2,n_1} \\
& - \sqrt{(N-n_1+2)(N-n_1+1)(n_1+l)(n_1-l)} \, \delta_{n_2,n_1-2} \\
& - \sqrt{(N-n_1)(N-n_1-1)(n_1+l+2)(n_1-l+2)} \, \delta_{n_2,n_1+2}
\end{aligned}$$

2DVM Casimir Operator Matrix Elements: Chain II

$$\begin{aligned}
\langle [N]; w_2^l|\hat{n}|[N]; w_1^l\rangle =& \left\{ \frac{(N-w_1)\left[(w_1-l+1)_2+(w_1+l+1)_2\right]}{2(2w_1+1)(2w_1+3)} \right. \\
&\left. + \frac{(N+w_1+1)\left[(w_1-l-1)_2+(w_1-l+1)_2\right]}{2(2w_1+1)(2w_1-1)} \right\} \delta_{w_2,w_1} \\
&+\sqrt{\frac{(N-w_1)(N+w_1+3)(w_1-l+1)_2(w_1+l+1)_2}{(2w_1+1)(2w_1+3)^2(2w_1+5)}}\delta_{w_2,w_1+2} \\
&+\sqrt{\frac{(N-w_1+2)(N+w_1+3)(w_1-l-1)_2(w_1+l-1)_2}{(2w_1-3)(2w_1+1)^2(2w_1+1)}}\delta_{w_2,w_1-2} \\
(a)_s =& a(a+1)\ldots(a+s-1) \quad \text{Pochhammer Symbol} \\
\langle [N]; w_2^l|\hat{W}^2|[N]; w_1^l\rangle =& w_1(w_1+2)\delta_{w_2,w_1} \\
\langle [N]; w_2^l|\hat{\ell}^2|[N]; w_1^l\rangle =& l^2\delta_{w_2,w_1}
\end{aligned}$$

Cylindrical Oscillator Dynamical Symmetry

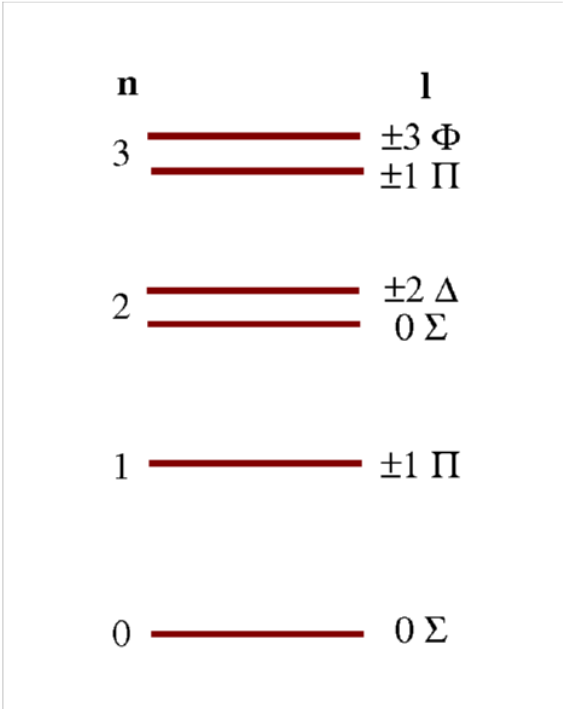
$$\begin{array}{ccccc} U(3) & \supset & U(2) & \supset & SO(2) \\ [N] & & n & & \ell \end{array}$$

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

Cylindrical Oscillator Dynamical Symmetry

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

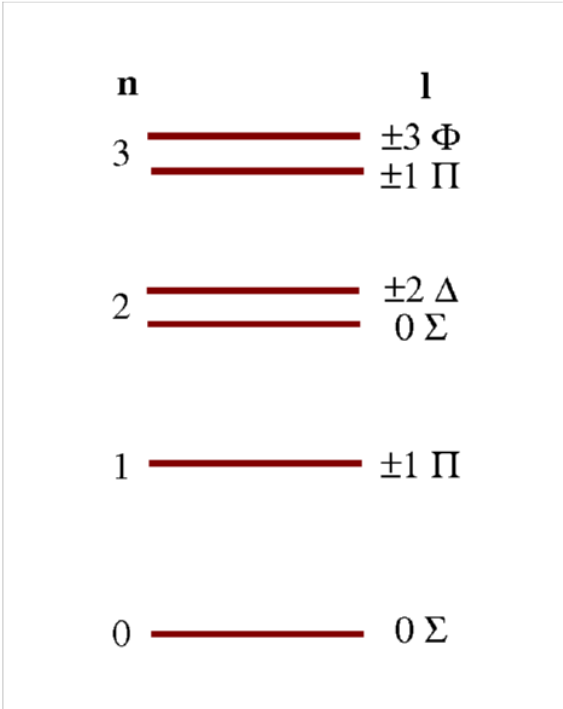
$$\begin{aligned} n &= N, N-1, N-2, \ldots, 0 \\ \ell &= \pm n, \pm(n-2), \ldots, 1(\text{or } 0) \end{aligned}$$

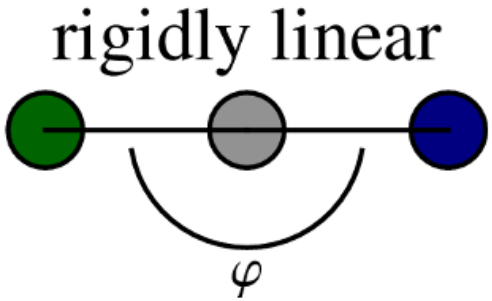


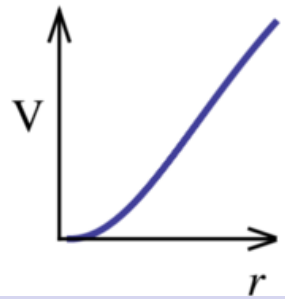
Cylindrical Oscillator Dynamical Symmetry

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

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







Displaced Oscillator Dynamical Symmetry

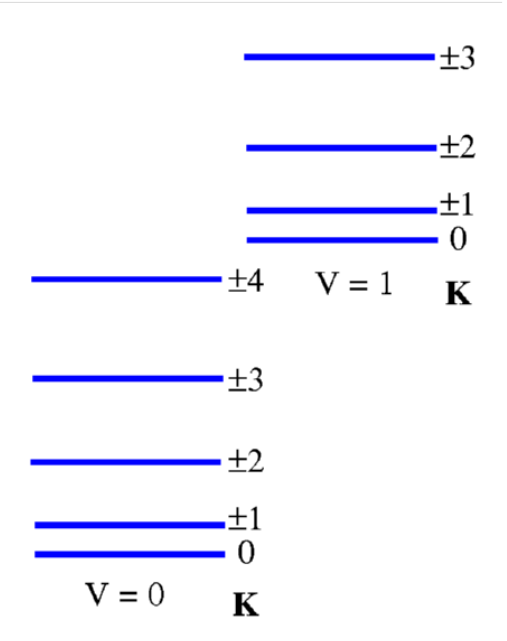
$$\begin{array}{ccccc} U(3) & \supset & SO(3) & \supset & SO(2) \\ N & & \omega & & \ell \end{array}$$

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

Displaced Oscillator Dynamical Symmetry

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

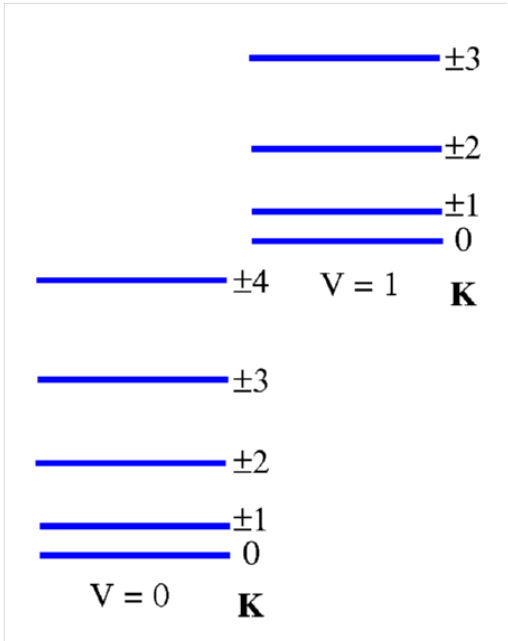
$$\begin{aligned} \omega &= N, N-2, N-4, \ldots, 1(\text{or } 0) \\ \ell &= \pm\omega, \pm(\omega-1), \ldots, 0 \\ v &= \frac{N-\omega}{2} = 0, 1, \ldots, \frac{N-1}{2}(\text{or } \frac{N}{2}) \\ \ell &= 0, \pm 1, \pm 2, \ldots, \pm(N-2v) \end{aligned}$$

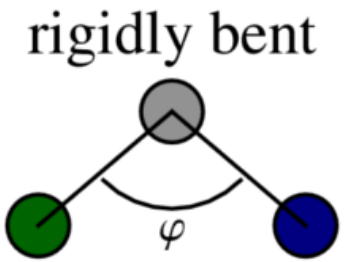


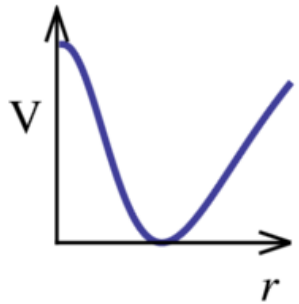
Displaced Oscillator Dynamical Symmetry

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

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

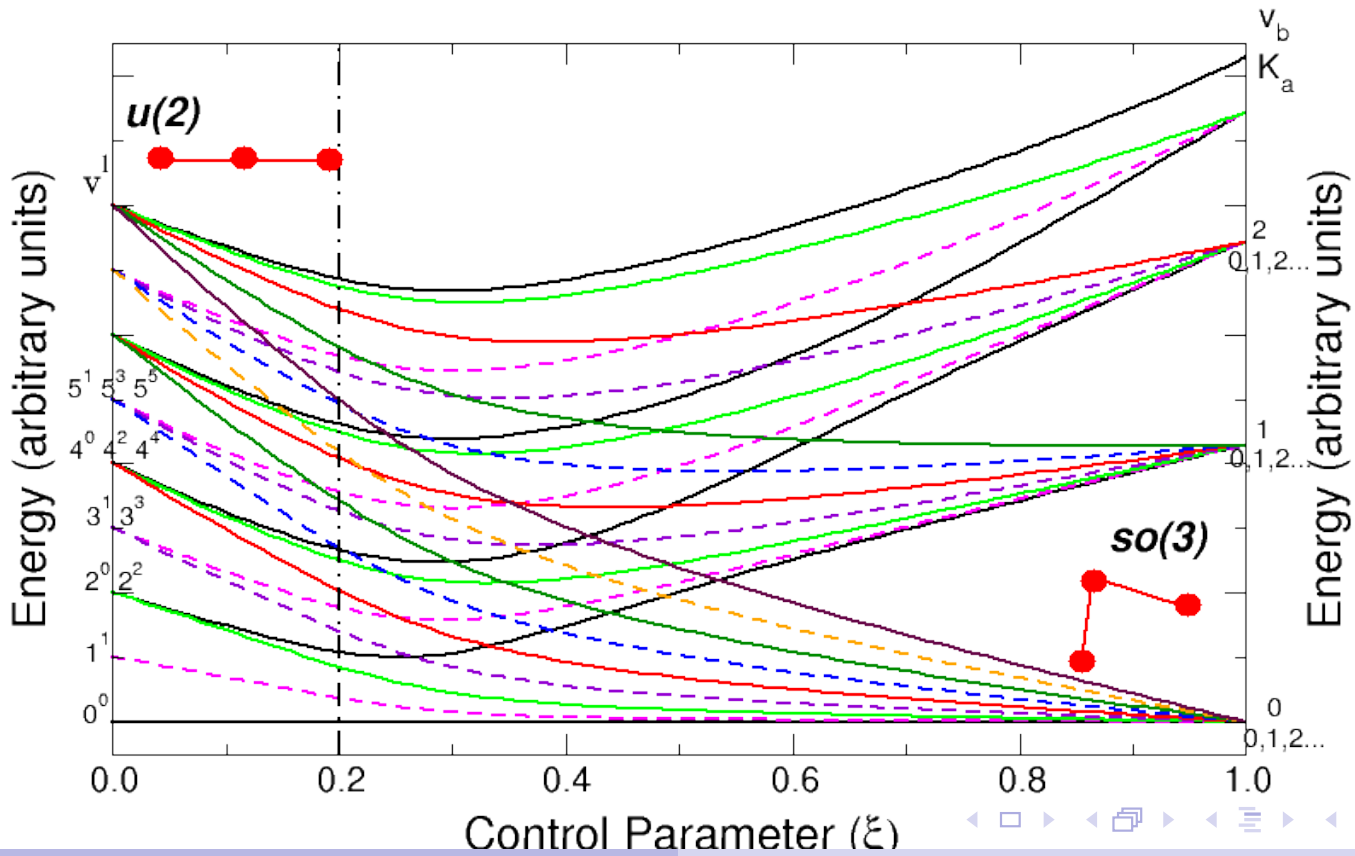




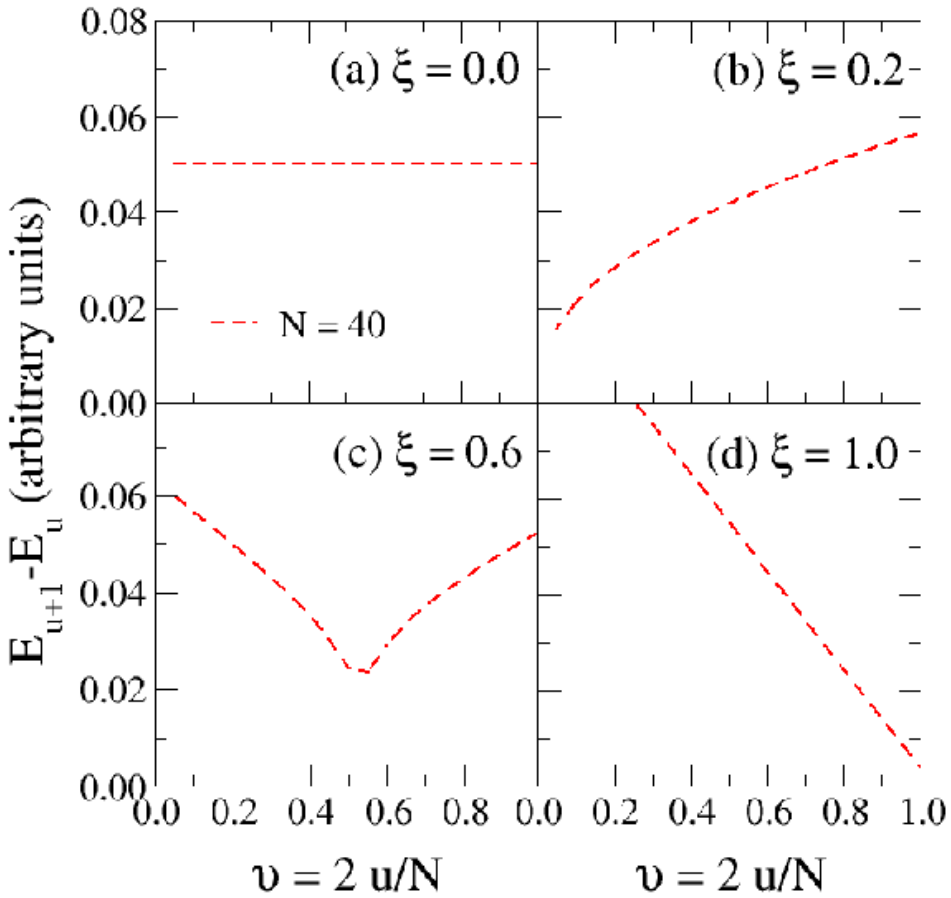


Correlation Energy Diagram

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

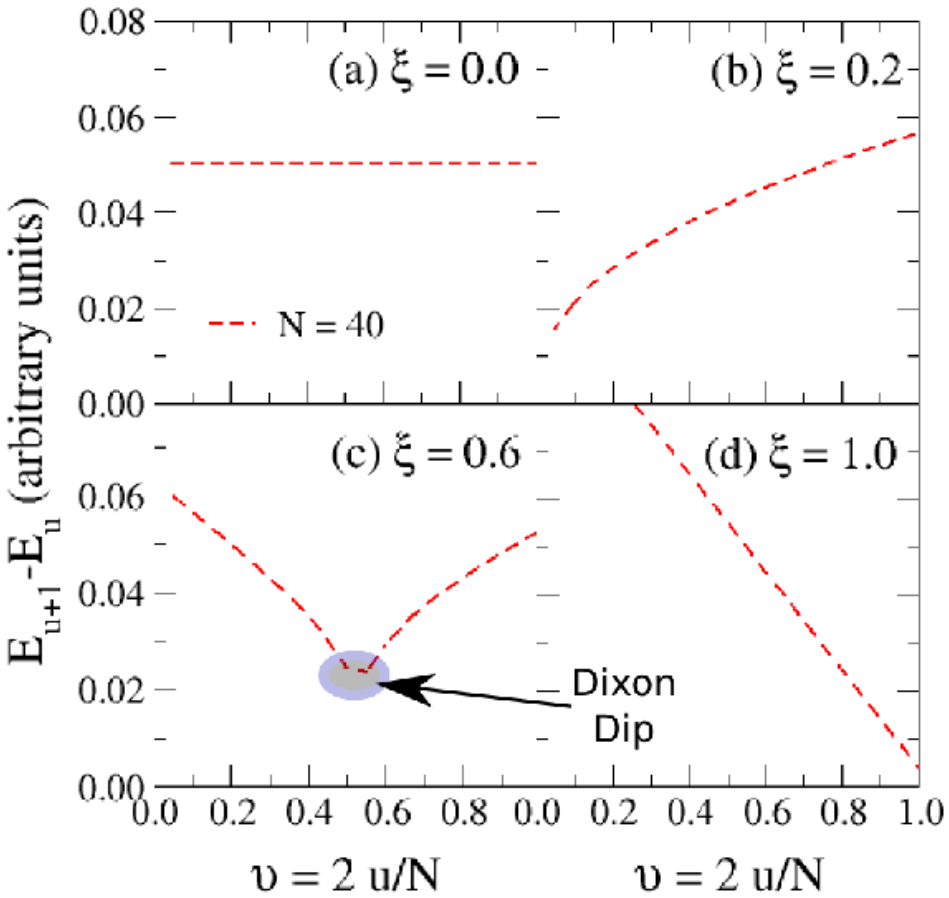


Spectroscopig Signatures: Birge-Sponer Plot



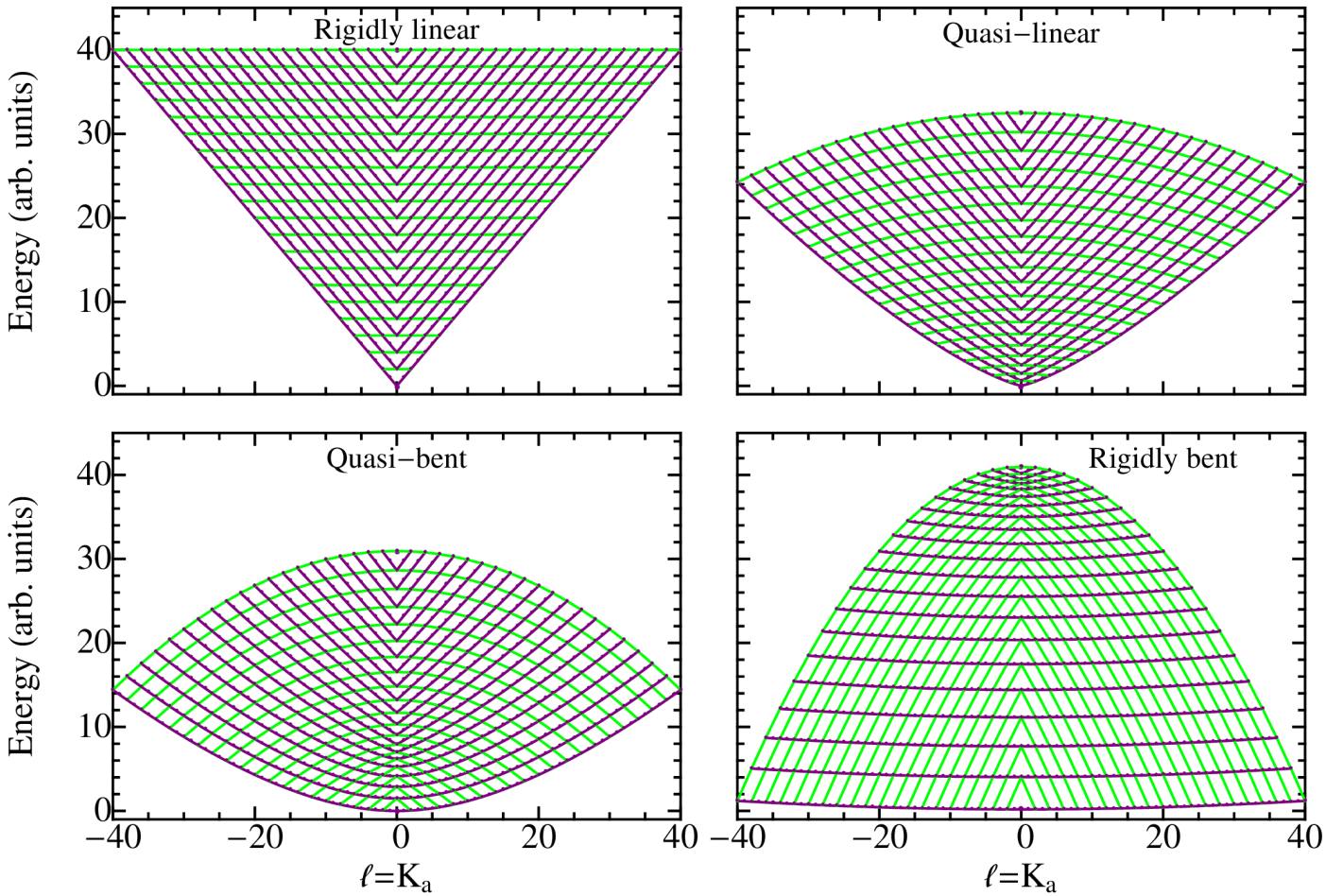
R. N. Dixon *Trans. Faraday Soc.* 60 1363 (1964).

Spectroscopig Signatures: Birge-Sponer Plot

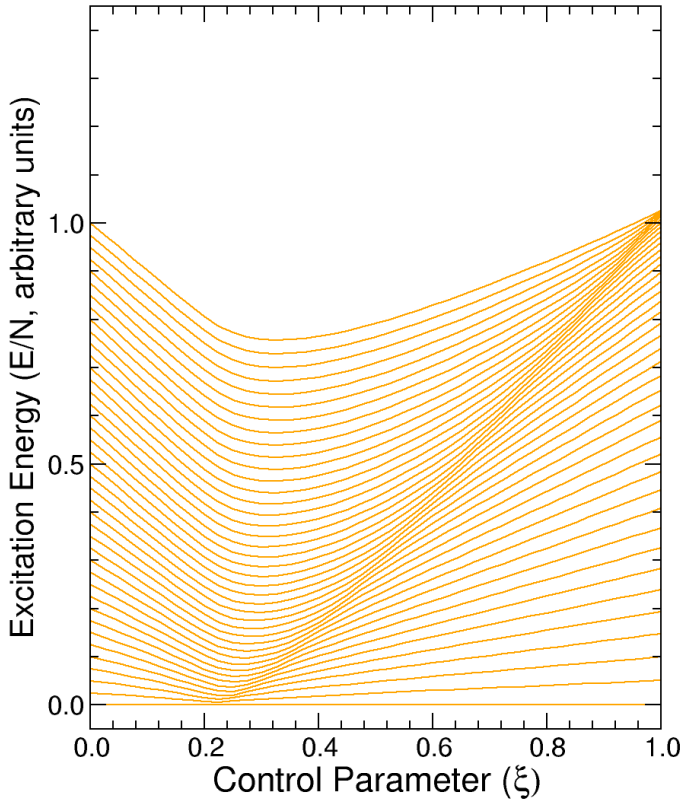


R. N. Dixon *Trans. Faraday Soc.* 60 1363 (1964).

Spectroscopig Signatures: Quantum Monodromy Plot



ESQPT in the 2DVM

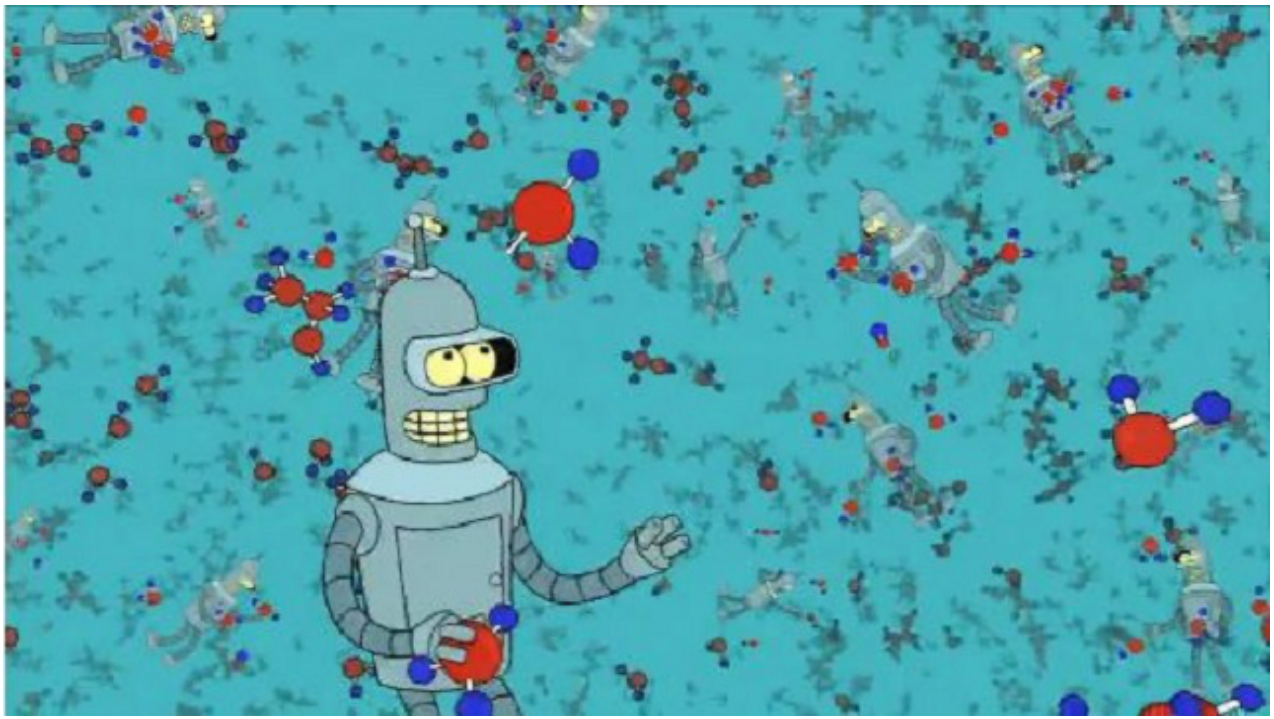


M.A. Caprio, P. Cejnar, F. Iachello. Ann. Phys. 323 1106 (2008).

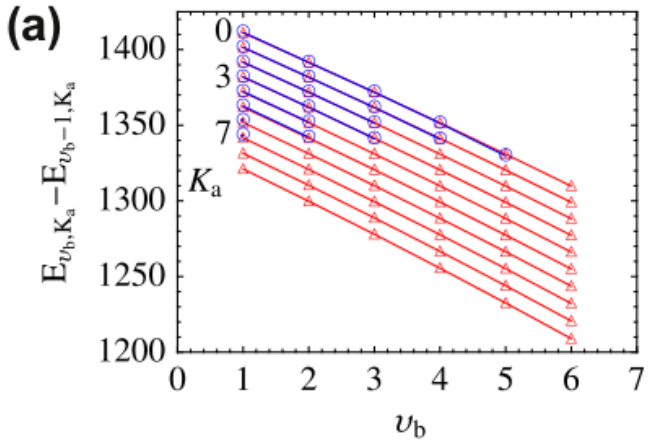
Outline

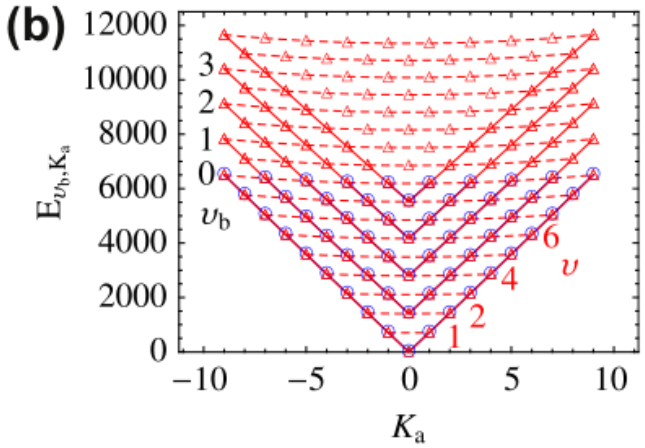
Application to Single Bender Molecular Species

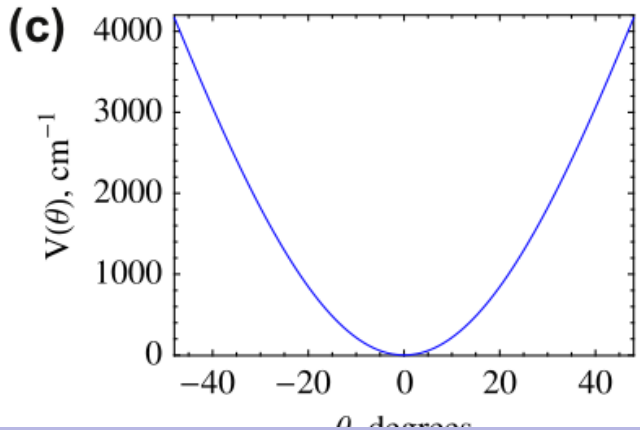
- D. Larese and F. Iachello. *J. Mol. Struct.* 1006 611 (2011).
- D. Larese, FPB, and F. Iachello. *J. Mol. Struct.* 1051 310 (2013).

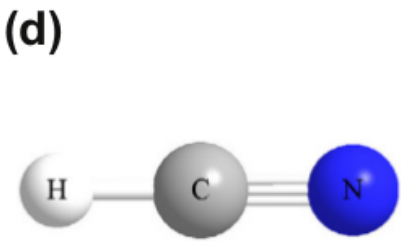


Dynamical Symmetry (I): HCN









(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Bending Potential

(d) Molecule Model

$N = 40$

$\varepsilon = 794.88$

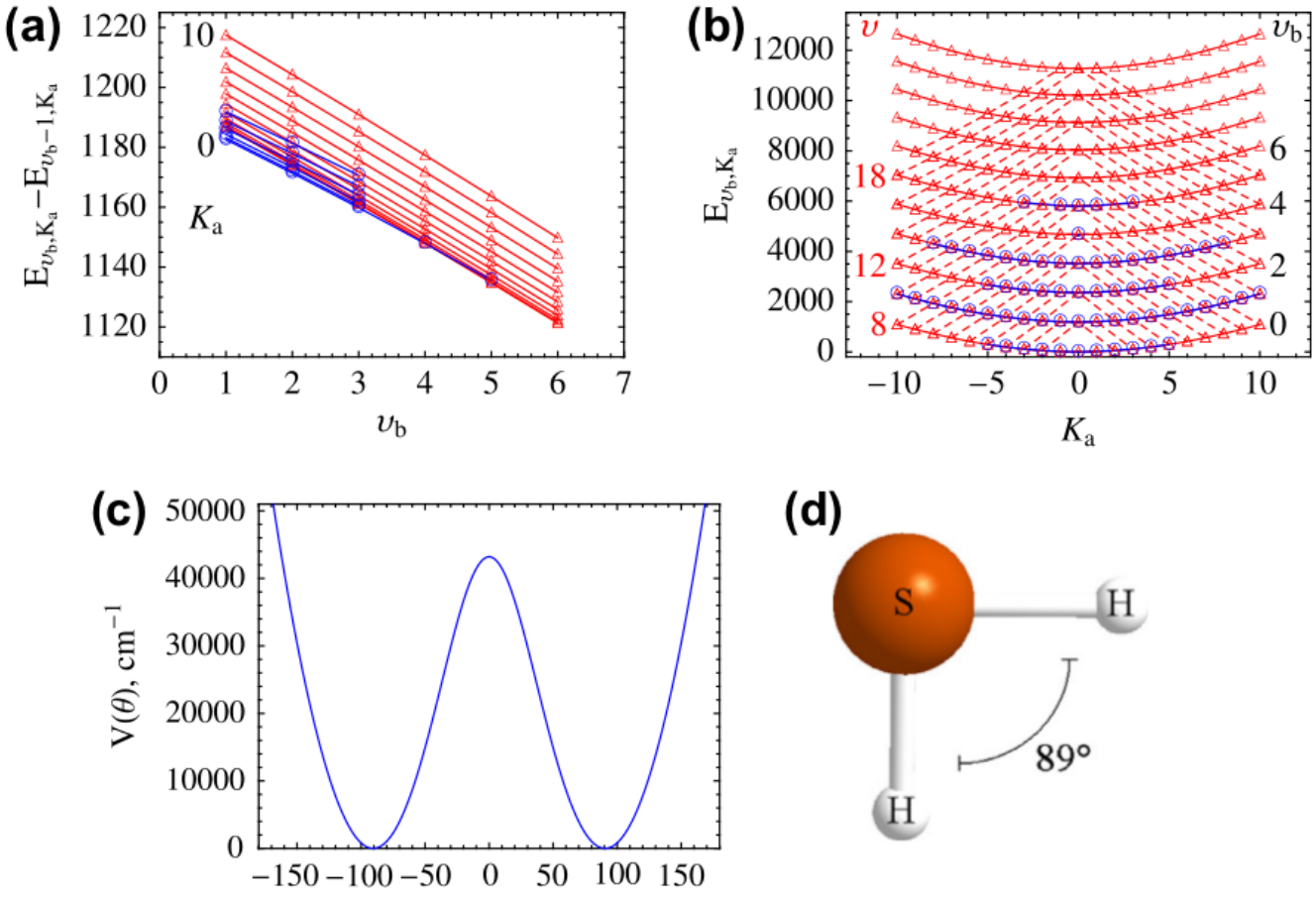
$\alpha = -3.96$

$\beta = 4.25$

$A = 0.36$

$rms = 0.7$ cm^{-1}

Dynamical Symmetry (II): H_2S



(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Bending Potential

(d) Molecule Model

$N = 140$

$\varepsilon = --$

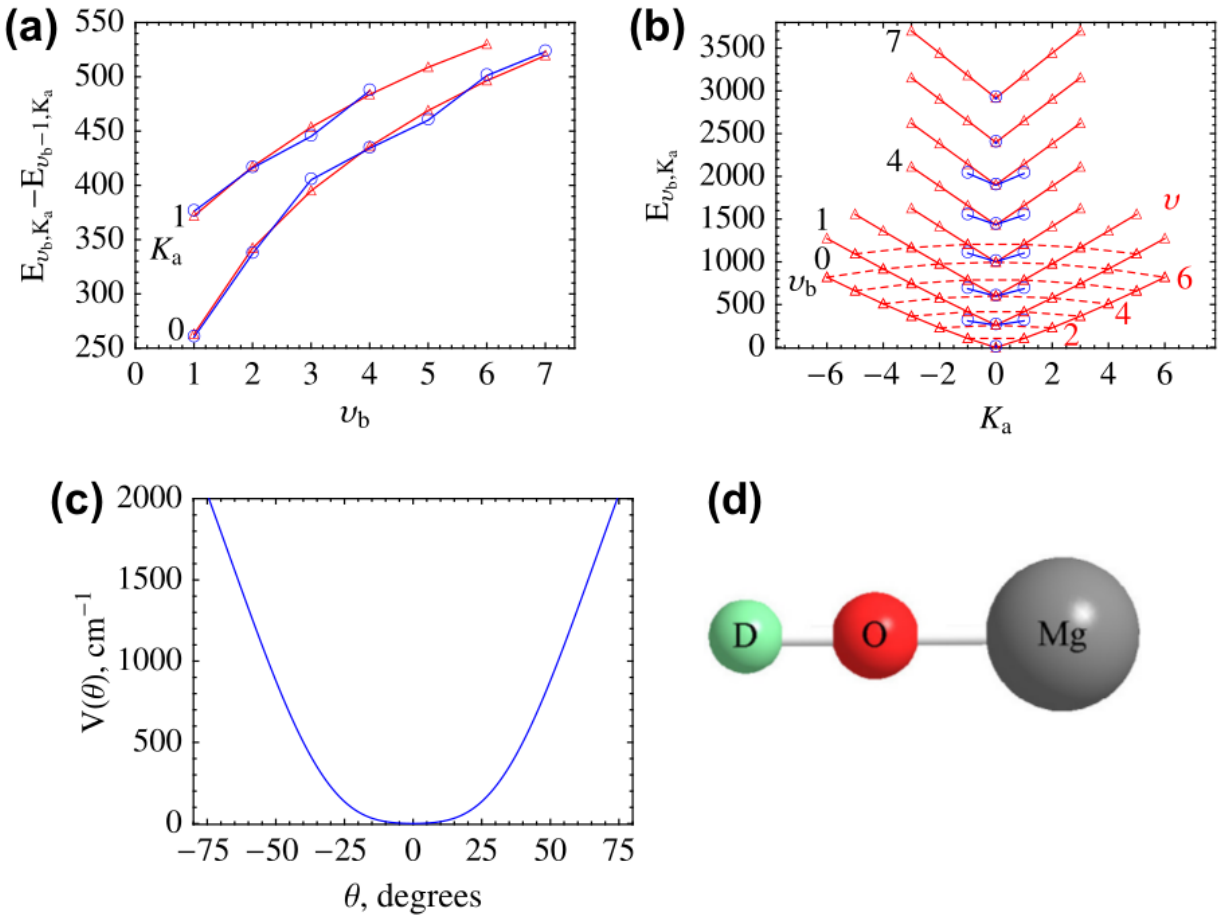
$\alpha = --$

$\beta = 12.10$

$A = 2.12$

$rms = 5.9\ \text{cm}^{-1}$

Quasilinear Species: MgOD



(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Bending Potential

(d) Molecule Model

$N = 27$

$\varepsilon = 299.4$

$\alpha = -2.1$

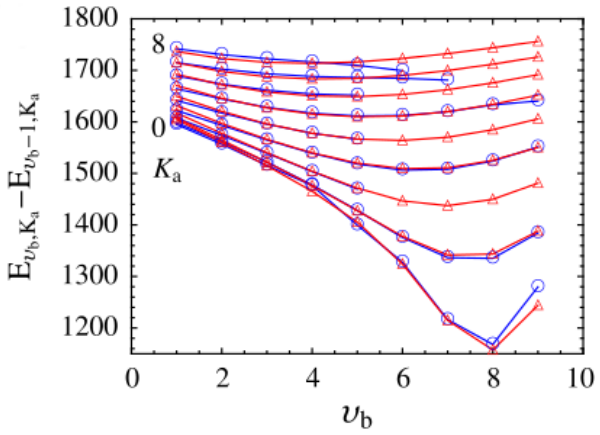
$\beta = --$

$A = 2.7$

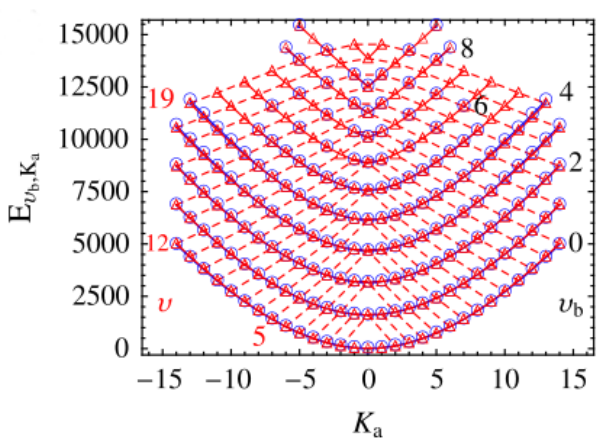
$rms = 4.2\ \mathrm{cm}^{-1}$

Nonrigid Species: H_2O

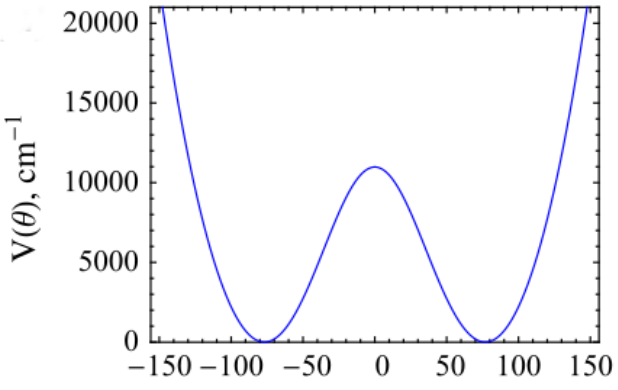
(a)



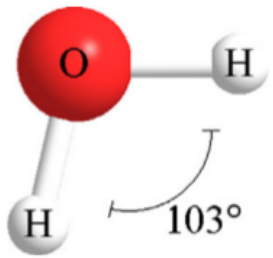
(b)



(c)



(d)



(a) Birge-Sponer Plot

(b) Monodromy Plot

(c) Bending Potential

(d) Molecule Model

$N = 143$

$\varepsilon = 4815.0$

$\alpha = -32.15$

$\beta = 15.44$

$A = 8.70$

$A_3 = 2.07 \times 10^{-5}$

$rms = 9.1\ \text{cm}^{-1}$

Outline

Simple Concepts on Classical Phase Transitions

Phase and Phase Transition

Simple Concepts on Classical Phase Transitions

Phase and Phase Transition

Phase state of matter that is uniform throughout, both in its chemical composition and its physical properties

Simple Concepts on Classical Phase Transitions

Phase and Phase Transition

Phase state of matter that is uniform throughout, both in its chemical composition and its physical properties

Phase Transition marked by an abrupt change in one or more properties of the system

Simple Concepts on Classical Phase Transitions

Phase and Phase Transition

Phase state of matter that is uniform throughout, both in its chemical composition and its physical properties

Phase Transition marked by an abrupt change in one or more properties of the system

- Most stable phase is the one with the lowest thermodynamical potential (Φ) which is a function of variable parameters (F(T,V), F(T,B); G(T,p), G(T,M)).

Simple Concepts on Classical Phase Transitions

Phase and Phase Transition

Phase state of matter that is uniform throughout, both in its chemical composition and its physical properties

Phase Transition marked by an abrupt change in one or more properties of the system

- Most stable phase is the one with the lowest thermodynamical potential (Φ) which is a function of variable parameters (F(T,V), F(T,B); G(T,p), G(T,M)).
- Φ is analogous to the potential energy, V(x), of a particle: systems like minimum energy states, in potential minima.

Transition Parameters and Classification

Control and Order Parameters

Control Parameters parameters of the thermodynamical potential Φ that can be changed arbitrarily and smoothly (e.g. T, p, external B).

Order Parameters observables that are changing as the control parameters are varied. Typically they are zero in one phase and different from zero in the other one.

Transition Parameters and Classification

Control and Order Parameters

Control Parameters parameters of the thermodynamical potential Φ that can be changed arbitrarily and smoothly (e.g. T, p, external B).

Order Parameters observables that are changing as the control parameters are varied. Typically they are zero in one phase and different from zero in the other one.

Classification

First Order Involve latent heat.

Continuous Does not involve latent heat.

Quantum Phase Transitions

Let's consider a system that is composed by two parts, having each one a different symmetry: G_1 and G_2.

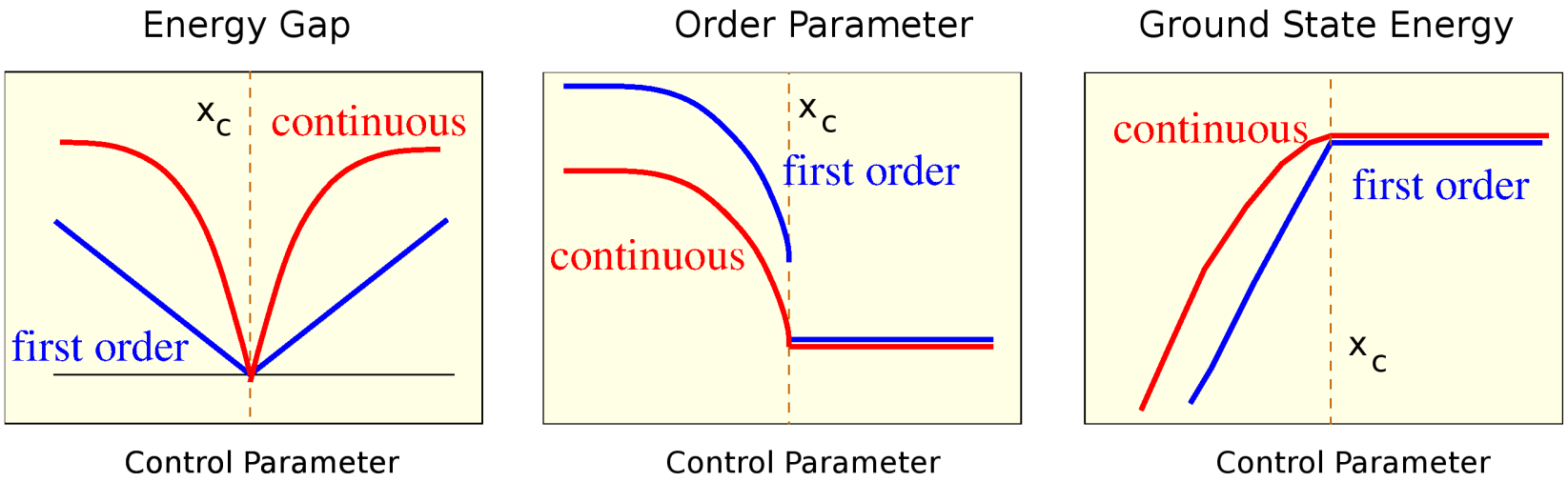
QPT occurs at some critical value (x_c) of the control parameter x, that controls an interaction strength in the system's Hamiltonian $H(x)$, is varied.

$$\hat{H} = x\ \hat{H}_1 + (1 - x)\ \hat{H}_2$$

At the critical point:

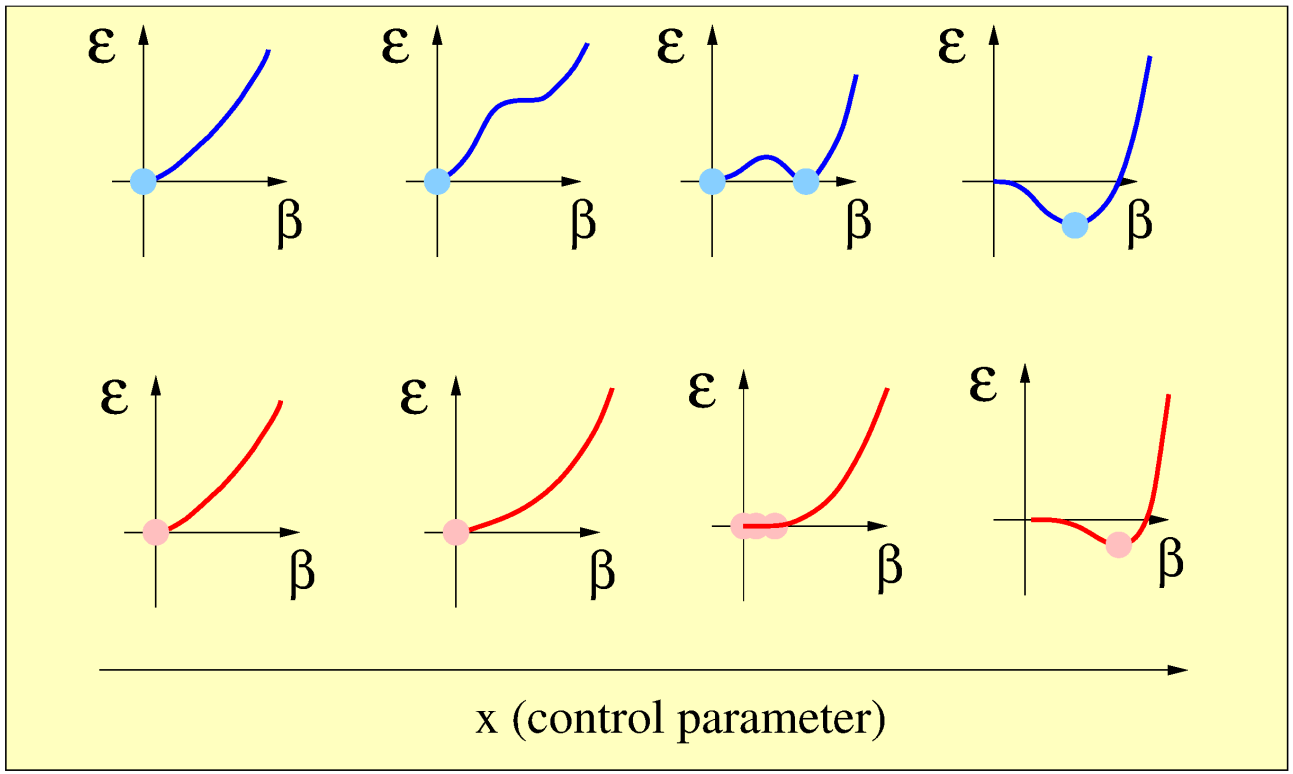
1. The ground state energy E_0 is nonanalytic.
2. The gap Δ between the first excited state and the ground state vanishes.

QPT Critical Point



Energy Surfaces

First order transitions (blue) and Continuous transitions (red)



Shape Phase Transitions

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)

P. Cejnar, J. Jolie and R. Casten. *Rev. Mod. Phys.* 82 2155 (2010)

Shape Phase Transitions

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)

P. Cejnar, J. Jolie and R. Casten. *Rev. Mod. Phys.* 82 2155 (2010)

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.

Shape Phase Transitions

Excited State Quantum Phase Transitions

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

ESQPT 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).

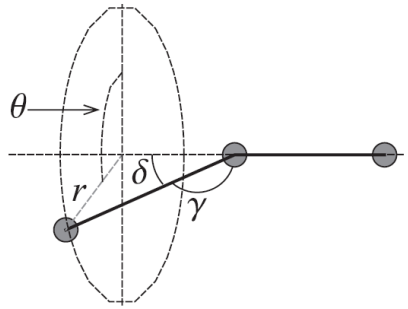
Shape phase transitions strictly take place at the thermodynamic limit (large N): importance of precursors for mesoscopic systems and the scaling behavior of the relevant quantities.

Outline

Intrinsic state: connection with the classical limit

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

$$b_c^\dagger = \frac{1}{\sqrt{1+r^2}}\left[\sigma^\dagger + x\tau_x^\dagger + y\tau_y^\dagger\right]$$



Model Hamiltonian and Energy per Particle

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

$$\mathcal{E}_\xi(r) = \frac{\langle[N]; r, \theta|\hat{\mathcal{H}}|[N]; r, \theta\rangle}{\epsilon N} = \left[(1-\xi)\frac{r^2}{1+r^2} + \xi\left(\frac{1-r^2}{1+r^2}\right)^2\right]$$

Ground State Energy

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

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

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

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

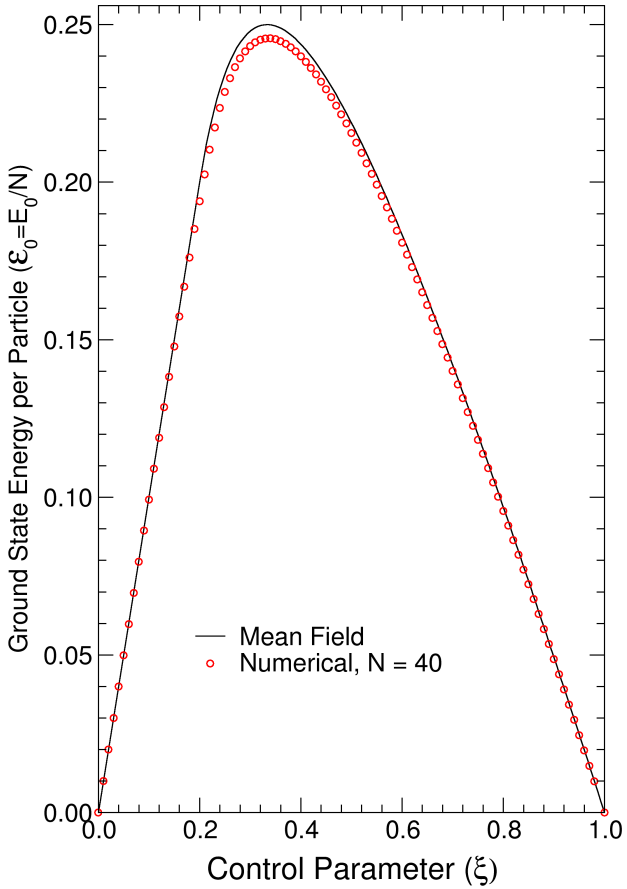
Ground State Energy

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

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

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

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



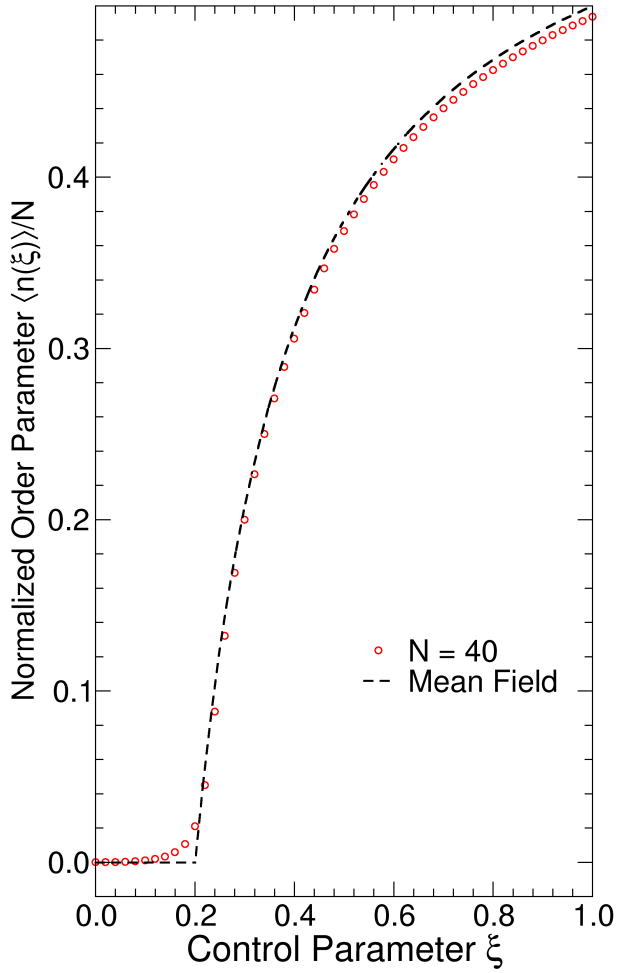
Expected value of $\hat{n}$, the number of τ bosons

$$\begin{aligned} \langle \hat{n} \rangle &= \langle [N]; r, \theta | \hat{n} | [N]; r, \theta \rangle \ , \\ \langle \hat{n} \rangle &= N \frac{r_e^2}{1 + r_e^2} = \begin{cases} 0 & 0 \leq \xi \leq \xi_c \\ \frac{5\xi - 1}{8\xi} & \xi_c < \xi \leq 1 \end{cases} \ . \end{aligned}$$

Expected value of $\hat{n}$, the number of τ bosons

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

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



Single Bender Mondel Hamiltonian Phase Diagram

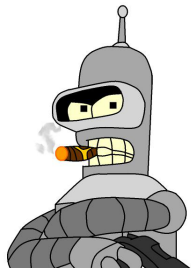
$$U(3) \supset U(2) \supset SO(2) \quad \text{Dynamical Symmetry (I)}$$
$$U(3) \supset SO(3) \supset SO(2) \quad \text{Dynamical Symmetry (II)}$$

Single Bender Mondel Hamiltonian Phase Diagram

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

Single Bender Model Hamiltonian

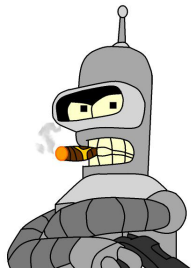
$$\hat{\mathcal{H}} = \varepsilon \left[(1-\xi)\hat{n} + \frac{\xi}{N-1}\hat{P} \right]$$



Single Bender Mondel Hamiltonian Phase Diagram

$$\begin{array}{ccccccc} U(3) & \supset & U(2) & \supset & SO(2) & \text{Dynamical Symmetry (I)} \\ U(3) & \supset & SO(3) & \supset & SO(2) & \text{Dynamical Symmetry (II)} \end{array}$$

Single Bender Model Hamiltonian



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

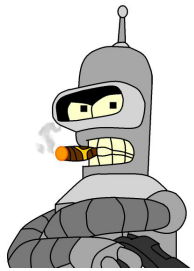
- ε: energy scale
- ξ: control parameter: $\xi \in [0,1]$
  - $\xi = 0.0$ rigidly-linear
  - $0.0 < \xi \leq 0.2$ quasilinear
  - $0.2 < \xi < 1.0$ non-rigid
  - $\xi = 1.0$ rigidly-bent

Single Bender Mondel Hamiltonian Phase Diagram

$$\begin{array}{ccccccc} U(3) & \supset & U(2) & \supset & SO(2) & \text{Dynamical Symmetry (I)} \\ U(3) & \supset & SO(3) & \supset & SO(2) & \text{Dynamical Symmetry (II)} \end{array}$$

Single Bender Model Hamiltonian

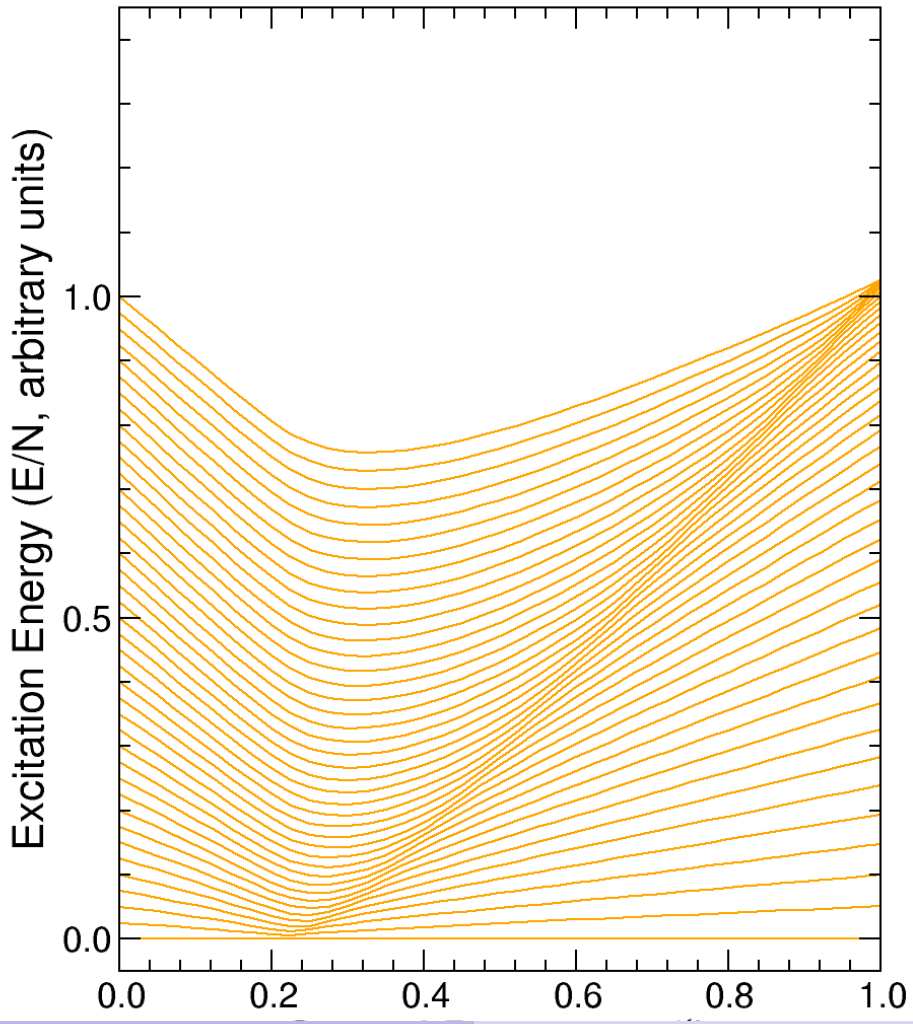
$$\hat{\mathcal{H}} = \varepsilon \left[(1-\xi)\hat{n} + \frac{\xi}{N-1}\hat{P} \right]$$



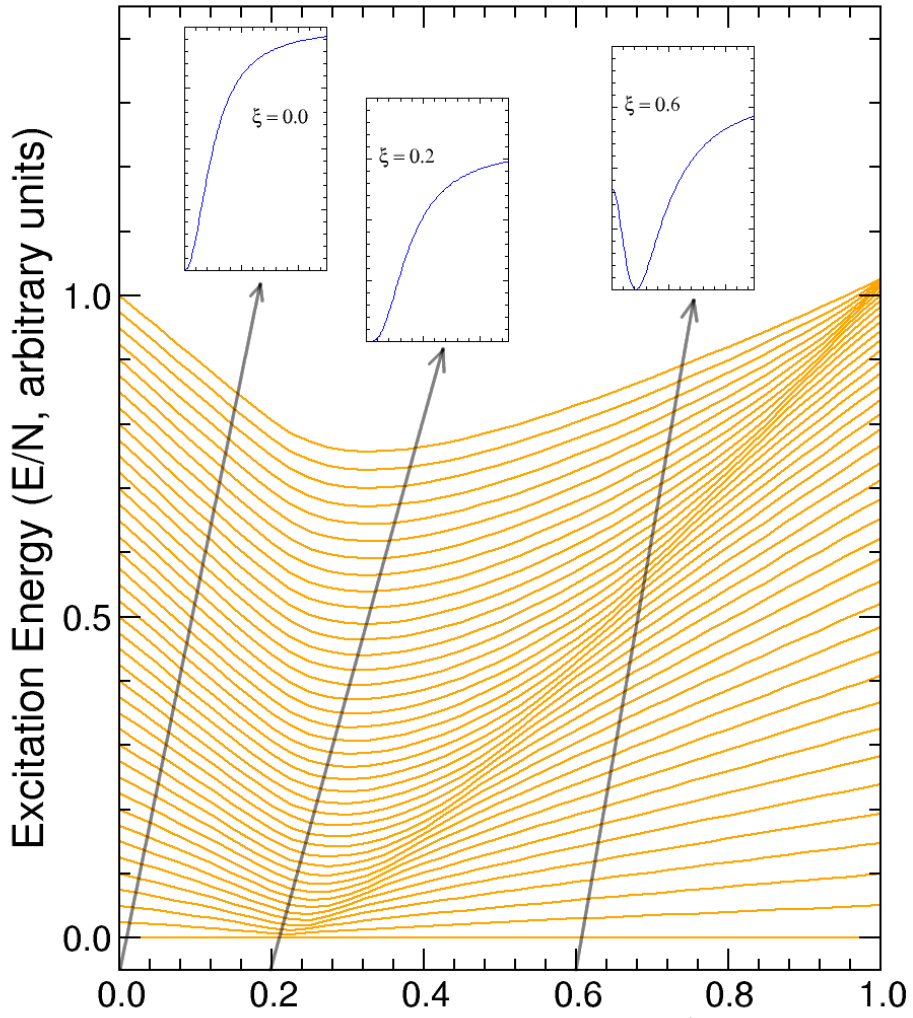
- ε: energy scale
- ξ: control parameter: $\xi \in [0,1]$
  - $\xi = 0.0$ rigidly-linear
  - $0.0 < \xi \leq 0.2$ quasilinear
  - $0.2 < \xi < 1.0$ non-rigid
  - $\xi = 1.0$ rigidly-bent

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

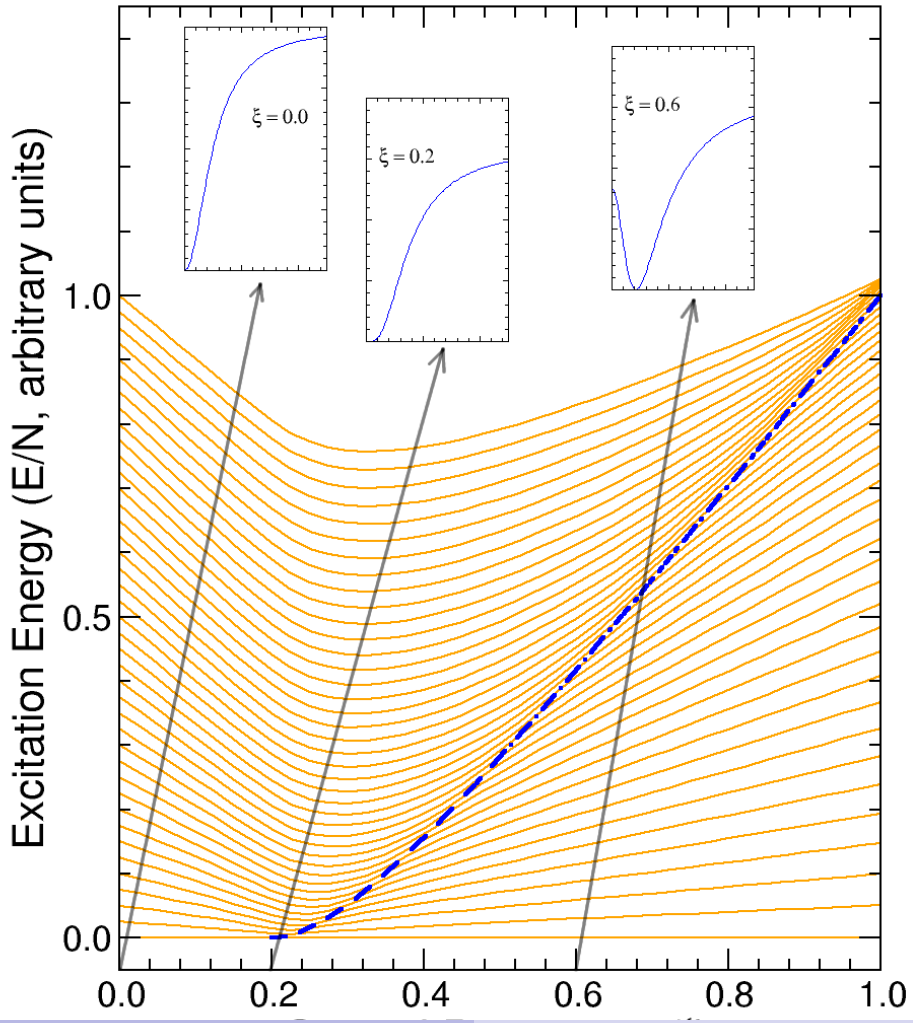
Single Bender Excited State Quantum Phase Transition



Single Bender Excited State Quantum Phase Transition



Single Bender Excited State Quantum Phase Transition

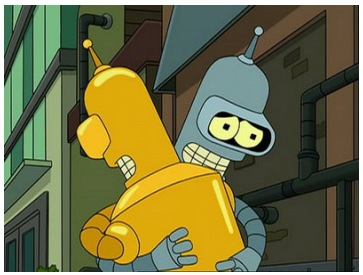


Outline

Algebraic approach to coupled benders

Two coupled benders dyn. algebra: $U_1(3) \times U_2(3)$:

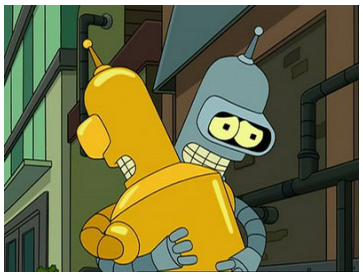
$$\sigma_j \ , \quad \tau^\dagger_{j,\pm} = \mp \frac{\tau^\dagger_{j,x} \pm i\tau^\dagger_{j,y}}{\sqrt{2}} \ , \quad j = 1, 2.$$



Algebraic approach to coupled benders

Two coupled benders dyn. algebra: $U_1(3) \times U_2(3)$:

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

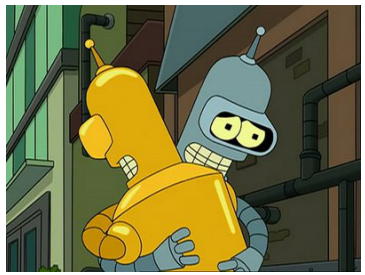


$$\begin{array}{ccccc} & & & & SO_1(2) \otimes SO_2(2) & & \text{(Ia)} \\ & & & \nearrow & & \searrow & \\ U_1(3) \otimes U_2(3) & \supset & U_1(2) \otimes U_2(2) & & & & SO_{12}(2), \\ & & & \searrow & & \nearrow & \\ & & & & U_{12}(2) & & \text{(Ib)} \end{array}$$

Algebraic approach to coupled benders

Two coupled benders dyn. algebra: $U_1(3) \times U_2(3)$:

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

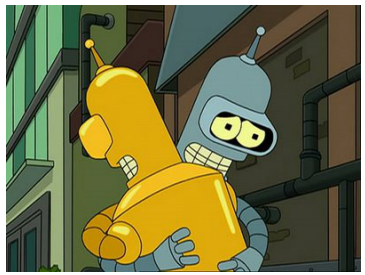


$$\begin{array}{lcll} & & SO_1(2) \otimes SO_2(2) & \text{(Ia)} \\ U_1(3) \otimes U_2(3) \supset & U_1(2) \otimes U_2(2) & \swarrow \quad \searrow & SO_{12}(2), \\ & & U_{12}(2) & \text{(Ib)} \\ & & SO_1(2) \otimes SO_2(2) & \text{(IIa)} \\ U_1(3) \otimes U_2(3) \supset & SO_1(3) \otimes SO_2(3) & \swarrow \quad \searrow & SO_{12}(2), \\ & & SO_{12}(3) & \text{(IIb)} \end{array}$$

Algebraic approach to coupled benders

Two coupled benders dyn. algebra: $U_1(3) \times U_2(3)$:

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



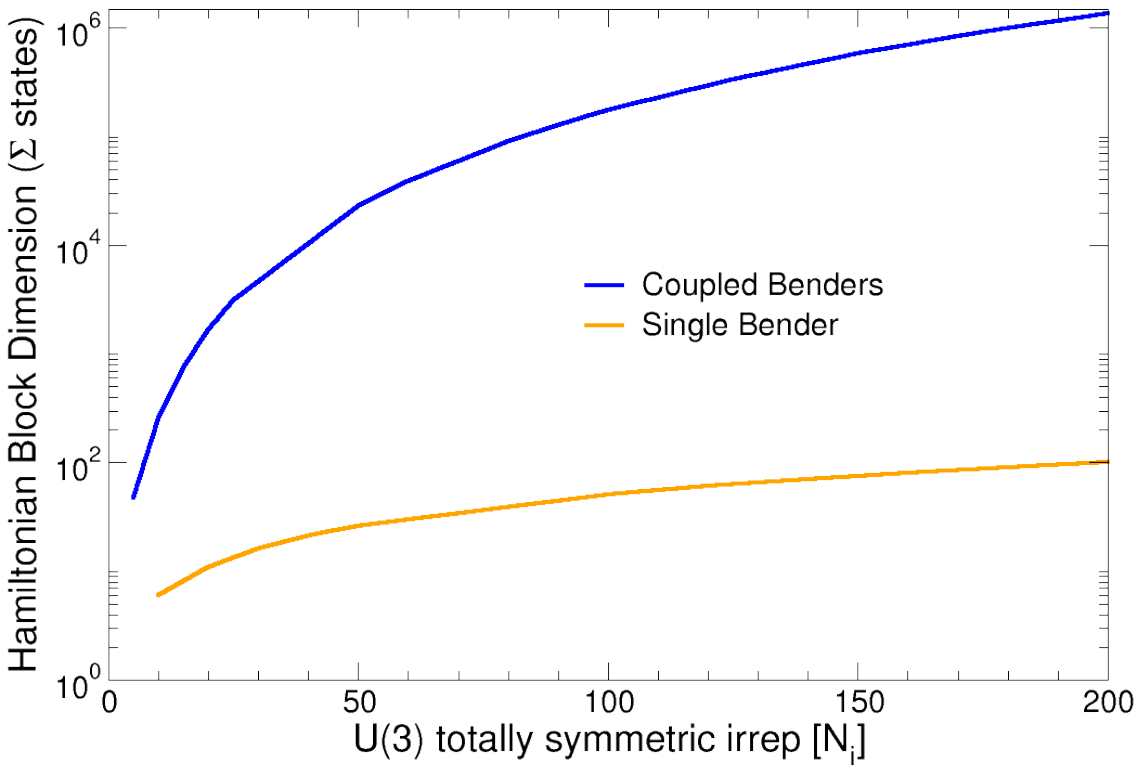
$$\begin{array}{lcl}
 & & SO_1(2) \otimes SO_2(2) \quad \text{(Ia)} \\
 & & \swarrow \qquad \searrow \\
U_1(3) \otimes U_2(3) \supset & U_1(2) \otimes U_2(2) & \qquad SO_{12}(2), \\
 & & \searrow \qquad \swarrow \\
 & & U_{12}(2) \quad \text{(Ib)} \\
 & & SO_1(2) \otimes SO_2(2) \quad \text{(IIa)} \\
 & & \swarrow \qquad \searrow \\
U_1(3) \otimes U_2(3) \supset & SO_1(3) \otimes SO_2(3) & \qquad SO_{12}(2), \\
 & & \searrow \qquad \swarrow \\
 & & SO_{12}(3) \quad \text{(IIb)} \\
 & & U_{12}(2) \quad \text{(IIIa)} \\
 & & \swarrow \qquad \searrow \\
U_1(3) \otimes U_2(3) \supset & U_{12}(3) & \qquad SO_{12}(2), \\
 & & \searrow \qquad \swarrow \\
 & & SO_{12}(3) \quad \text{(IIIb)}
\end{array}$$

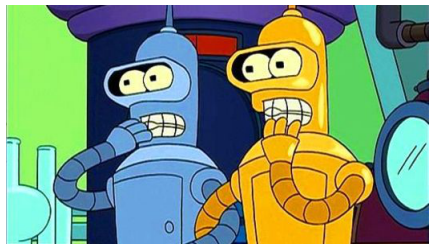
Block Dimensions in the Coupled Benders Hamiltonian

The two-fluid model implies a huge increase in Hamiltonian block dimensions.

Block Dimensions in the Coupled Benders Hamiltonian

The two-fluid model implies a huge increase in Hamiltonian block dimensions.





Coupled Benders Hamiltonian (ABBA molecules)

General Hamiltonian (9 parameters)

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

Coupled Benders Hamiltonian (ABBA molecules)

General Hamiltonian (9 parameters)

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

Model Hamiltonian (3 control parameters: $0 \leq \xi \leq 1$, η_1, and $\eta_2 < 0$)

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

Coupled Benders Hamiltonian (ABBA molecules)

General Hamiltonian (9 parameters)

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

Model Hamiltonian (3 control parameters: $0 \leq \xi \leq 1$, η_1, and $\eta_2 < 0$)

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

Rigidly-bent molecular species (4 parameters: λ, A, A_{12} and τ)

$$\hat{H} = E_0' + \lambda(\hat{D}_1\cdot\hat{D}_2 + \hat{R}_1\cdot\hat{R}_2) + A(\hat{W}_1^2 + \hat{W}_2^2) + A_{12}\hat{W}_1\cdot\hat{W}_2 + \tau(\hat{\ell}_1 - \hat{\ell}_2)^2$$

Coupled Benders Hamiltonian (ABBA molecules)

General Hamiltonian (9 parameters)

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

Model Hamiltonian (3 control parameters: $0 \leq \xi \leq 1$, η_1, and $\eta_2 < 0$)

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

Rigidly-bent molecular species (4 parameters: λ, A, A_{12} and τ)

$$\hat{H} = E_0' + \lambda(\hat{D}_1\cdot\hat{D}_2 + \hat{R}_1\cdot\hat{R}_2) + A(\hat{W}_1^2 + \hat{W}_2^2) + A_{12}\,\hat{W}_1\cdot\hat{W}_2 + \tau(\hat{\ell}_1 - \hat{\ell}_2)^2$$

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

FPB and L. Fortunato, Phys. Lett. A 376 236 (2012); D. Larese *et al.*, J. Chem. Phys. 140, 014304 (2014)

Outline

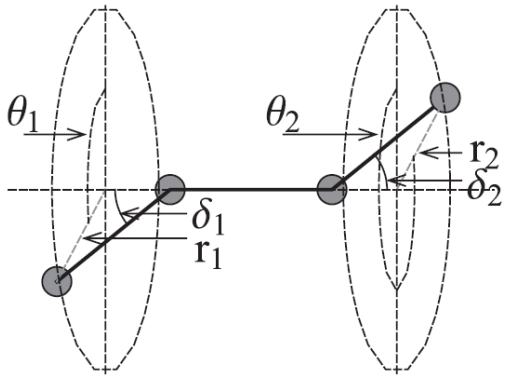
Projective coherent states (coupled case)

We define the intrinsic state and the boson condensate as

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

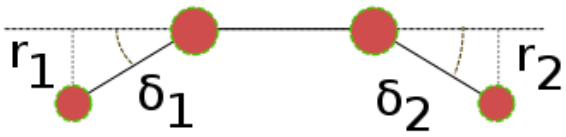
$$b^\dagger_{c,i} = \frac{1}{\sqrt{1+r^2}}\left[\sigma^\dagger_i+\left(x_i\tau^\dagger_{i,x}+y_i\tau^\dagger_{i,y}\right)\right]$$

where (r_i,θ_i) are associated to the bending angles.



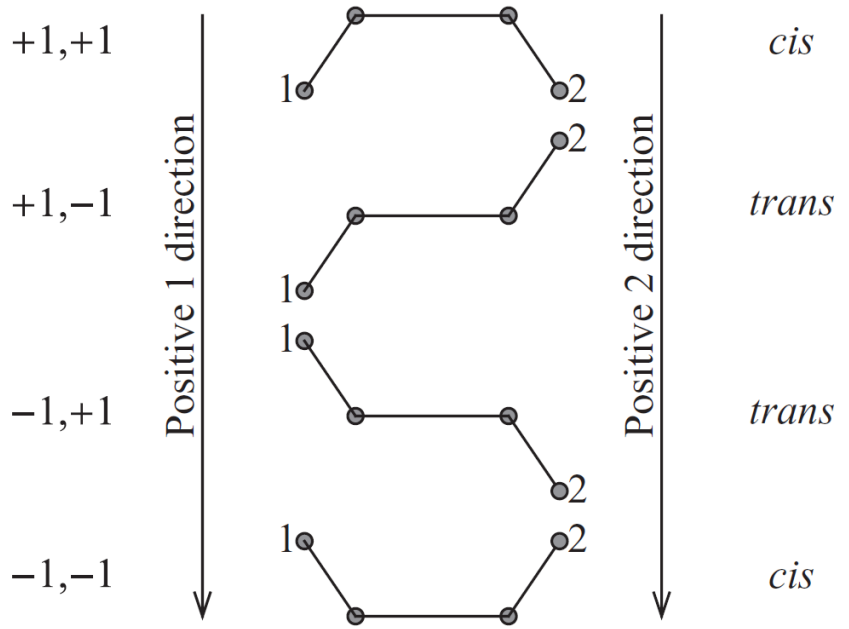
Geometrical interpretation of r_1 and r_2. Planar case.

The r_1 and r_2 parameters are related to the angles measuring the deviation from linearity and thus they are finite and can take positive or negative values.



$$r_1 = s_1 \delta_1$$

$$r_2 = s_2 \delta_2$$



Coupled Benders Model Hamiltonian Energy Functional

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

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

Coupled Benders Model Hamiltonian Energy Functional

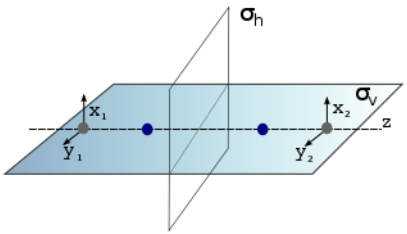
$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

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

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

$r_1 = r_2 = 0$

(C_2H_2, $\tilde{X}$)

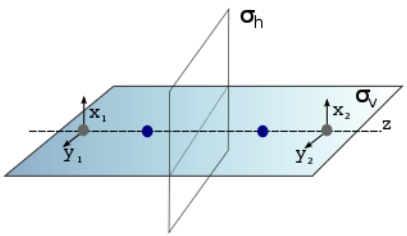


Coupled Benders Model Hamiltonian Energy Functional

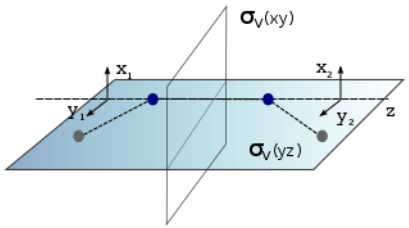
$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

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

Linear, $\mathcal{D}_{\infty h}$
$r_1 = r_2 = 0$
(C_2H_2, $\tilde{X}$)



Cis, $\mathcal{C}_{2v}$
$r_1 r_2 > 0, \phi = 0$
(C_2H_2, *cis*-$\tilde{A}$)

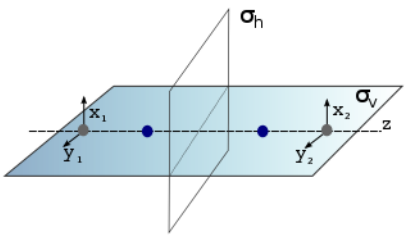


Coupled Benders Model Hamiltonian Energy Functional

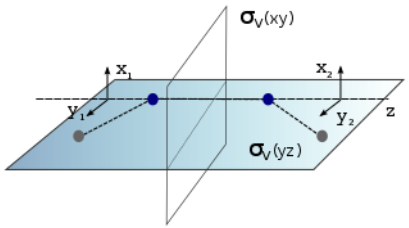
$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

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

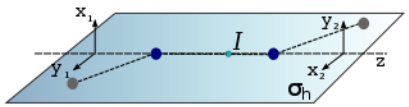
Linear, $\mathcal{D}_{\infty h}$
$r_1 = r_2 = 0$
(C_2H_2, $\tilde{X}$)



Cis, $\mathcal{C}_{2v}$
$r_1 r_2 > 0, \phi = 0$
(C_2H_2, *cis*-$\tilde{A}$)



Trans, $\mathcal{C}_{2h}$
$r_1 r_2 < 0, \phi = 0$
(C_2H_2, *trans*-$\tilde{A}$)

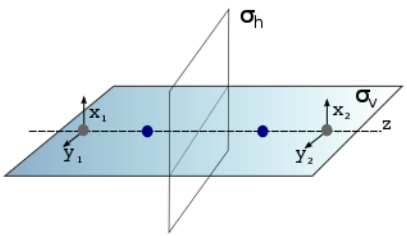


Coupled Benders Model Hamiltonian Energy Functional

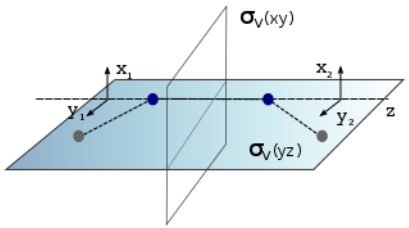
$$\hat{\mathcal{H}} = \varepsilon \left\{ (1-\xi) \left[\hat{n}_1 + \hat{n}_2 + \frac{\eta_1}{N} \hat{Q}_1 \cdot \hat{Q}_2 \right] + \frac{\xi}{N} \left[\hat{P}_1 + \hat{P}_2 + 2\eta_2 \hat{W}_1 \cdot \hat{W}_2 \right] \right\}$$

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

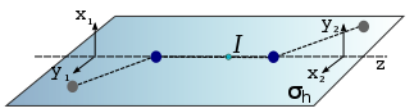
Linear, $\mathcal{D}_{\infty h}$
$r_1 = r_2 = 0$
(C_2H_2, $\tilde{X}$)



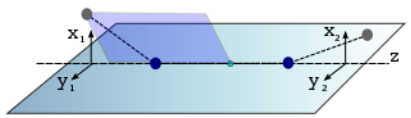
Cis, $\mathcal{C}_{2v}$
$r_1 r_2 > 0, \phi = 0$
(C_2H_2, *cis*-$\tilde{A}$)



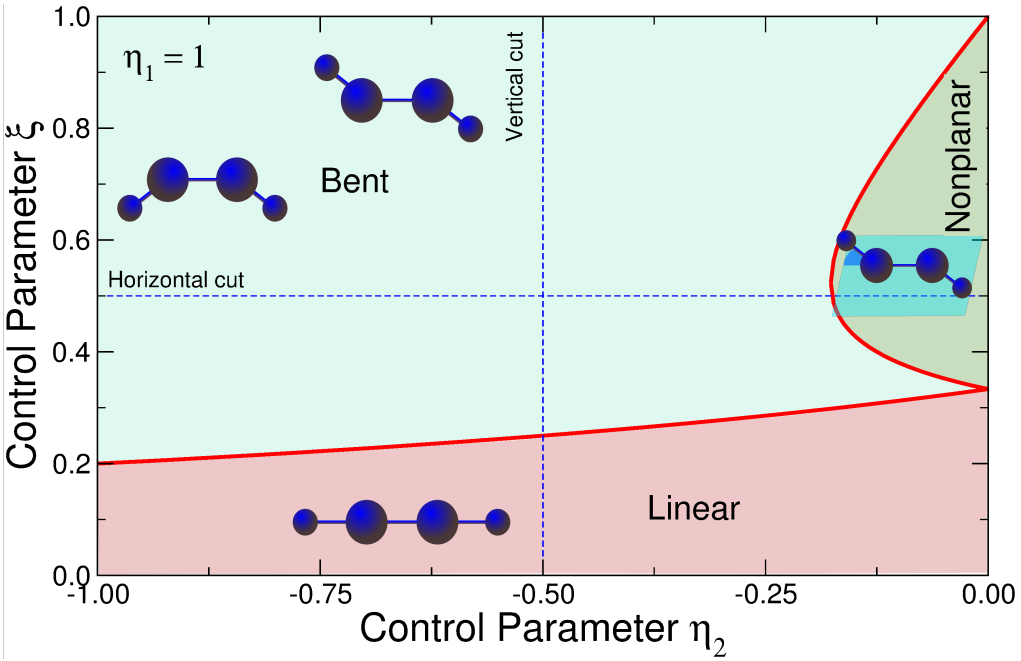
Trans, $\mathcal{C}_{2h}$
$r_1 r_2 < 0, \phi = 0$
(C_2H_2, *trans*-$\tilde{A}$)



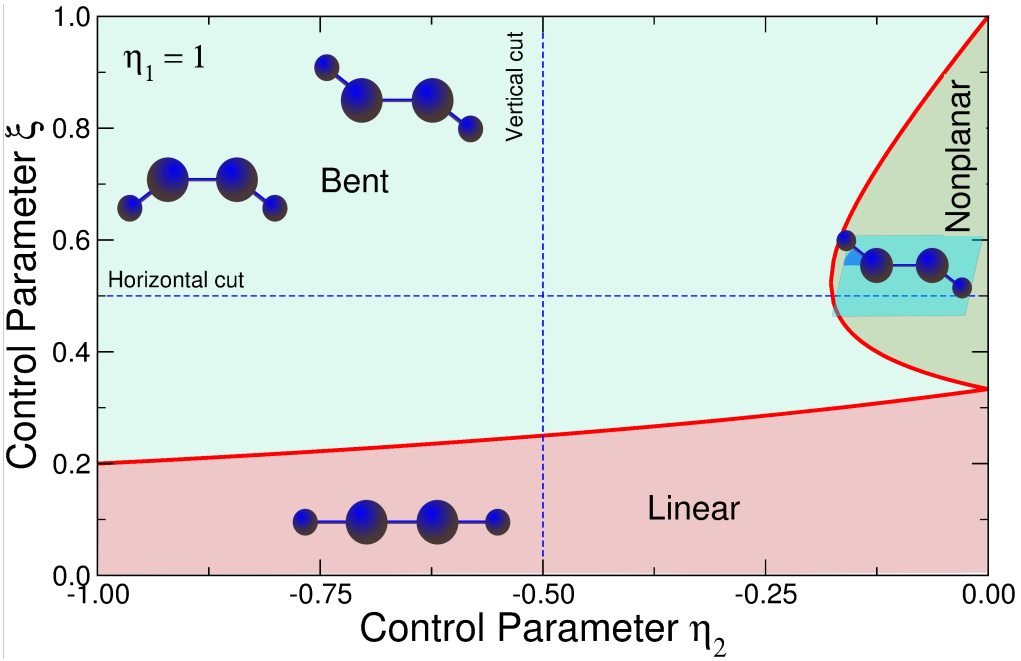
Non-planar, $\mathcal{C}_2$
$r_1 = r_2 \neq 0$
$0 < \phi \leq \frac{\pi}{2}$ (H_2O_2)

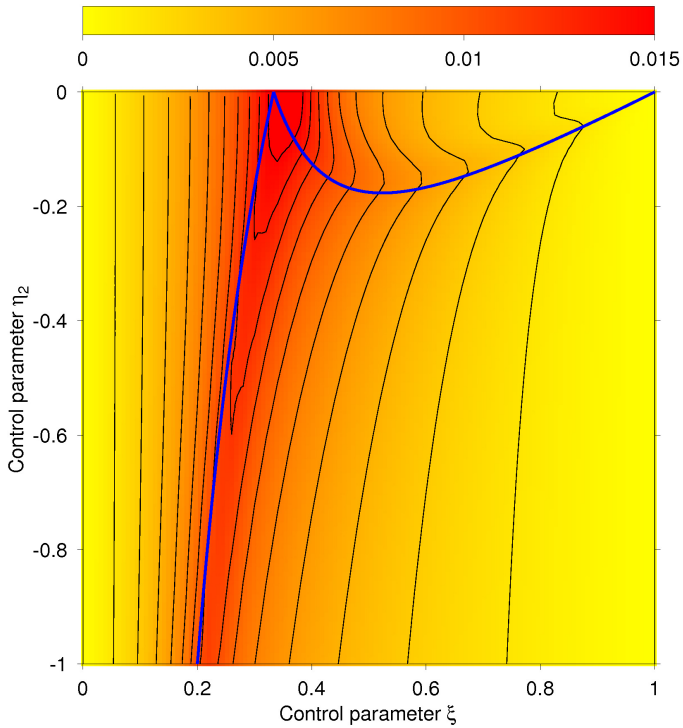


Phase diagram



Phase diagram





FPB and L. Fortunato, Phys. Lett. A 376 236 (2012)

D. Larese *et al.*, J. Chem. Phys. 140, 014304 (2014).

Outline

Symmetry adapted basis: planar *cis* ($\mathcal{C}_{2v}$) case

Starting point: Local type Ia basis

$$|[N_1, N_2]; n_1^{\ell_1} n_2^{\ell_2}\rangle = \prod_{i=1,2} N_{n_i \ell_i} \left(\sigma_i^\dagger\right)^{N_i - n_i} \left(\tau_{i,+}^\dagger\right)^{\frac{n_i+\ell_i}{2}} \left(\tau_{i,-}^\dagger\right)^{\frac{n_i-\ell_i}{2}} |0\rangle \quad ,$$

Normalization constant N_{n_i,l_i}

$$N_{n_i l_i} = \sqrt{(N_i - n_i)! \left(\frac{n_i + \ell_i}{2}\right)! \left(\frac{n_i - \ell_i}{2}\right)!} \quad .$$

Symmetry adapted basis: planar *cis* ($\mathcal{C}_{2v}$) case

Starting point: Local type Ia basis

$$|[N_1, N_2]; n_1^{\ell_1} n_2^{\ell_2}\rangle = \prod_{i=1,2} N_{n_i \ell_i} \left(\sigma_i^\dagger\right)^{N_i - n_i} \left(\tau_{i,+}^\dagger\right)^{\frac{n_i+\ell_i}{2}} \left(\tau_{i,-}^\dagger\right)^{\frac{n_i-\ell_i}{2}} |0\rangle \quad ,$$

Normalization constant N_{n_i,l_i}

$$N_{n_i l_i} = \sqrt{(N_i - n_i)! \left(\frac{n_i + \ell_i}{2}\right)! \left(\frac{n_i - \ell_i}{2}\right)!} \quad .$$

Truncated HO basis in polar coordinates (r_i, θ_i)

$$\Psi_{n_1^{\ell_1} n_2^{\ell_2}}(r_1, \theta_1, r_2, \theta_2) = \prod_{j=1,2} \mathcal{N}_{n_j \ell_j} f_{n_j \ell_j}(\alpha_j r_j) e^{i \ell_j \theta_j} \;\; ; \;\; f_{n_j \ell_j}(r_j) = r_j^{|\ell|} e^{-\frac{r_j^2}{2}} L^{|\ell_j|}_{\frac{n_j - |\ell_j|}{2}}(r_j^2)$$

with inverse oscillator length and normalization constant

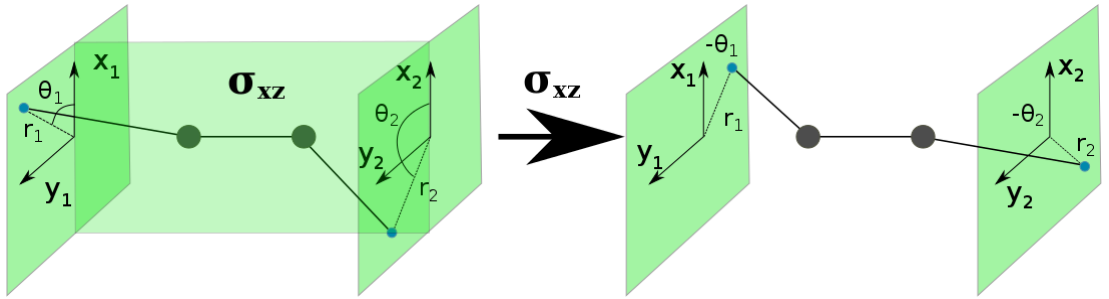
$$\alpha_j = \sqrt{\omega_j \mu_j / \hbar} \;\; ; \;\; \mathcal{N}_{n_j \ell_j} = \sqrt{\alpha_j^2 \frac{\left(\frac{n_j - |\ell_j|}{2}\right)!}{\pi \left(\frac{n_j + |\ell_j|}{2}\right)!}} \quad .$$

Symmetry adapted basis: planar *cis* ($\mathcal{C}_{2v}$) case

$\mathcal{C}_{2v}$	E	C_{2x}	σ_{xz}	σ_{xy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
A_2	1	-1	1	-1

Symmetry adapted basis: planar *cis* ($\mathcal{C}_{2v}$) case

$\mathcal{C}_{2v}$	E	C_{2x}	σ_{xz}	σ_{xy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
A_2	1	-1	1	-1

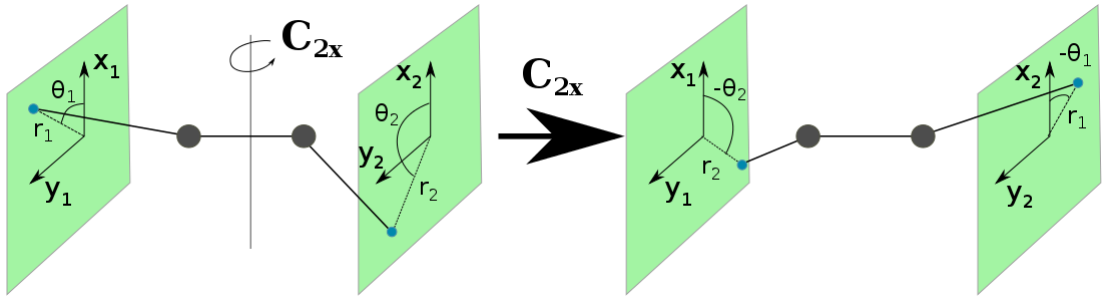


σ_{xz} $\theta_1 \rightarrow -\theta_1$ and $\theta_2 \rightarrow -\theta_2$

σ_{xz} $\sigma_{xz}|n_1^{\ell_1} n_2^{\ell_2}\rangle = |n_1^{-\ell_1} n_2^{-\ell_2}\rangle$

Symmetry adapted basis: planar *cis* ($\mathcal{C}_{2v}$) case

$\mathcal{C}_{2v}$	E	C_{2x}	σ_{xz}	σ_{xy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
A_2	1	-1	1	-1



σ_{xz} $\theta_1 \to -\theta_1$ and $\theta_2 \to -\theta_2$

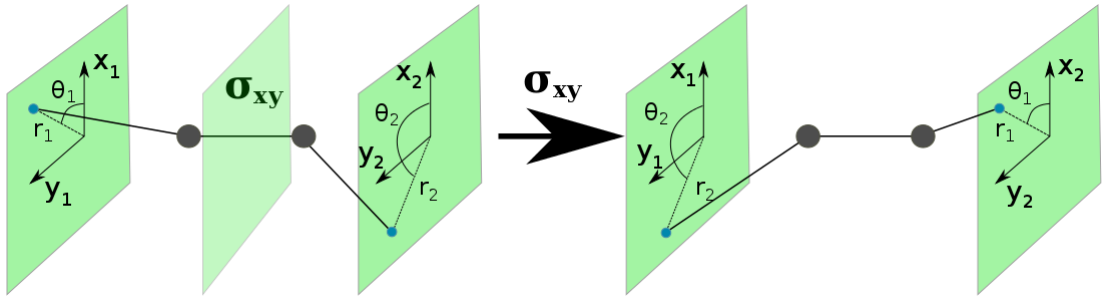
C_{2x} $\theta_1 \to -\theta_2$ and $\theta_2 \to -\theta_1$

σ_{xz} $\sigma_{xz}|n_1^{\ell_1} n_2^{\ell_2}\rangle = |n_1^{-\ell_1} n_2^{-\ell_2}\rangle$

C_{2x} $C_{2x}|n_1^{\ell_1} n_2^{\ell_2}\rangle = |n_2^{-\ell_2} n_1^{-\ell_1}\rangle$

Symmetry adapted basis: planar *cis* ($\mathcal{C}_{2v}$) case

$\mathcal{C}_{2v}$	E	C_{2x}	σ_{xz}	σ_{xy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
A_2	1	-1	1	-1



σ_{xz} $\theta_1 \to -\theta_1$ and $\theta_2 \to -\theta_2$

C_{2x} $\theta_1 \to -\theta_2$ and $\theta_2 \to -\theta_1$

σ_{xy} $\theta_1 \to \theta_2$ and $\theta_2 \to \theta_1$

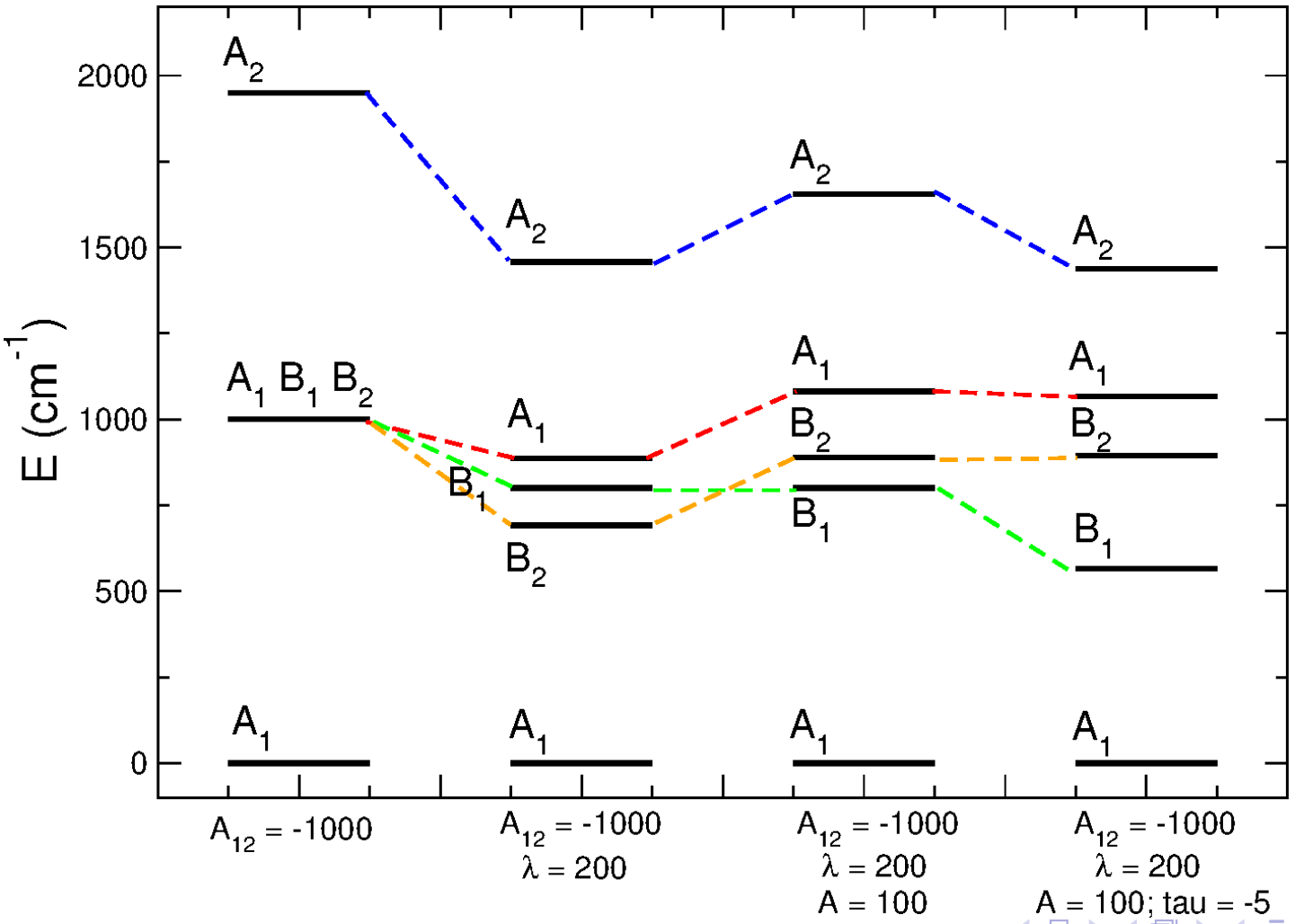
σ_{xz} $\sigma_{xz}|n_1^{\ell_1} n_2^{\ell_2}\rangle = |n_1^{-\ell_1} n_2^{-\ell_2}\rangle$

C_{2x} $C_{2x}|n_1^{\ell_1} n_2^{\ell_2}\rangle = |n_2^{-\ell_2} n_1^{-\ell_1}\rangle$

σ_{xy} $\sigma_{xy}|n_1^{\ell_1} n_2^{\ell_2}\rangle = |n_2^{\ell_2} n_1^{\ell_1}\rangle$

The symmetry adapted basis is built through diagonalization of a CSCO, in particular $O_{CSCO} = 3C_{2x} + \sigma_{xz}$.

Schematic spectrum for a *Cis* molecular species

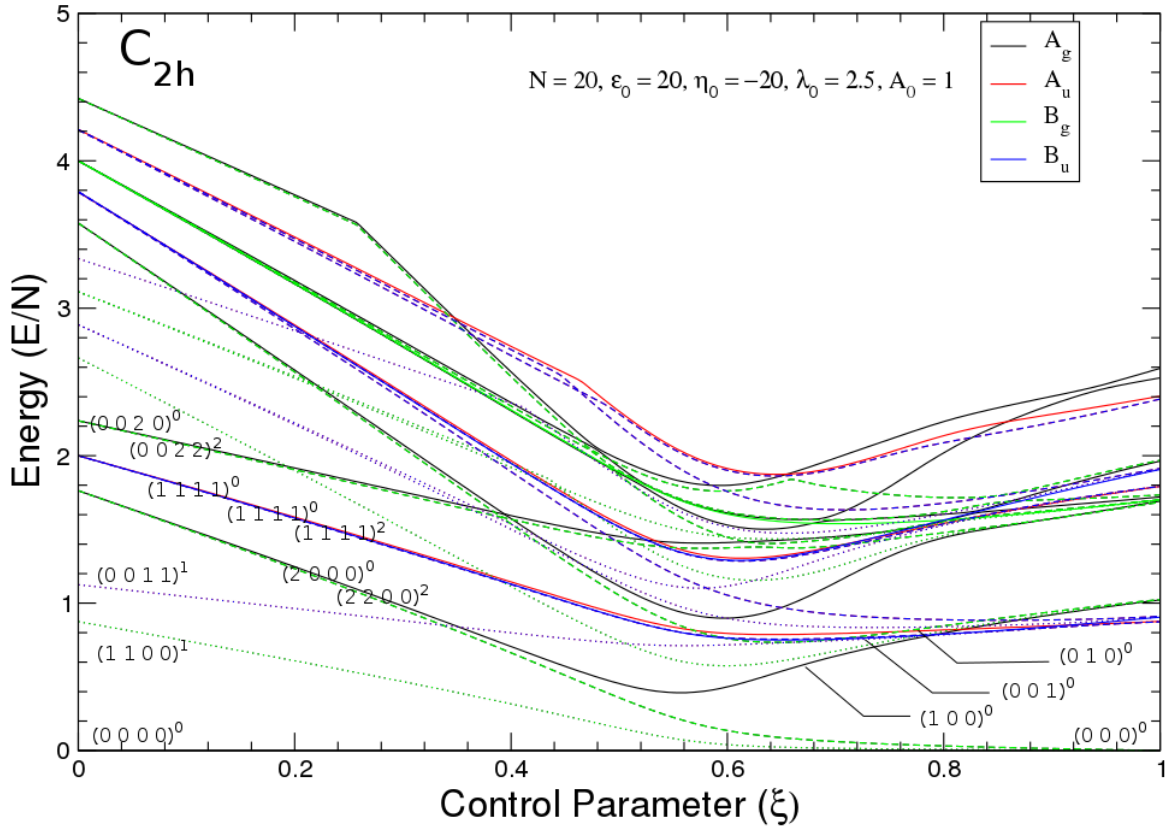


Correlation energy diagram: from linear to *trans* configuration

$$\hat{\mathcal{H}}/\varepsilon = (1-\xi)\epsilon_0\left(\hat{n}_1+\hat{n}_2\right)+\xi\left[A_0\frac{\hat{P}_1+\hat{P}_2}{N}+2\eta_{20}\frac{\hat{W}_1\cdot\hat{W}_2}{N}\right] \quad (1)$$
$$+2\left(\xi-\frac{1}{2}\right)\lambda_0\frac{\hat{M}}{N}$$

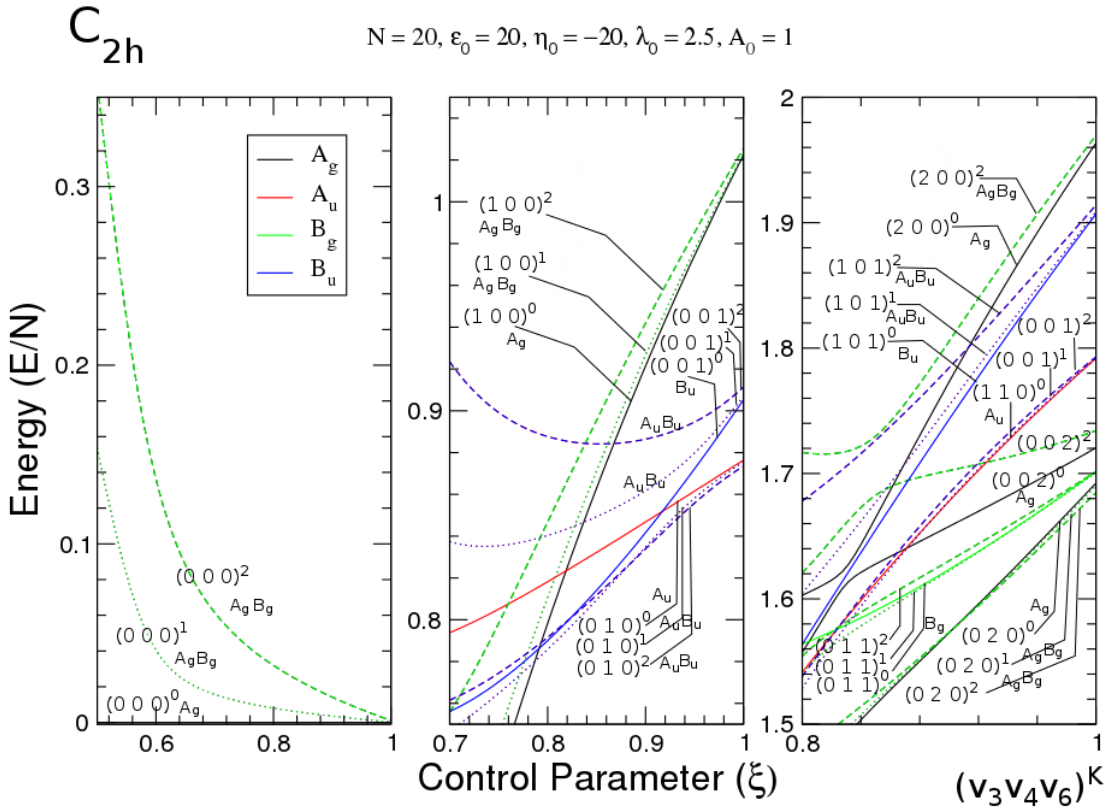
Correlation energy diagram: from linear to *trans* configuration

$$\hat{\mathcal{H}}/\varepsilon = (1-\xi)\epsilon_0\left(\hat{n}_1+\hat{n}_2\right)+\xi\left[A_0\frac{\hat{P}_1+\hat{P}_2}{N}+2\eta_{20}\frac{\hat{W}_1\cdot\hat{W}_2}{N}\right]+2\left(\xi-\frac{1}{2}\right)\lambda_0\frac{\hat{M}}{N}\ ,$$



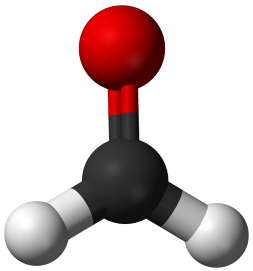
Correlation energy diagram: from linear to *trans* configuration

$$\hat{\mathcal{H}}/\varepsilon = (1-\xi)\epsilon_0\left(\hat{n}_1+\hat{n}_2\right)+\xi\left[A_0\frac{\hat{P}_1+\hat{P}_2}{N}+2\eta_{20}\frac{\hat{W}_1\cdot\hat{W}_2}{N}\right]+2\left(\xi-\frac{1}{2}\right)\lambda_0\frac{\hat{M}}{N}\ ,$$



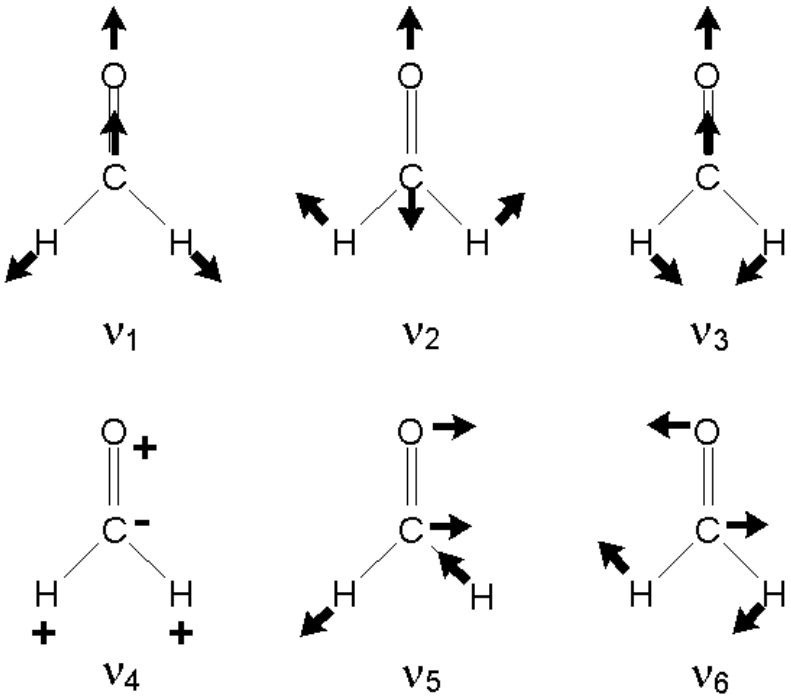
Outline

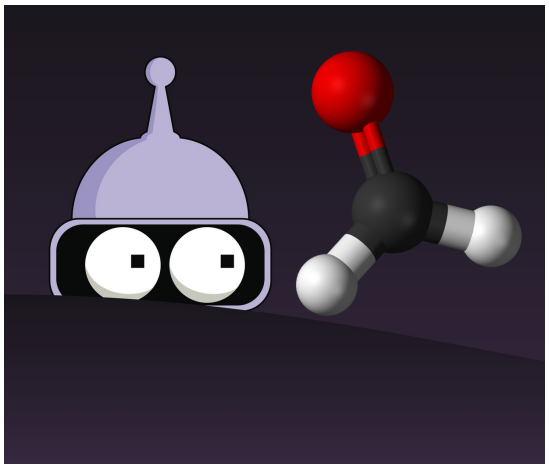
Formaldehyde normal modes of vibration



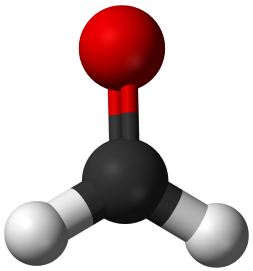
Point group symmetry $\mathcal{C}_{2v}$

$3N - 6 = 6$ non-degenerate normal modes of vibration.



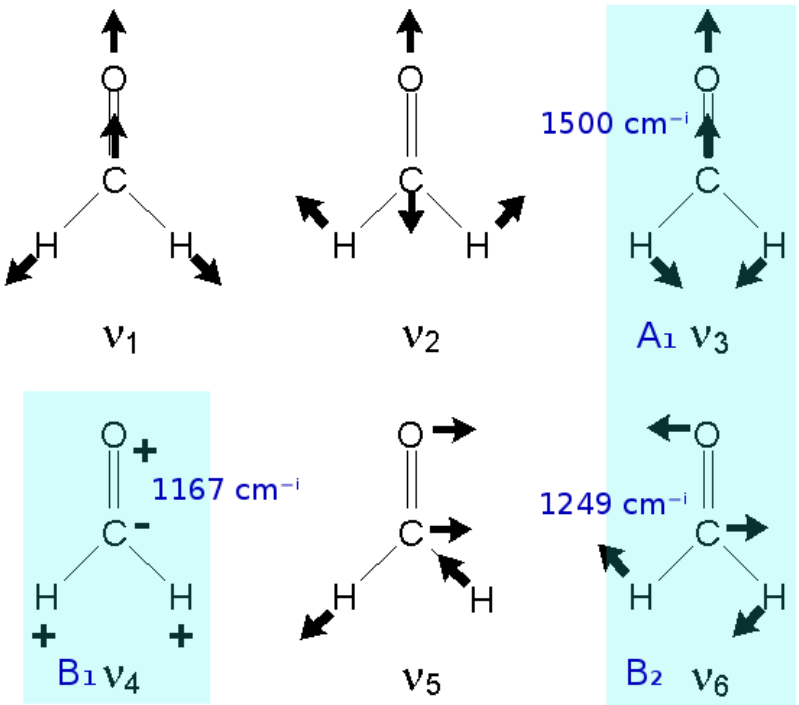


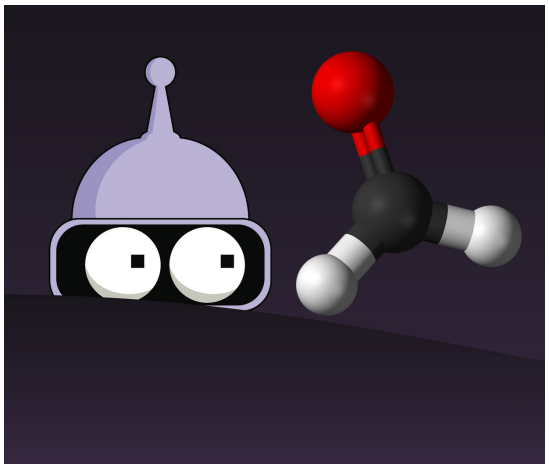
Formaldehyde normal modes of vibration



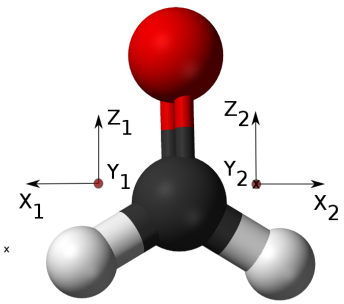
Point group symmetry $\mathcal{C}_{2v}$

$3N - 6 = 6$ non-degenerate normal modes of vibration.



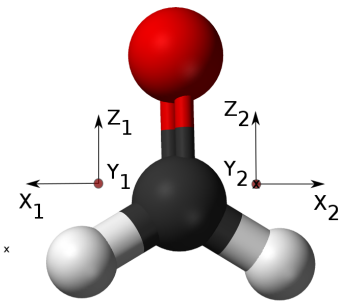


Fit to formaldehyde bending spectrum



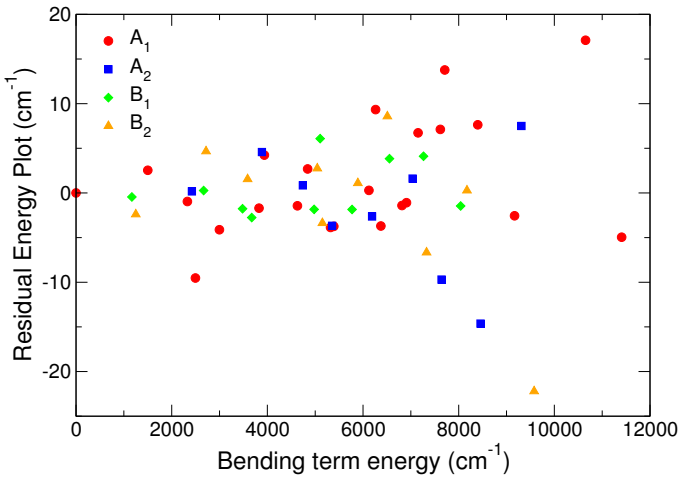
$$\hat{H}_C = \frac{A_1}{N}(\hat{P}_1 + \hat{P}_2) + \frac{\eta_2}{N}\hat{W}_1 \cdot \hat{W}_2 + \frac{\lambda_1}{N} + \frac{A_{11}}{N^2}(\hat{P}_1^2 + \hat{P}_2^2)\hat{M}_C$$
$$+ \frac{A_{12}}{N^2}(\hat{P}_1\hat{P}_2) + \frac{A\eta_2}{N^2}\left[(\hat{P}_1 + \hat{P}_2)\cdot(\hat{W}_1 \cdot \hat{W}_2)\right]_+ + \frac{A\lambda_1}{N^2}\left[(\hat{P}_1 + \hat{P}_2)\hat{M}_C\right]_+$$
$$+ \frac{\eta_{22}}{N^2}(\hat{W}_1 \cdot \hat{W}_2)^2 + \frac{\lambda\eta_2}{N^2}\left[(\hat{W}_1 \cdot \hat{W}_2)\cdot\hat{M}_C\right]_+ + \frac{\lambda_{11}}{N^2}(\hat{M}_C)^2 \ ,$$

Fit to formaldehyde bending spectrum



$$\hat{H}_C = \frac{A_1}{N}(\hat{P}_1+\hat{P}_2) + \frac{\eta_2}{N}\hat{W}_1\cdot\hat{W}_2 + \frac{\lambda_1}{N} + \frac{A_{11}}{N^2}(\hat{P}_1^2+\hat{P}_2^2)\hat{M}_C + \frac{A_{12}}{N^2}(\hat{P}_1\hat{P}_2) + \frac{A\eta_2}{N^2}\left[(\hat{P}_1+\hat{P}_2)\cdot(\hat{W}_1\cdot\hat{W}_2)\right]_+ + \frac{A\lambda_1}{N^2}\left[(\hat{P}_1+\hat{P}_2)\hat{M}_C\right]_+ + \frac{\eta_{22}}{N^2}(\hat{W}_1\cdot\hat{W}_2)^2 + \frac{\lambda\eta_2}{N^2}\left[(\hat{W}_1\cdot\hat{W}_2)\cdot\hat{M}_C\right]_+ + \frac{\lambda_{11}}{N^2}(\hat{M}_C)^2 \ ,$$

N_{data}	rms (cm^{-1})	N
52	6.2	80
A_1 (cm^{-1})	η_2 (cm^{-1})	λ_1 (cm^{-1})
467.71	−1763.23	550.46
A_{11} (cm^{-1})	A_{12} (cm^{-1})	$A\eta_2$ (cm^{-1})
−13.098	8.8980	−11.2666
$A\lambda_1$ (cm^{-1})	η_{22} (cm^{-1})	$A\eta_2$ (cm^{-1})
−6.26605	16.3662	−15.2127



Concluding Remarks

- Take-home message: algebraic methods based on symmetry considerations are a powerful tool for the modeling of many physical systems, in particular molecular structure.
- Molecular spectroscopy can access highly–excited states giving experimental evidence for QPTs and ESQPTs.
- Coupled systems display a rich gamut of interesting physical situations where the phase transition formalism can thrive.
- Many interesting open questions and problems: experimental study of QPT and ESQPT, ESQPT in coupled systems, normal-local transitions in benders, continuum effects in algebraic models, endohedral systems, lattice systems...

Concluding Remarks

- Take-home message: algebraic methods based on symmetry considerations are a powerful tool for the modeling of many physical systems, in particular molecular structure.
- Molecular spectroscopy can access highly–excited states giving experimental evidence for QPTs and ESQPTs.
- Coupled systems display a rich gamut of interesting physical situations where the phase transition formalism can thrive.
- Many interesting open questions and problems: experimental study of QPT and ESQPT, ESQPT in coupled systems, normal-local transitions in benders, continuum effects in algebraic models, endohedral systems, lattice systems...

Thanks for your kind attention...

The Usual Suspects

- Francesco Iachello, Patrick H. Vaccaro (Yale University, USA)
- Andrea Vitturi, Lorenzo Fortunato (Padova University, Italy)
- Jorge Dukelsky and Armando Relaño (IEM-CSIC, Spain)
- Pavel Cejnar (Charles University, Czech Republic)
- Piet van Isacker (GANIL, France)
- Manuel Calixto and Elvira Romera (University of Granada, Spain)
- Octavio Castaños, Renato Lemus, Alejandro Frank (ICN-UNAM, Mexico)
- José Miguel Arias, Miguel Carvajal, José E. García-Ramos, **CPB**, Pedro Pérez-Fernández (US-UHU, Spain)