5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$
    State labels by symmetry $O(3) \supset D_{\infty h}$
        Coriolis and λ-doubling levels
    Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
    Tableau dimension formulae for X_4 and XY_4 molecules
        CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
    Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
    Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
    Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
    Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES)   (UnZIPPed)
    REES for high-J Coriolis spectra in SF_6
    REES for high-J Coriolis spectra in υ_3 CF_4
.   REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

AMOP reference links *(Updated list given on **2nd** and 3rd pages of each class presentation)*

Web Resources - front page
UAF Physics UTube channel

Quantum Theory for the Computer Age
Principles of Symmetry, Dynamics, and Spectroscopy
Classical Mechanics with a Bang!
Modern Physics and its Classical Foundations

2014 AMOP
2017 Group Theory for QM
2018 AMOP

Representaions Of Multidimensional Symmetries In Networks - harter-jmp-1973

Alternative Basis for the Theory of Complex Spectra

- Alternative_Basis_for_the_Theory_of_Complex_Spectra_I_-_harter-pra-1973
- Alternative_Basis_for_the_Theory_of_Complex_Spectra_II_-_harter-patterson-pra-1976
- Alternative_Basis_for_the_Theory_of_Complex_Spectra_III_-_patterson-harter-pra-1977

Frame Transformation Relations And Multipole Transitions In Symmetric Polyatomic Molecules - RMP-1978
Asymptotic eigensolutions of fourth and sixth rank octahedral tensor operators - Harter-Patterson-JMP-1979
Rotational energy surfaces and high- J eigenvalue structure of polyatomic molecules - Harter - Patterson - 1984
Galloping waves and their relativistic properties - ajp-1985-Harter
Rovibrational Spectral Fine Structure Of Icosahedral Molecules - Cpl 1986 (Alt Scan)

Theory of hyperfine and superfine levels in symmetric polyatomic molecules.

I) Trigonal and tetrahedral molecules: Elementary spin-1/2 cases in vibronic ground states - PRA-1979-Harter-Patterson (Alt scan)
II) Elementary cases in octahedral hexafluoride molecules - Harter-PRA-1981 (Alt scan)

Rotation–vibration spectra of icosahedral molecules.

I) Icosahedral symmetry analysis and fine structure - harter-weeks-jcp-1989 (Alt scan)
II) Icosahedral symmetry, vibrational eigenfrequencies, and normal modes of buckminsterfullerene - weeks-harter-jcp-1989 (Alt scan)
III) Half-integral angular momentum - harter-reimer-jcp-1991

Rotation-vibration scalar coupling zeta coefficients and spectroscopic band shapes of buckminsterfullerene - Weeks-Harter-CPL-1991 (Alt scan)
Nuclear spin weights and gas phase spectral structure of 12C60 and 13C60 buckminsterfullerene -Harter-Reimer-Cpl-1992 - (Alt1, Alt2 Erratum)
Gas Phase Level Structure of C60 Buckyball and Derivatives Exhibiting Broken Icosahedral Symmetry - reimer-diss-1996
Fullerene symmetry reduction and rotational level fine structure/ the Buckyball isotopomer 12C 13C59 - jcp-Reimer-Harter-1997 (HiRez)
Wave Node Dynamics and Revival Symmetry in Quantum Rotors - harter - jms - 2001
Molecular Symmetry and Dynamics - Ch32-Springer Handbooks of Atomic, Molecular, and Optical Physics - Harter-2006

Resonance and Revivals

I) QUANTUM ROTOR AND INFINITE-WELL DYNAMICS - ISMSLi2012 (Talk) OSU knowledge Bank
II) Comparing Half-integer Spin and Integer Spin - Alva-ISMS-Ohio2013-R777 (Talks)
III) Quantum Resonant Beats and Revivals in the Morse Oscillators and Rotors - (2013-Li-Diss)

Resonance and Revivals in Quantum Rotors - Comparing Half-integer Spin and Integer Spin - Alva-ISMS-Ohio2013-R777 (Talk)
Molecular Eigensolution Symmetry Analysis and Fine Structure - IJMS-harter-mitchell-2013
Quantum Revivals of Morse Oscillators and Farey-Ford Geometry - Li-Harter-cpl-2013
QTCA Unit 10 Ch 30 - 2013
AMOP Ch 0 Space-Time Symmetry - 2019

**In development - a web based A.M.O.P. oriented reference page, with thumbnail/previews, greater control over the information display, and eventually full on* Apache-SOLR *Index and search for* nuanced, whole-site content/metadata level *searching.*

AMOP reference links *(Updated list given on 2nd and 3rd pages of each class presentation)*

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 ,   QTCA Unit 7 Ch. 23-26),   (PSDS - Ch. 5, 7)

Int.J.Mol.Sci, 14, 714(2013), QTCA Unit 8 Ch. 23-25, QTCA Unit 9 Ch. 26, PSDS Ch. 5, PSDS Ch. 7

Intro spin ½ coupling
Unit 8 Ch. 24 p3

H atom hyperfine-B-level crossing
Unit 8 Ch. 24 p15

Hyperf. theory Ch. 24 p48.

Hyperf. theory Ch. 24 p48.
Deeper theory ends p53

Intro 2p3p coupling
Unit 8 Ch. 24 p17.

Intro LS-jj coupling
Unit 8 Ch. 24 p22.

CG coupling derived (start)
Unit 8 Ch. 24 p39.

CG coupling derived (formula)
Unit 8 Ch. 24 p44.

Lande' g-factor
Unit 8 Ch. 24 p26.

Irrep Tensor building
Unit 8 Ch. 25 p5.

Irrep Tensor Tables
Unit 8 Ch. 25 p12.

Wigner-Eckart tensor Theorem.
Unit 8 Ch. 25 p17.

Tensors Applied to d,f-levels.
Unit 8 Ch. 25 p21.

Tensors Applied to high J levels.
Unit 8 Ch. 25 p63.

Intro 3-particle coupling.
Unit 8 Ch. 25 p28.

Intro 3,4-particle Young Tabl
GrpThLect29 p42.

Young Tableau Magic Formu
GrpThLect29 p46-48.

**In development - a web based A.M.O.P. oriented reference page, with thumbnail/previews, greater control over the information display, and eventually full on* Apache-SOLR *Index and search for* nuanced, whole-site content/metadata level *searching.*

AMOP reference links *(Updated list given on 2nd and* ***3rd*** *and* ***4th*** *pages of each class presentation)*

Predrag Cvitanovic's: Birdtrack Notation, Calculations, and Simplification

Chaos_Classical_and_Quantum_-_2018-Cvitanovic-ChaosBook
Group Theory - PUP_Lucy_Day_-_Diagrammatic_notation_-_Ch4
Simplification_Rules_for_Birdtrack_Operators_-_Alcock-Zeilinger-Weigert-zeilinger-jmp-2017
Group Theory - Birdtracks_Lies_and_Exceptional_Groups_-_Cvitanovic-2011
Simplification_rules_for_birdtrack_operators-_jmp-alcock-zeilinger-2017
Birdtracks for SU(N) - 2017-Keppeler

Frank Rioux's: UMA method of vibrational induction

Quantum_Mechanics_Group_Theory_and_C60_-_Frank_Rioux_-_Department_of_Chemistry_Saint_Johns_U
Symmetry_Analysis_for_H20-_H20GrpTheory-_Rioux
Quantum_Mechanics-Group_Theory_and_C60_-_JChemEd-Rioux-1994
Group_Theory_Problems-_Rioux-_SymmetryProblemsX
Comment_on_the_Vibrational_Analysis_for_C60_and_Other_Fullerenes_Rioux-RSP

Supplemental AMOP Techniques & Experiment

Many Correlation Tables are Molien Sequences - Klee (Draft 2016)
High-resolution_spectroscopy_and_global_analysis_of_CF4_rovibrational_bands_to_model_its_atmospheric_absorption-_carlos-Boudon-jqsrt-2017
Symmetry and Chirality - Continuous_Measures_-_Avnir
*

Special Topics & Colloquial References

r-process_nucleosynthesis_from_matter_ejected_in_binary_neutron_star_mergers-PhysRevD-Bovard-2017

**In development - a web based A.M.O.P. oriented reference page, with thumbnail/previews, greater control over the information display, and eventually full on* Apache-SOLR *Index and search for* nuanced, whole-site content/metadata level *searching.*

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

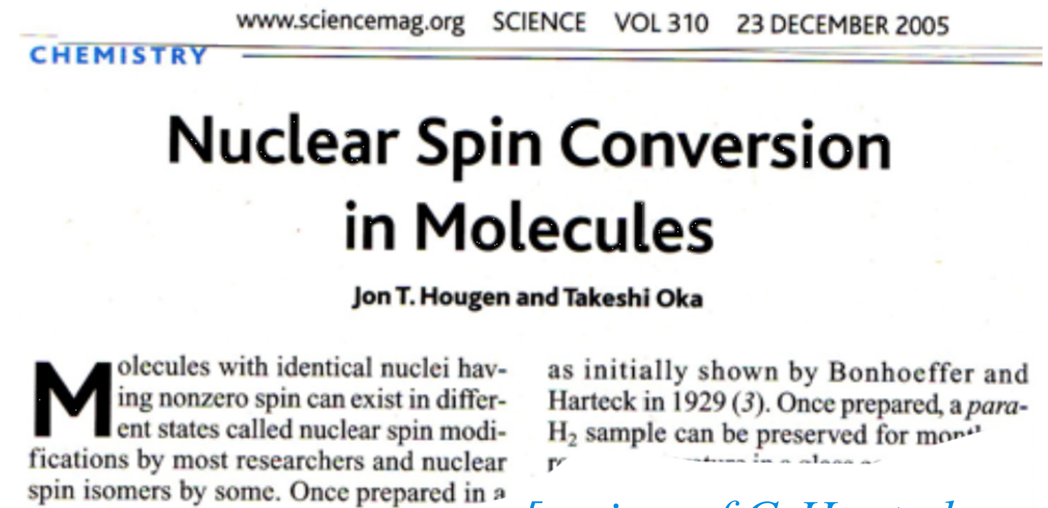
Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$
State labels by symmetry $O(3) \supset D_{\infty h}$
Coriolis and λ-doubling levels
Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
Tableau dimension formulae for X_4 and XY_4 molecules
CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)
REES for high-J Coriolis spectra in SF_6
REES for high-J Coriolis spectra in υ_3 CF_4
. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

CONSERVATION OF ROVIBRONIC SPIN-SPECIES - *Two Views:*

Old *versus* ***New (1978- 2005)***

(1939, 1945, and 1966)


www.sciencemag.org SCIENCE VOL 310 23 DECEMBER 2005

CHEMISTRY

Nuclear Spin Conversion in Molecules

Jon T. Hougen and Takeshi Oka

Molecules with identical nuclei having nonzero spin can exist in different states called nuclear spin modifications by most researchers and nuclear spin isomers by some. Once prepared in a ... as initially shown by Bonhoeffer and Harteck in 1929 (3). Once prepared, a *para*-H_2 sample can be preserved for mon...

[review of C_2H_4 study: Sun, Takagi, Matsushima, Science ***310****, 1938(2005)]*

"...transitions between...species (A_1,..E,..T_2..) ...are **very strictly forbidden***..."*

Strictly *versus* ***NOT!***

Conservation and preservation?

...for diatomic molecules...I p. 150
...for D_2 asymmetric tops...II p.468
...for D_n symmetric tops...II p.415
...for O-T_d spherical tops...II p.441-453

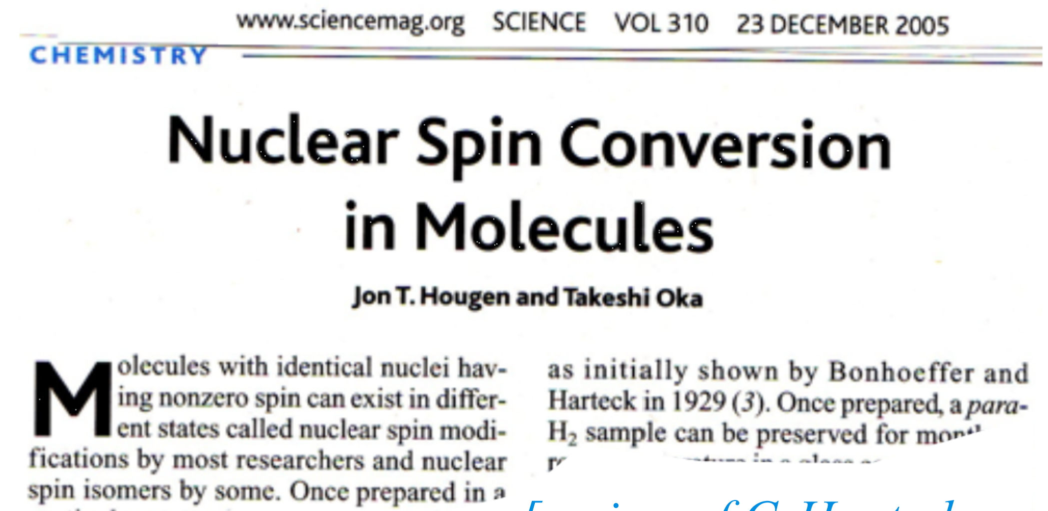
No Way! *versus* ***WAY!***

Conversion, perversion or transition?

...during transitions involving...
...rotational states,...III p.246
...vibrational states,... " "
... electronic states,... " "
... collisional states... " "

CONSERVATION OF ROVIBRONIC SPIN-SPECIES - *Two Views:*

Old *(1939, 1945, and 1966)* *versus* **New (1978- 2005)**


www.sciencemag.org SCIENCE VOL 310 23 DECEMBER 2005

CHEMISTRY

Nuclear Spin Conversion in Molecules

Jon T. Hougen and Takeshi Oka

Molecules with identical nuclei having nonzero spin can exist in different states called nuclear spin modifications by most researchers and nuclear spin isomers by some. Once prepared in a ... as initially shown by Bonhoeffer and Harteck in 1929 (3). Once prepared, a *para*-H_2 sample can be preserved for mont...

*[review of C_2H_4 study: Sun, Takagi, Matsushima, Science **310**, 1938(2005)]*

"...transitions between...species (A_1,..E,..T_2..) ...are **very strictly forbidden** *..."*

Strictly *versus* **NOT!**

...for diatomic molecules...I p. 150
...for D_2 asymmetric tops...II p.468
...for D_n symmetric tops...II p.415
...for O-T_d spherical tops...II p.441-453

Conservation and preservation?

To conserve vs. To convert

To preserve vs. To pervert

No Way! *versus* **WAY!**

...during transitions involving...
...rotational states,...III p.246
...vibrational states,... " "
... electronic states,... " "
... collisional states... " "

Conversion, perversion or transition?

Widespread and extreme mixing of species reported in CF4, SiF_4 and SF_6 :

perversion

Ch. Borde, Phys. Rev. ***A20****,254(1978)(expt.)*
Harter, Phys. Rev. ***A24****,192 (1981)(theory)*

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? *versus* ***What mixes it up?***

No Way!

WAY!

and...

What is it?

SPIN SYMMETRY correlation has a new name...

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? *versus* ***What mixes it up?***

No Way!

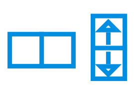
WAY!

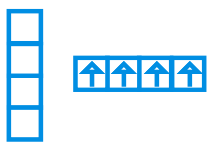
and...

What is it?

SPIN SYMMETRY correlation ***has a new name...***

it's now called ENTANGLEMENT!





Herzberg's terms:
"..Overall ...symmetry..."

Better terms:
..Under-all ... or internal symmetry...spin frame..... "Bare" rotor

(From an overall "Coupled" state we SUBTRACT *vibronic "Activity" to get underlying "Bare" rotor.)*

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

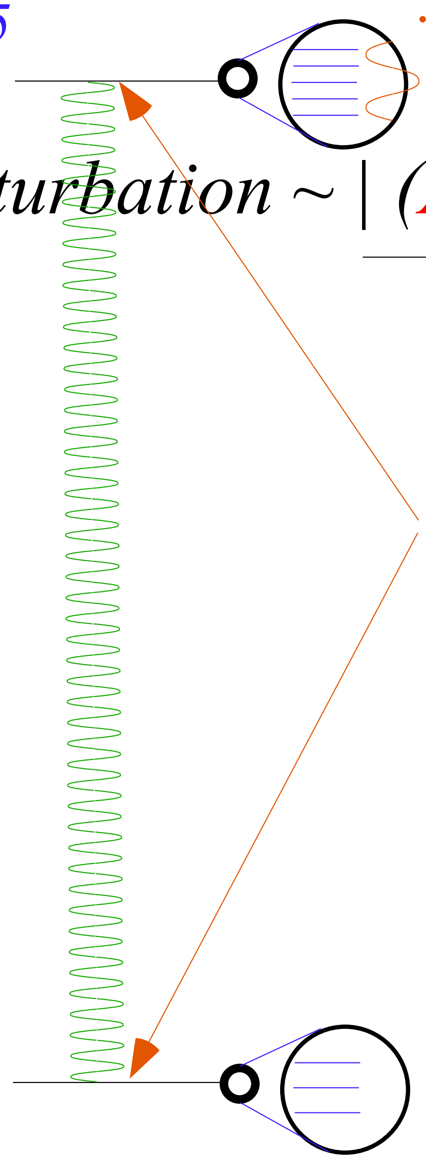
What preserves it? versus *What messes it up?*

$A_{2u}{}^{1}$

No Way!

...because nuclear moments...
...are so very slight...”

$E_{2g}{}^{5}$



$A_{1g}{}^{3}$

...too darn small (~kHz)...

$$\text{perturbation} \sim \frac{|\,(A_{1g}{}^{3}|\text{spin-rovib.}|E_{2g}{}^{5})\,|^2}{E_{A_{1g}{}^{3}} - E_{E_{2g}{}^{5}}}$$

...too darn big (*like*10MHz)...

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

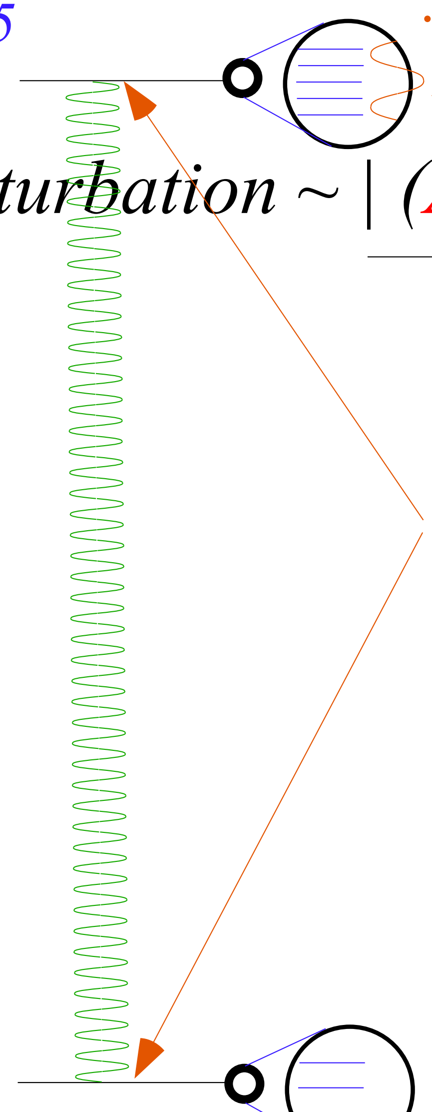
What preserves it? versus **What mixes it up?**

$A_{2u}^{\ 1}$

No Way!

"...because nuclear moments...
...are so very slight..."

$E_{2g}^{\ 5}$

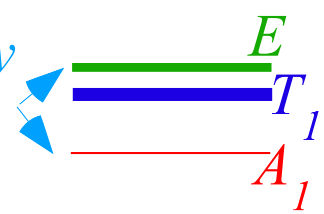


...too darn small (~kHz)...

$$\text{perturbation} \sim \frac{|\,(A_{1g}^{\ 3}|\text{spin-rovib.}|E_{2g}^{\ 5})\,|^2}{E_{A_{1g}^{\ 3}} - E_{E_{2g}^{\ 5}}}$$

...too darn big (*like* 10MHz)...

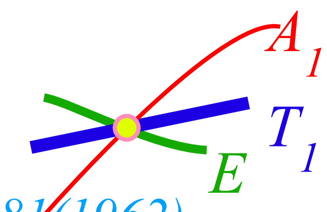
...exponentially tiny! (like 10^{-50}Hz)



$A_{1g}^{\ 3}$

WAY!

...because levels of different species are forced together by angular wave localization or "level-clustering" or (rarely) by "accidental" degeneracy.



"Accidental" degeneracy
Lea, Leask & Wolf JPCSol.23,1381(1962)

Level-clustering
Dorney and Watson JMS 42,135(1972)
Harter and Patterson PRL38,224(1977)
JCP 66,4872(1977)

RE Surface precession vs. tunneling
Harter and Patterson JMP 20,1453(1979)
JCP 80,4241(1984)

RE Superhyperfine transitions
Hyperfine effects may rule! A_1 T_1 E T_2 A_2 get seriously mixed up.

Harter, Patterson, and daPaixao, Rev.Mod.Phys. 50, 37(1978)
Harter and Patterson, Phys. Rev. A19,2277(1979) (CF_4)
Harter, Phys. Rev. A24,192-262(1981) (SF_6)

JPCS=Journal Phys. Chem. Solids
JMS=Journal Molecular Spectroscopy
PRL=Phys. Rev. Letters
JCP=Journal of Chemical Physics
JMP=Journal of Mathematical Physics

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

State labels by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling “hook-up” vs. stronger “BOA-constricted” wavefunctions

Semiclassical Rotor-“Gyro”-Spin coupling

Semiclassical Rotor-“Gyro”-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

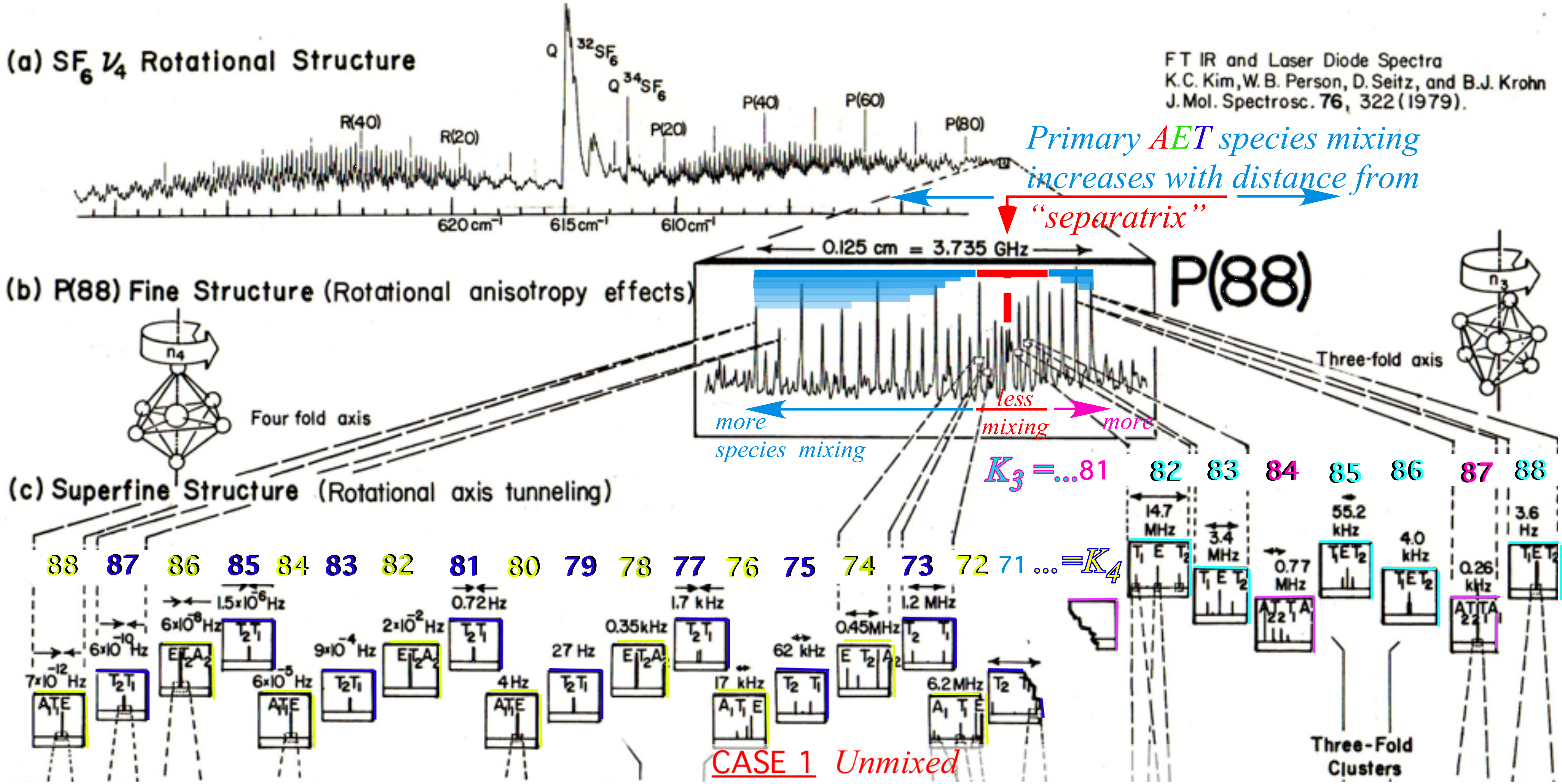
REES for high-J Coriolis spectra in SF_6

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

*ZIPP (Zero-Interaction-Potential-`Proximation

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

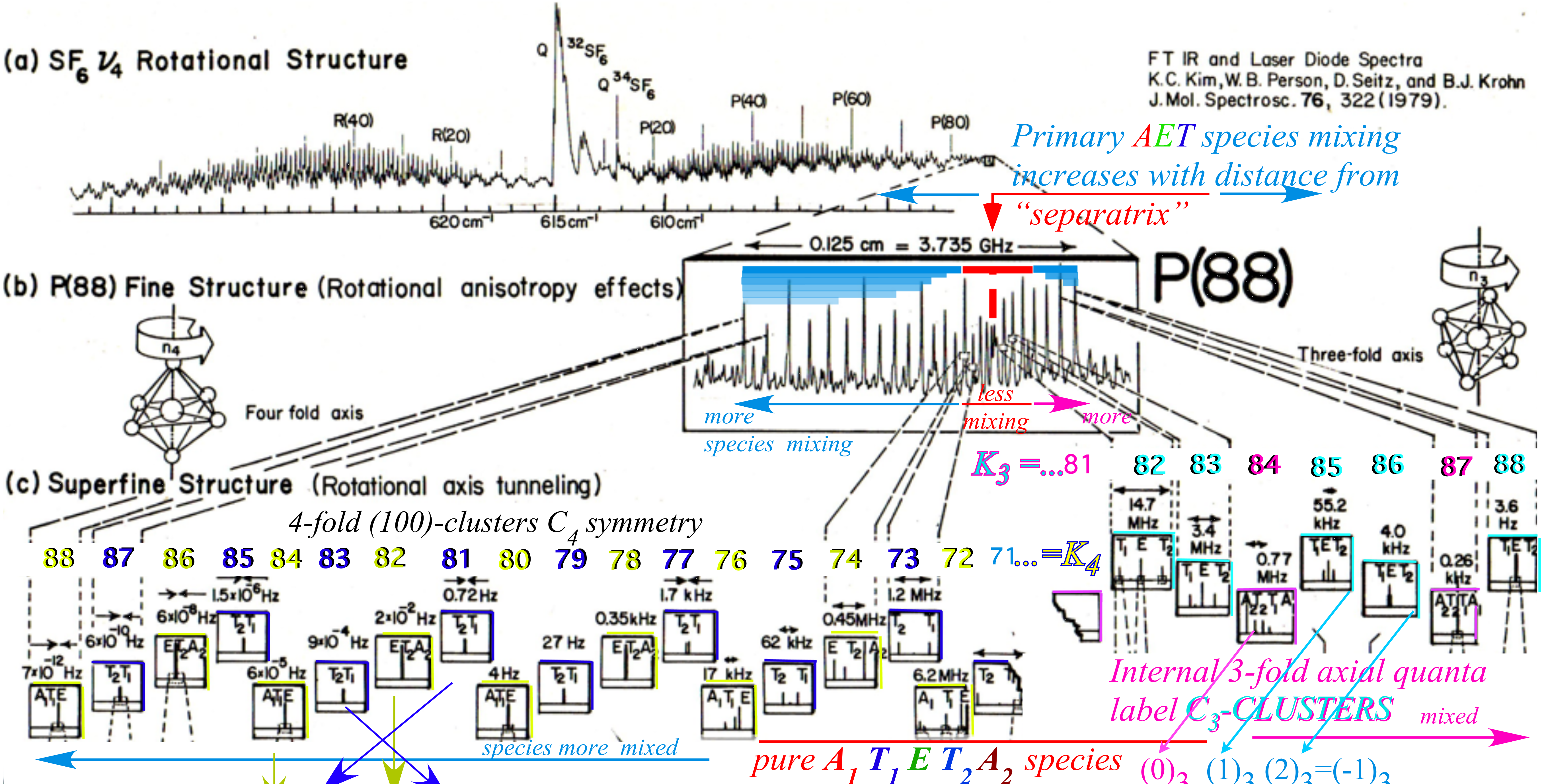


PQR structure due to Coriolis scalar interaction between vibrational angular momentum ℓ and total momentum $\mathbf{J} = \ell + \mathbf{N}$ *of rotating nuclei*

P(N)=P(88) structure due to tensor centrifugal/Coriolis due to vibrational ℓ and total momentum $\mathbf{J} = \ell + \mathbf{N}$

Superfine structure modeled by **J***-tunneling in body frame (Underlying F-spin-permutation symmetry is involved, too.)*

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking



	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4=(-1)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

Cubic Octahedral symmetry O

3 modulo 4 equals -1 modulo 4 (and 83 mod 4)

83=84-1

4-fold (1oo) C_4 symmetry clusters

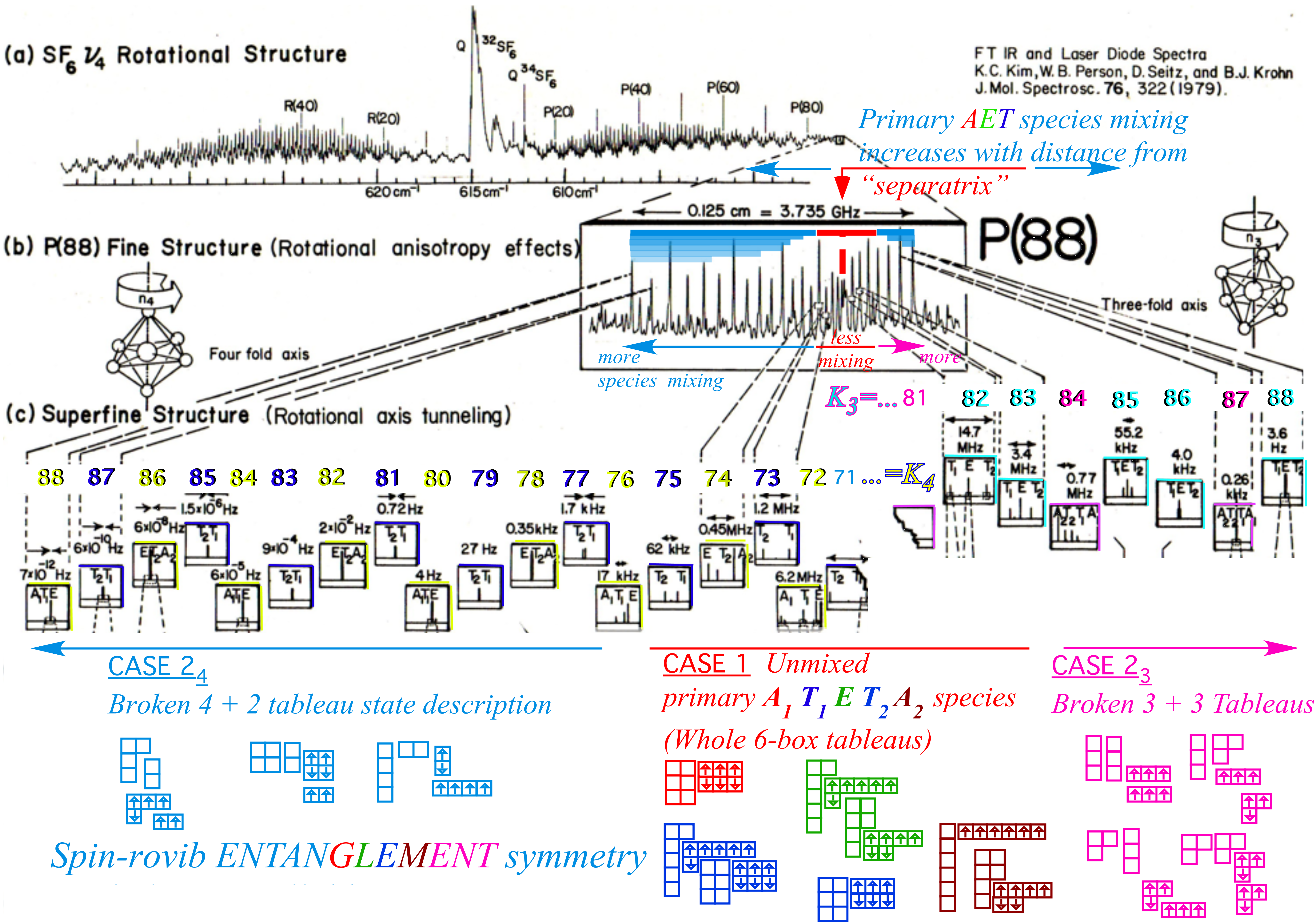
3-fold (111) C_3 symmetry clusters

	$(0)_3$	$(1)_3$	$(2)_3=(-1)_3$
A_1	1	•	•
A_2	1	•	•
E	•	1	1
T_1	1	1	1
T_2	1	1	1

(2 modulo 3 equals -1 modulo 3 and 86 mod 3)

86=88-1

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking



AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6 **ZIPP (Zero-Interaction-Potential-`Proximation*

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

PSDS Ch.5 pdf p.10.

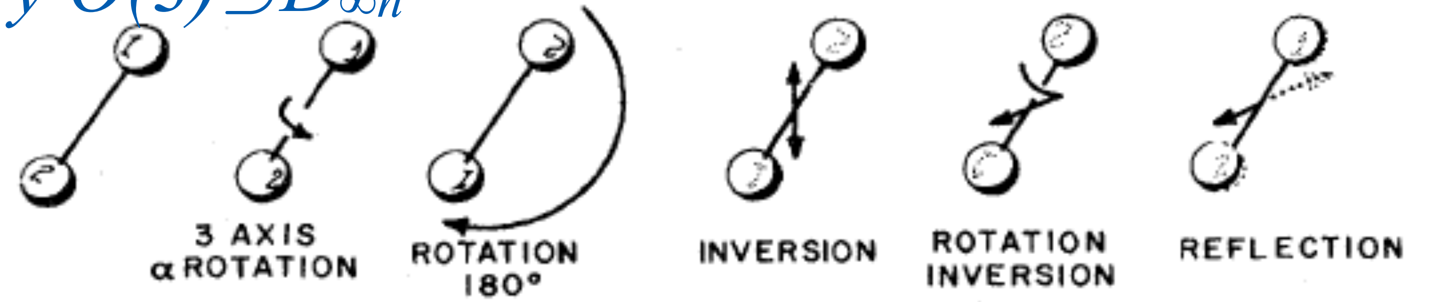
$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1



1 $\quad$ $R(\alpha 0 0)$ $\quad$ $R(-\alpha\, 180°\, \alpha)$ $\quad$ I $\quad$ $I.R(\alpha 0 0)$ $\quad$ $I.R(-\alpha\, 180°\, \alpha)$

$A_{1g} = \Sigma_g^+$

$A_{1u} = \Sigma_u^+$

$A_{2g} = \Sigma_g^-$

$A_{2u} = \Sigma_u^-$

$E_{1g} = \pi_g$

$E_{1u} = \pi_u$

$E_{2g} = \Delta_g$

$E_{2u} = \Delta_u$

$\cdot$

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of $A \otimes B$

Rev. Mod. Phys. 50,1,1 (1978)pdf p.19.

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

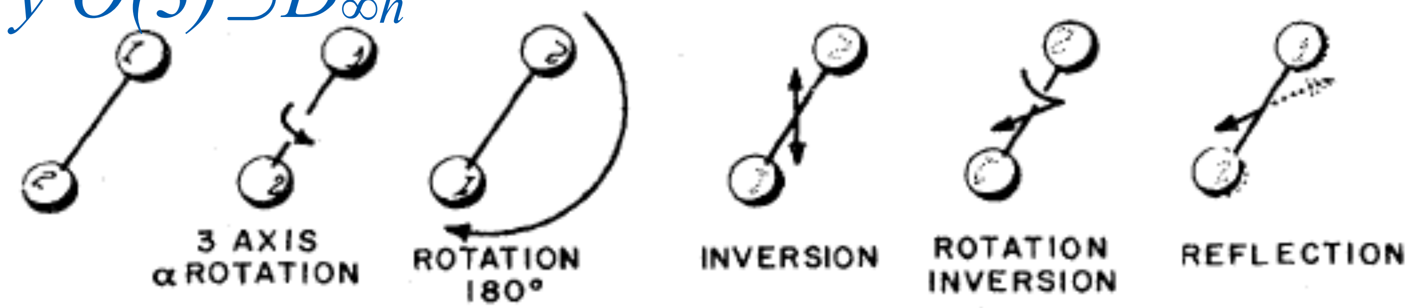
$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	*atomic label*	*molecular label*
$\ell=0$	*s or S*	σ or Σ
$\ell=1$	*p or P*	π or Π
$\ell=2$	*d or D*	δ or Δ
$\ell=3$	*f or F*	ϕ or Φ

A, B, or C Correlations

$B=$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1



	1	$R(\alpha 0 0)$	$R(-\alpha 180° \alpha)$	I	$I.R(\alpha 0 0)$	$I.R(-\alpha 180° \alpha)$
$A_{1g}=\Sigma_g^+$	1	1	1	1	1	1
$A_{1u}=\Sigma_u^+$	1	1	-1	-1	-1	1
$A_{2g}=\Sigma_g^-$	1	1	-1	1	1	-1
$A_{2u}=\Sigma_u^-$	1	1	1	-1	-1	-1
$E_{1g}=\pi_g$	2	$2\cos\alpha$	0	2	$2\cos\alpha$	0
$E_{1u}=\pi_u$	2	$2\cos\alpha$	0	-2	$-2\cos\alpha$	0
$E_{2g}=\Delta_g$	2	$2\cos 2\alpha$	0	2	$2\cos 2\alpha$	0
$E_{2u}=\Delta_u$	2	$2\cos 2\alpha$	0	-2	$-2\cos 2\alpha$	0
·	·	·	·	·	·	·

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of $A\otimes B$

Rev. Mod. Phys. 50,1,1 (1978)pdf p.19.

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

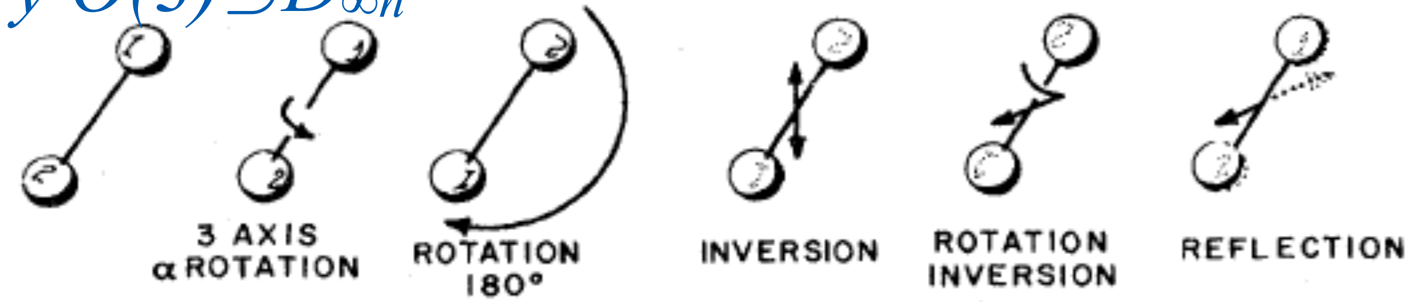
$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

$B=$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1



	1	R(α00)	R(-α180°α)	I	I.R(α00)	I.R(-α180°α)
$A_{1g}=\Sigma_g^+$	1	1	1	1	1	1
$A_{1u}=\Sigma_u^+$	1	1	-1	-1	-1	1
$A_{2g}=\Sigma_g^-$	1	1	-1	1	1	-1
$A_{2u}=\Sigma_u^-$	1	1	1	-1	-1	-1
$E_{1g}=\pi_g$	2	$2\cos\alpha$	0	2	$2\cos\alpha$	0
$E_{1u}=\pi_u$	2	$2\cos\alpha$	0	-2	$-2\cos\alpha$	0
$E_{2g}=\Delta_g$	2	$2\cos 2\alpha$	0	2	$2\cos 2\alpha$	0
$E_{2u}=\Delta_u$	2	$2\cos 2\alpha$	0	-2	$-2\cos 2\alpha$	0
·	·	·	·	·	·	·

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of $A\otimes B$

Rev. Mod. Phys. 50,1,1 (1978) pdf p.19.

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

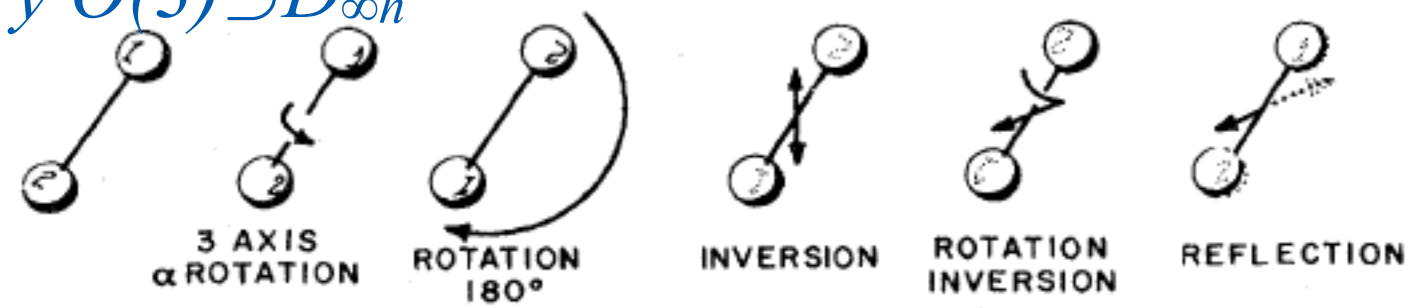
$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

$B=$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
$1+$	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
$2+$	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
$3+$	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1



	1	R(α00)	R(-α180°α)	I	I.R(α00)	I.R(-α180°α)
$A_{1g}=\Sigma_g^+$	1	1	1	1	1	1
$A_{1u}=\Sigma_u^+$	1	1	-1	-1	-1	1
$A_{2g}=\Sigma_g^-$	1	1	-1	1	1	-1
$A_{2u}=\Sigma_u^-$	1	1	1	-1	-1	-1
$E_{1g}=\pi_g$	2	$2\cos\alpha$	0	2	$2\cos\alpha$	0
$E_{1u}=\pi_u$	2	$2\cos\alpha$	0	-2	$-2\cos\alpha$	0
$E_{2g}=\Delta_g$	2	$2\cos 2\alpha$	0	2	$2\cos 2\alpha$	0
$E_{2u}=\Delta_u$	2	$2\cos 2\alpha$	0	-2	$-2\cos 2\alpha$	0
⋮	⋮	⋮	⋮	⋮	⋮	⋮

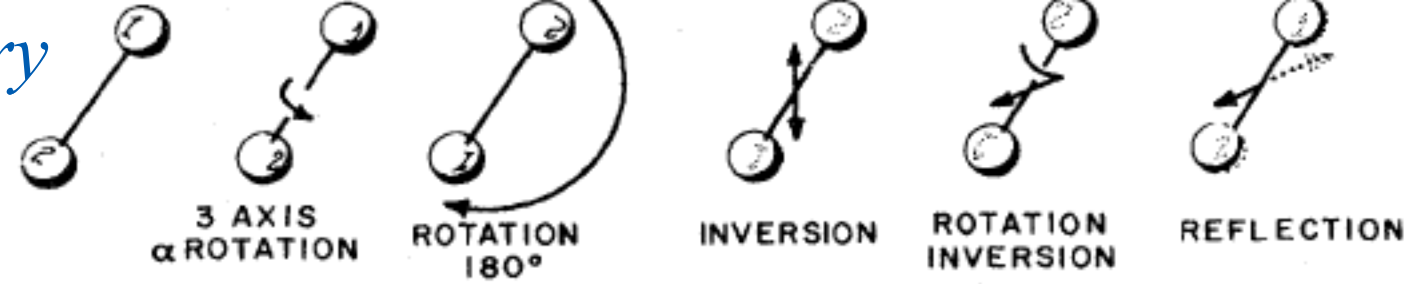
FIG. 15. Characters of $D_{\infty h}=O_{2i}$ symmetry of X_2 rotor.

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of $A\otimes B$

Rev. Mod. Phys. 50,1,1 (1978) pdf p.19.

Diatomic or linear molecule symmetry



O(3) $D_{\infty h}$ spin-symmetry species

3D Orthogonal group O(3) correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
$1+$	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
$2+$	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
$3+$	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

	1	R(α00)	R(−α180°α)	I	I.R(α00)	I.R(−α180°α)
$A_{1g}=\Sigma_g^+$	1	1	1	1	1	1
$A_{1u}=\Sigma_u^+$	1	1	−1	−1	−1	1
$A_{2g}=\Sigma_g^-$	1	1	−1	1	1	−1
$A_{2u}=\Sigma_u^-$	1	1	1	−1	−1	−1
$E_{1g}=\pi_g$	2	2 cos α	0	2	2 cos α	0
$E_{1u}=\pi_u$	2	2 cos α	0	−2	−2 cos α	0
$E_{2g}=\Delta_g$	2	2 cos 2α	0	2	2 cos 2α	0
$E_{2u}=\Delta_u$	2	2 cos 2α	0	−2	−2 cos 2α	0
⋮	⋮	⋮	⋮	⋮	⋮	⋮

TABLE VIII. $O_3 \downarrow (O_{2i}=D_{\infty h})$ correlation of representations.

O_3 \ O_{2i}	$B=\Sigma_g^+$	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u	Φ_g	Φ_u	Γ_g ...
$N^p=0^+$	1	...	...	...	...	...	...	...	...	...	
$=0^-$	...	...	...	1	...	...	...	...	...	...	
$=1^+$	...	...	1	...	1	...	...	...	...	...	
$=1^-$	...	1	...	...	...	1	...	...	...	...	
$=2^+$	1	...	...	...	1	...	1	...	...	...	
$=2^-$	...	...	...	1	...	1	...	1	...	...	
$=3^+$	...	...	1	...	1	...	1	...	1	...	
$=3^-$	...	1	...	...	...	1	...	1	...	1	
$=4^+$	1	...	...	...	1	...	1	...	1	...	1

Types of symmetry labels
A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of A⊗B

Rev. Mod. Phys. 50,1,1 (1978) pdf p.19.

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6 **ZIPP (Zero-Interaction-Potential-`Proximation*

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

Diatomic or linear molecule:State labels by symmetry O(3)⊃D∞h

A=Σ symmetry Λ=0 *(no e or v activity)*

A=Π symmetry Λ=±1

(unit quantum of e or v activity "riding" on rotor)

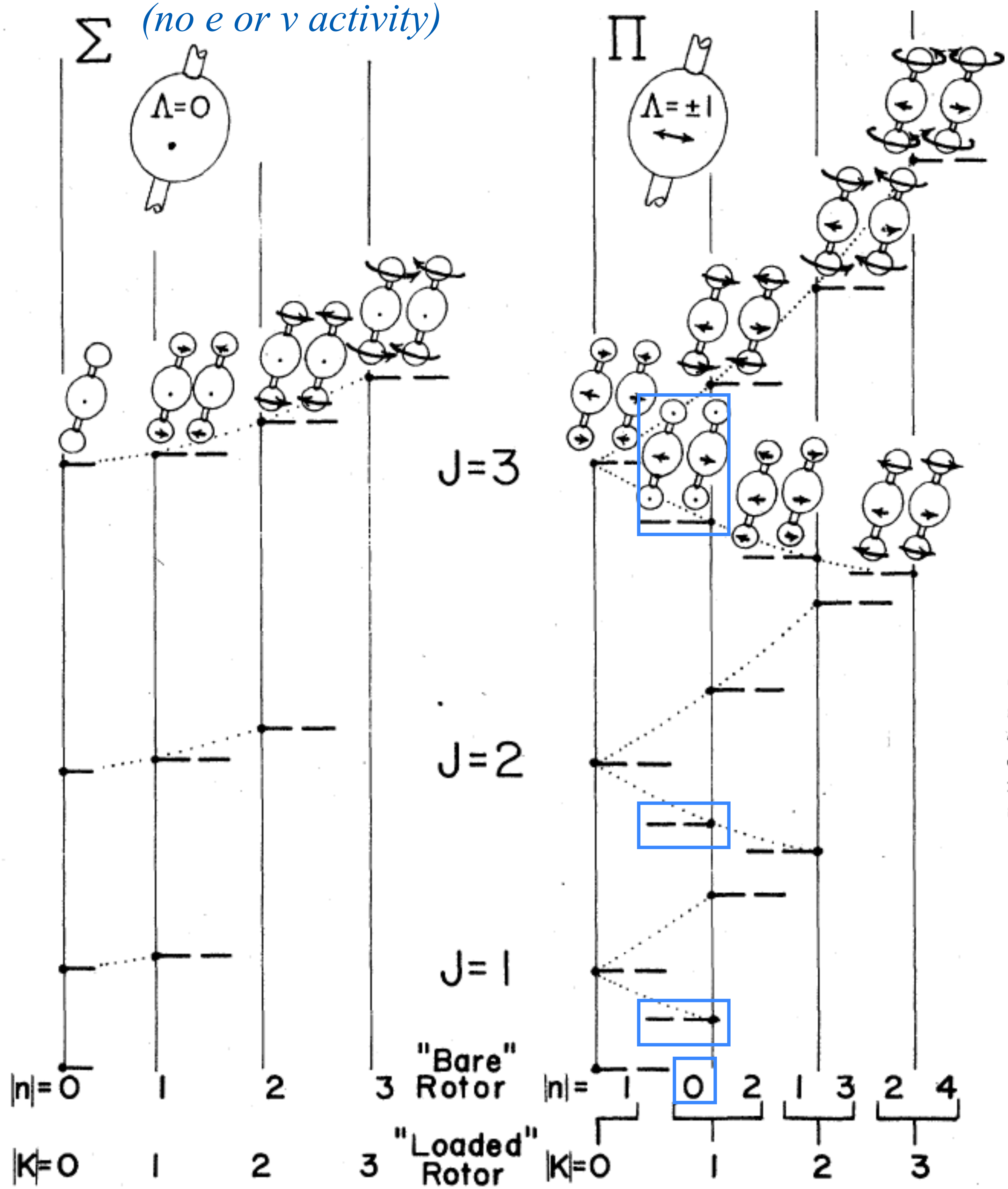


FIG. 18. Σ and Π BOA states for symmetric top molecule. The electronic or vibronic "load" is indicated by an ellipsoid surrounding a "bare" dumb-bell rotor. Arrows indicate the direction of rotation of moving wave states and relative amounts of momentum n or K. Only for the $(n=0, \Pi)$ states will it be necessary to make up standing waves to form the "Λ-doublet" states which are shown in Fig. 19.

Rev. Mod. Phys. 50,1,1 (1978)[*pdf p.21.*]

Types of symmetry labels

A=Activity (of vibrations, electrons)
B=Bare rotor (rotations, nuclear spin)
C=Coupling or Constriction of A⊗B

Diatomic or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

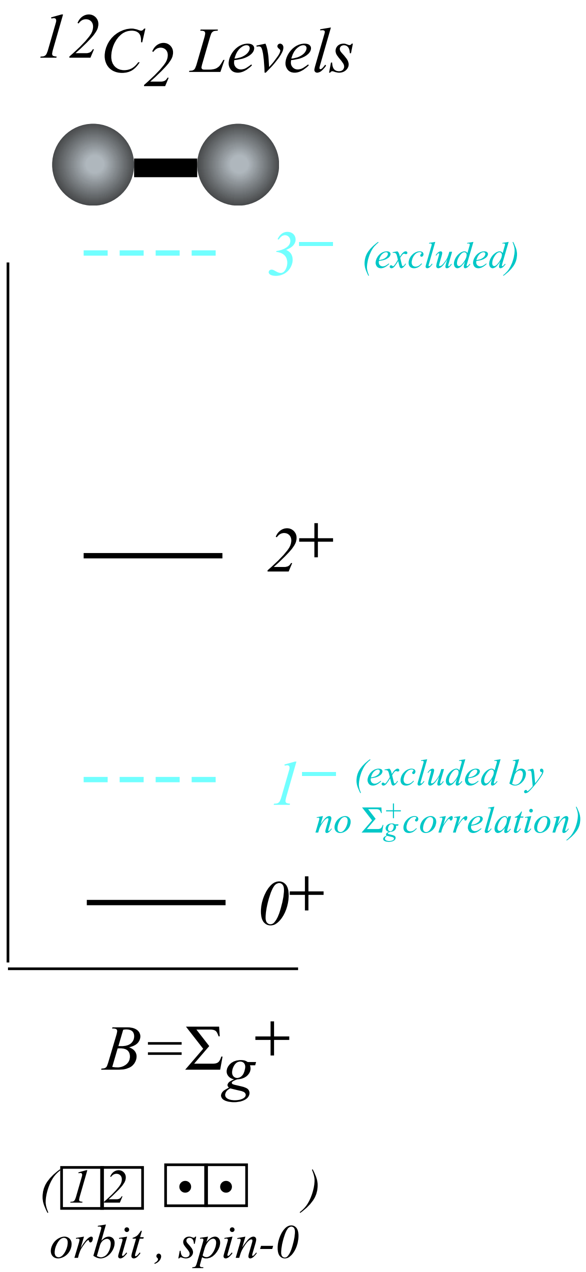
Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

$B=$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

^{12}C has nuclear spin-0



Ortho-Species (only)

^{13}C has nuclear spin-½

Pairs of Fermi (spin-$\frac{1}{2}$) nuclei required by Pauli principle to be totally antisymmetric:

Para-Species

Ortho-Species

Either Even-Odd or Odd-Even

Diatomic or linear molecule: Labeling by symmetry $O(3)\supset D_{\infty h}\supset C_{\infty v}$

$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

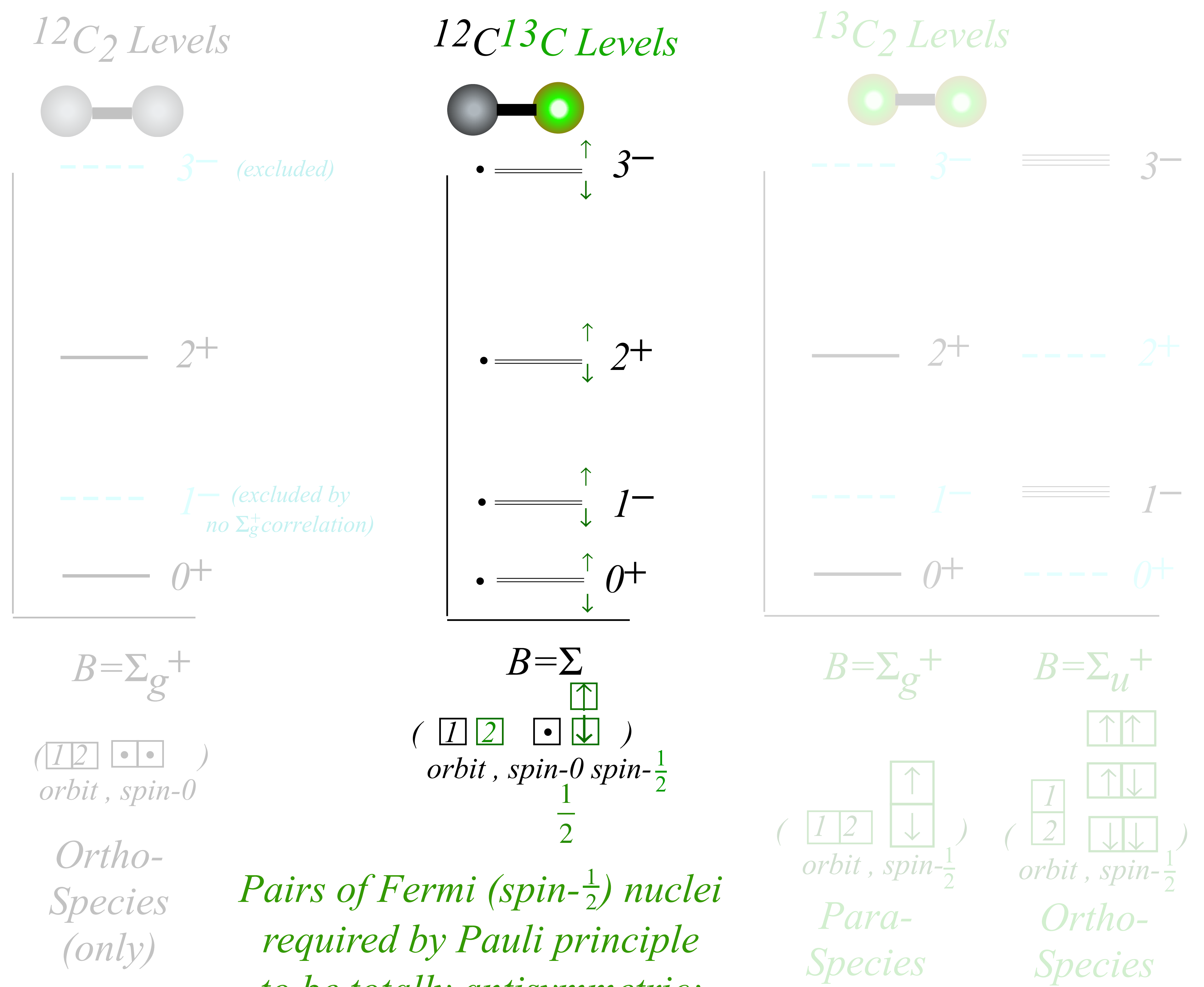
A, B, or C Correlations

$B=$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

^{12}C has nuclear spin-0

^{13}C has nuclear spin-½



Pairs of Fermi (spin-$\frac{1}{2}$) nuclei required by Pauli principle to be totally antisymmetric:

Either Even-Odd or Odd-Even

Diatomic or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

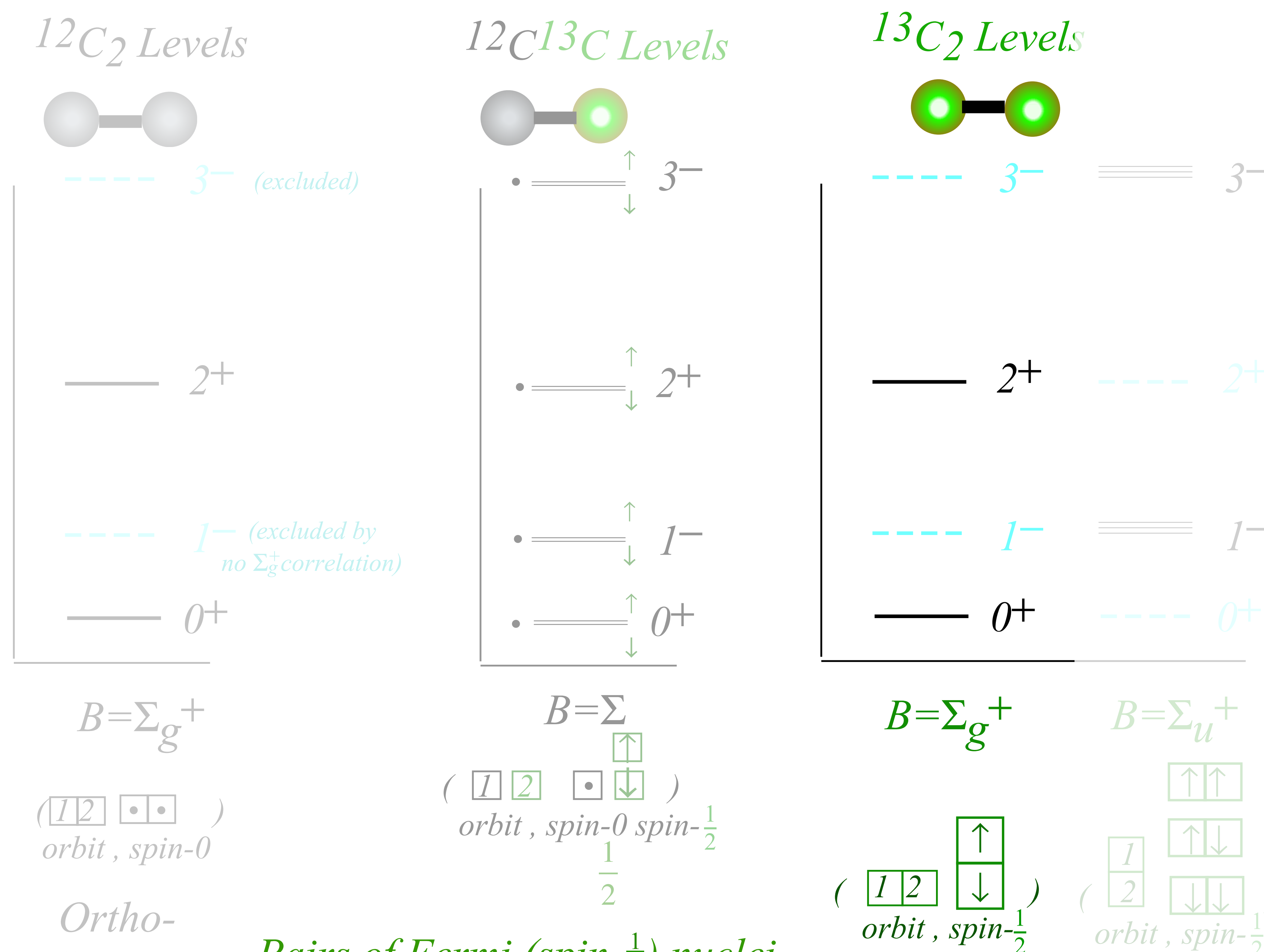
Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

$B=$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

^{12}C has nuclear spin-0 $\qquad$ ^{13}C has nuclear spin-½



Ortho-Species (only)

Pairs of Fermi (spin-$\frac{1}{2}$) nuclei required by Pauli principle to be totally antisymmetric:

Para-Species $\qquad$ Ortho-Species

Either Even-Odd or Odd-Even

Diatomic or linear molecule:Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

$O(3)$ $D_{\infty h}$ spin-symmetry species

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

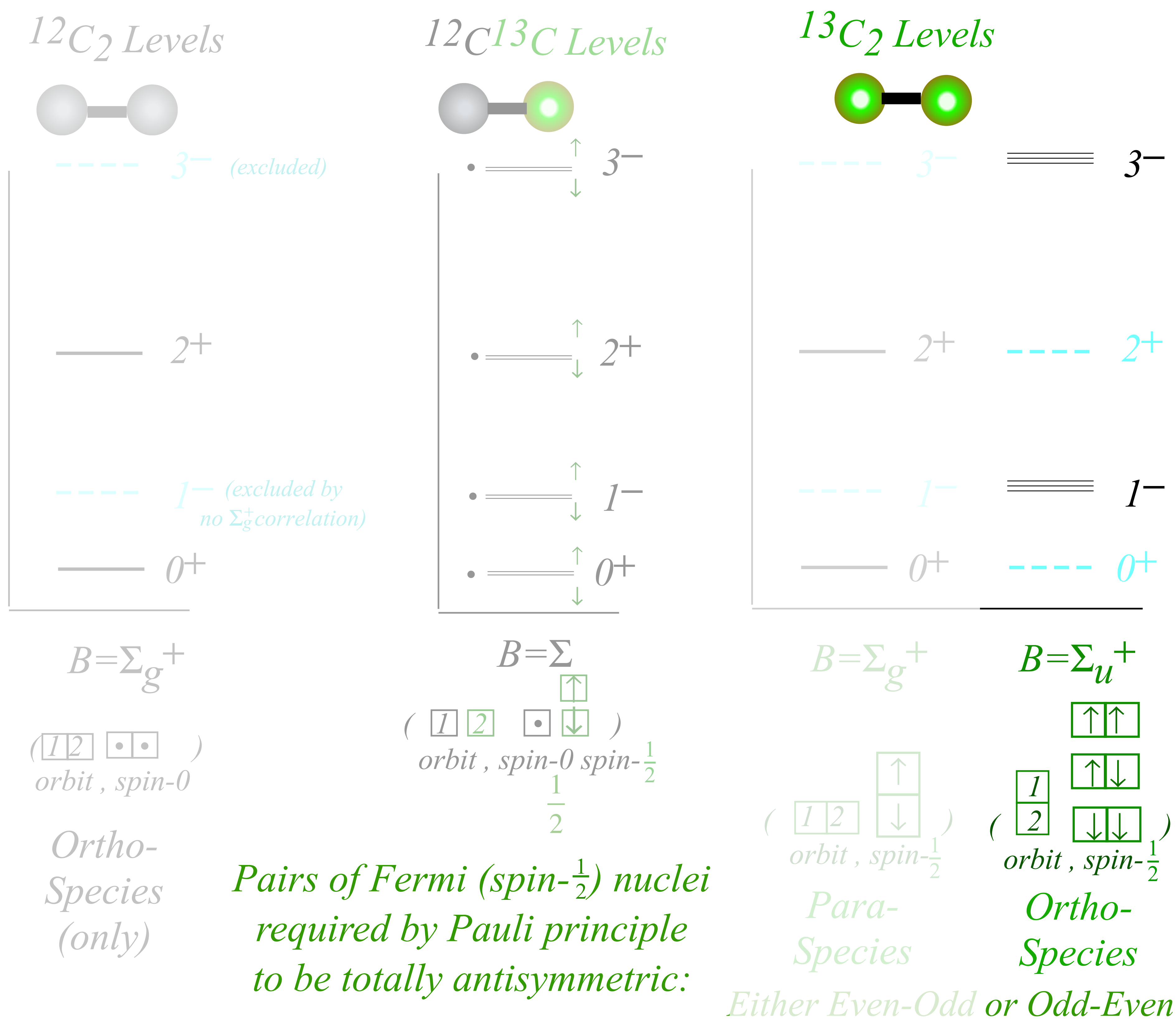
Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
$1+$	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
$2+$	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
$3+$	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

^{12}C has nuclear spin-0

^{13}C has nuclear spin-½



Diatomic or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

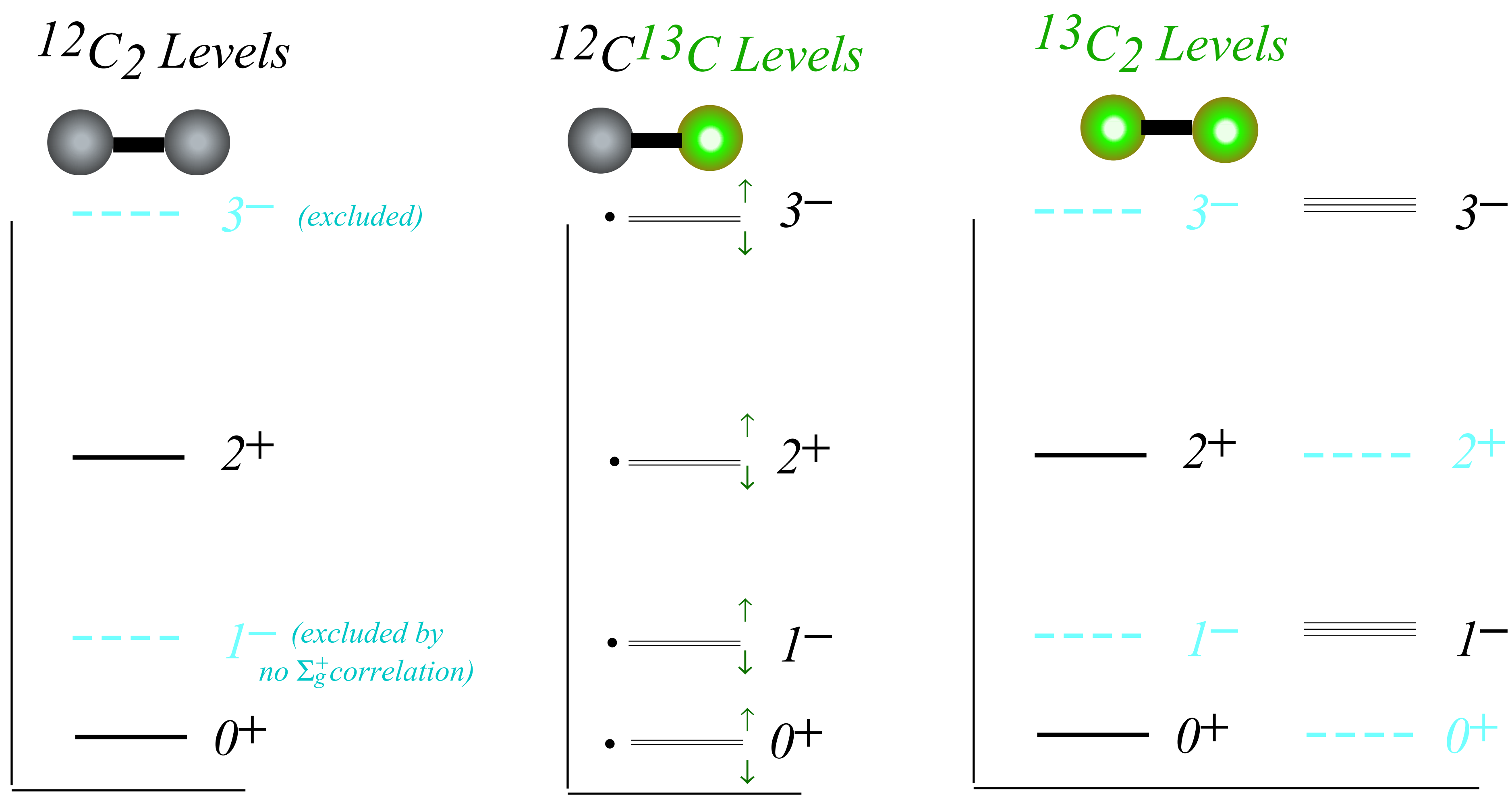
A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

^{12}C has nuclear spin-0

^{13}C has nuclear spin-½



$B=\Sigma_g^+$

($\boxed{1}\boxed{2}$ $\boxed{\cdot}\boxed{\cdot}$)
orbit, spin-0

Ortho-Species (only)

$B=\Sigma$

($\boxed{1}$ $\boxed{2}$ $\boxed{\cdot}$ $\boxed{\uparrow}\boxed{\downarrow}$)
orbit, spin-0 spin-$\frac{1}{2}$ $\frac{1}{2}$

Pairs of Fermi (spin-$\frac{1}{2}$) nuclei required by Pauli principle to be totally antisymmetric:

$B=\Sigma_g^+$

($\boxed{1}\boxed{2}$ $\boxed{\uparrow}\boxed{\downarrow}$)
orbit, spin-$\frac{1}{2}$

Para-Species

$B=\Sigma_u^+$

($\boxed{1}\boxed{2}$ $\boxed{\uparrow}\boxed{\uparrow}$ $\boxed{\uparrow}\boxed{\downarrow}$ $\boxed{\downarrow}\boxed{\downarrow}$)
orbit, spin-$\frac{1}{2}$

Ortho-Species

Either Even-Odd or Odd-Even

Diatomic or linear molecule: Labeling by symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

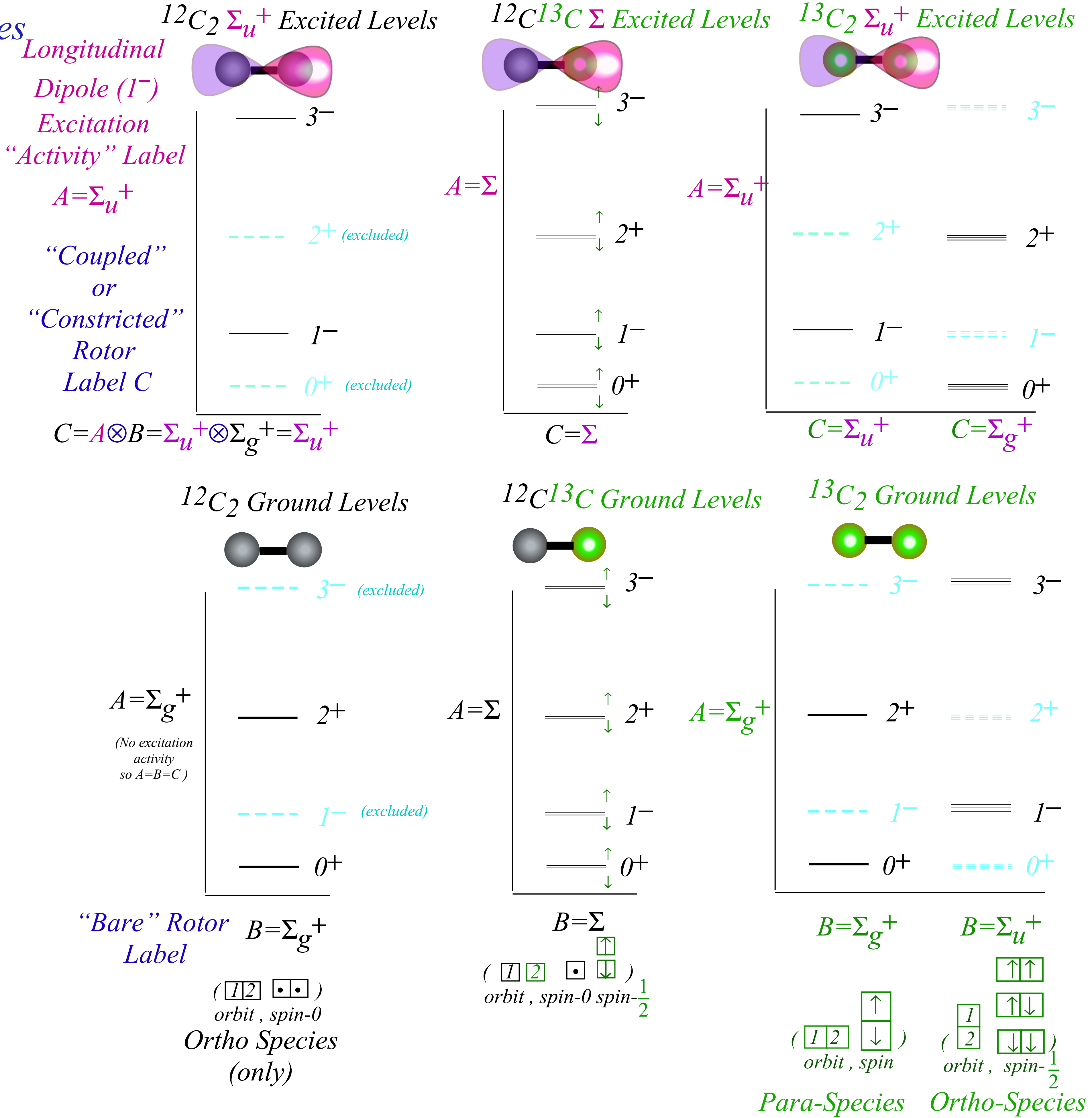
$O(3)$ $D_{\infty h}$ spin-symmetry species

3D Orthogonal group $O(3)$ correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$\ell=0$	s or S	σ or Σ
$\ell=1$	p or P	π or Π
$\ell=2$	d or D	δ or Δ
$\ell=3$	f or F	ϕ or Φ

A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u...
0^+	1	·	·	·	·	·	·	·
0^-	·	·	·	1	·	·	·	·
1^+	·	·	1	·	1	·	·	·
1^-	·	1	·	·	·	1	·	·
2^+	1	·	·	·	1	·	1	·
2^-	·	·	·	1	·	1	·	1
3^+	·	·	1	·	1	·	1	·
3^-	·	1	·	·	·	1	·	1



AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

- State labels by symmetry $O(3) \supset D_{\infty h}$
  - Coriolis and λ-doubling levels
- Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

- Tableau dimension formulae for X_4 and XY_4 molecules
  - CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
- Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

- Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
- Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

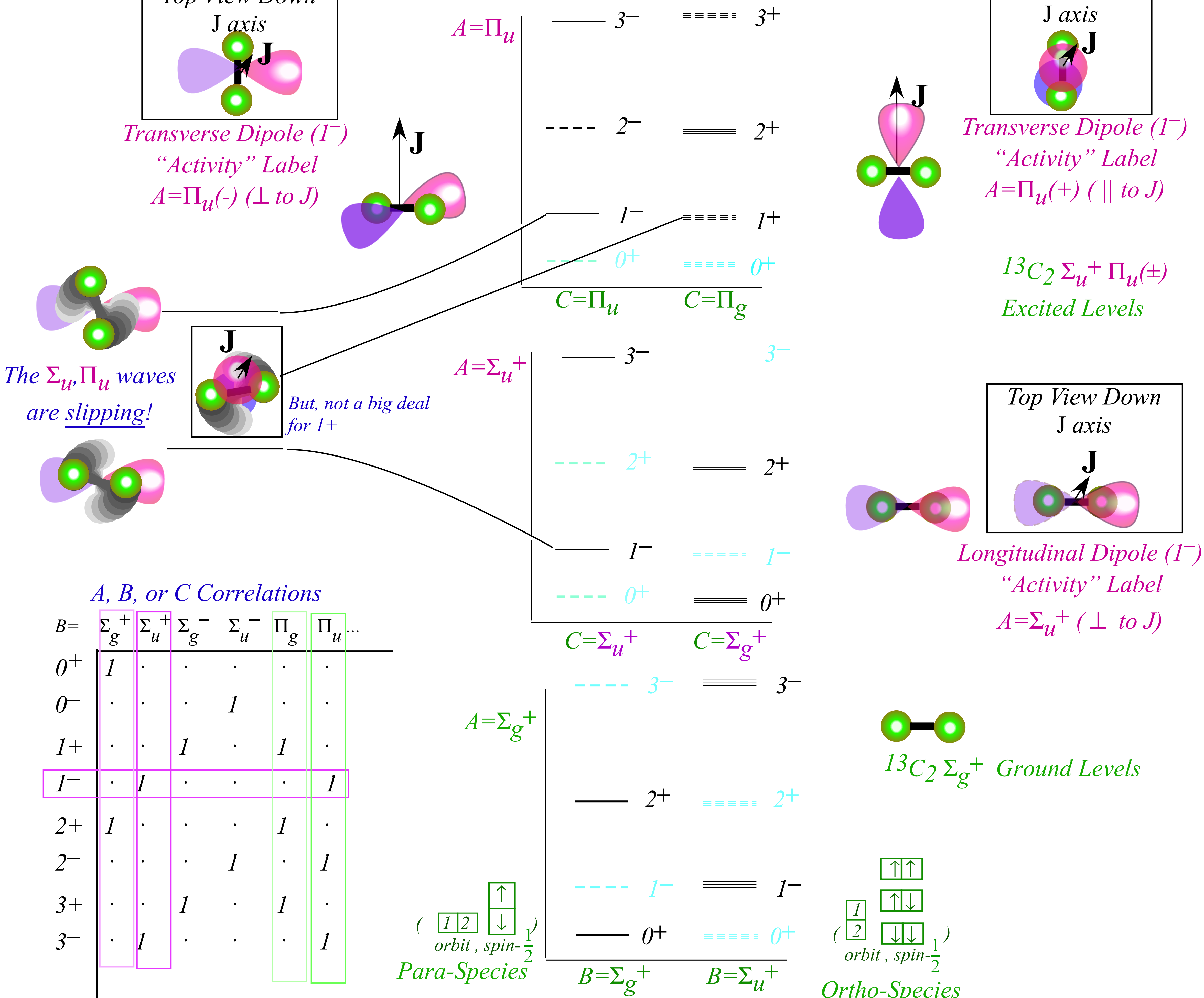
- Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

- REES for high-J Coriolis spectra in SF_6
- REES for high-J Coriolis spectra in υ_3 CF_4
- REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

Coriolis and λ-doubling levels



A, B, or C Correlations

B=	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u...
0^+	1	·	·	·	·	·
0^-	·	·	·	1	·	·
$1+$	·	·	1	·	1	·
1^-	·	1	·	·	·	1
$2+$	1	·	·	·	1	·
2^-	·	·	·	1	·	1
$3+$	·	·	1	·	1	·
3^-	·	1	·	·	·	1

Diatomic or linear molecule: Coriolis and λ-doubling levels

$$\mathbf{H} = \mathbf{H}_e + (\mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{J}_{\bar{x}}\mathbf{L}_{\bar{x}} - 2\mathbf{J}_{\bar{y}}\mathbf{L}_{\bar{y}} - 2\mathbf{J}_{\bar{z}}\mathbf{L}_{\bar{z}})/2I_{\bar{x}\bar{y}}$$

$$\begin{array}{cc} & \begin{array}{ccc} |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \end{array} \\ \langle \mathbf{H} \rangle = & \begin{vmatrix} \epsilon_\Sigma + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_\pi + 2 & 0 \\ 0 & 0 & \epsilon_\pi + 2 \end{vmatrix} /2I_{\bar{x}\bar{y}} \end{array}$$

(J =1)-case

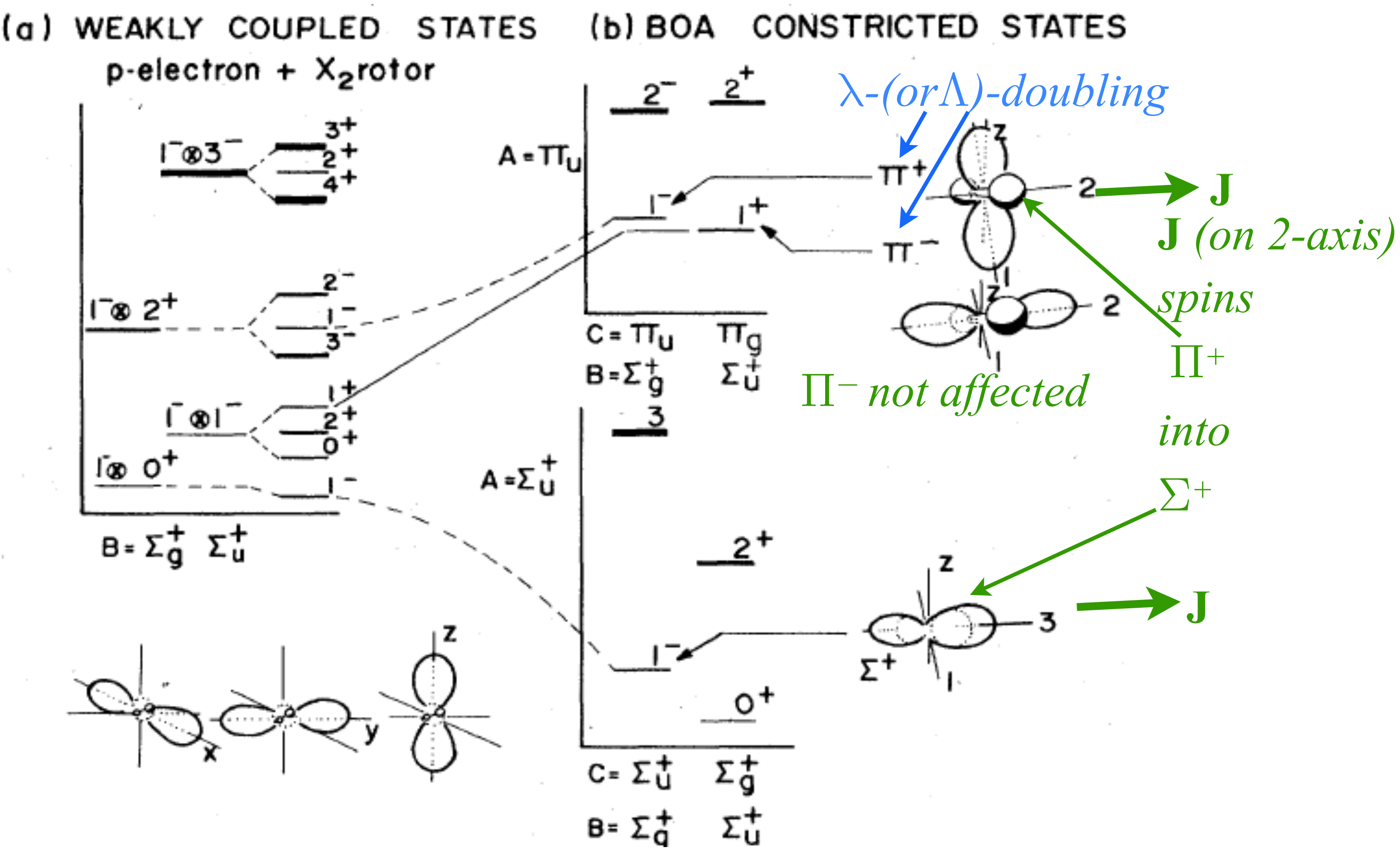


FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an X_2 rotor. (a) Weakly-coupled states. (N^P, B, and J^P are good labels.) (b) BOA-constricted states. (A, B, C, and J^P are good labels.) States with the same $B=\Sigma_g^+$ and $J^P=1^-$ are connected by dotted lines. The $B=\Sigma_u^+$ and $J^P=1^+$ state (solid line) turns out to be the same for either side as long as $l=1$ is unspoiled. Note that $A=\Pi_u$-doublets are represented by standing waves in the body system. The lower doublet is alternatively + and − parity.

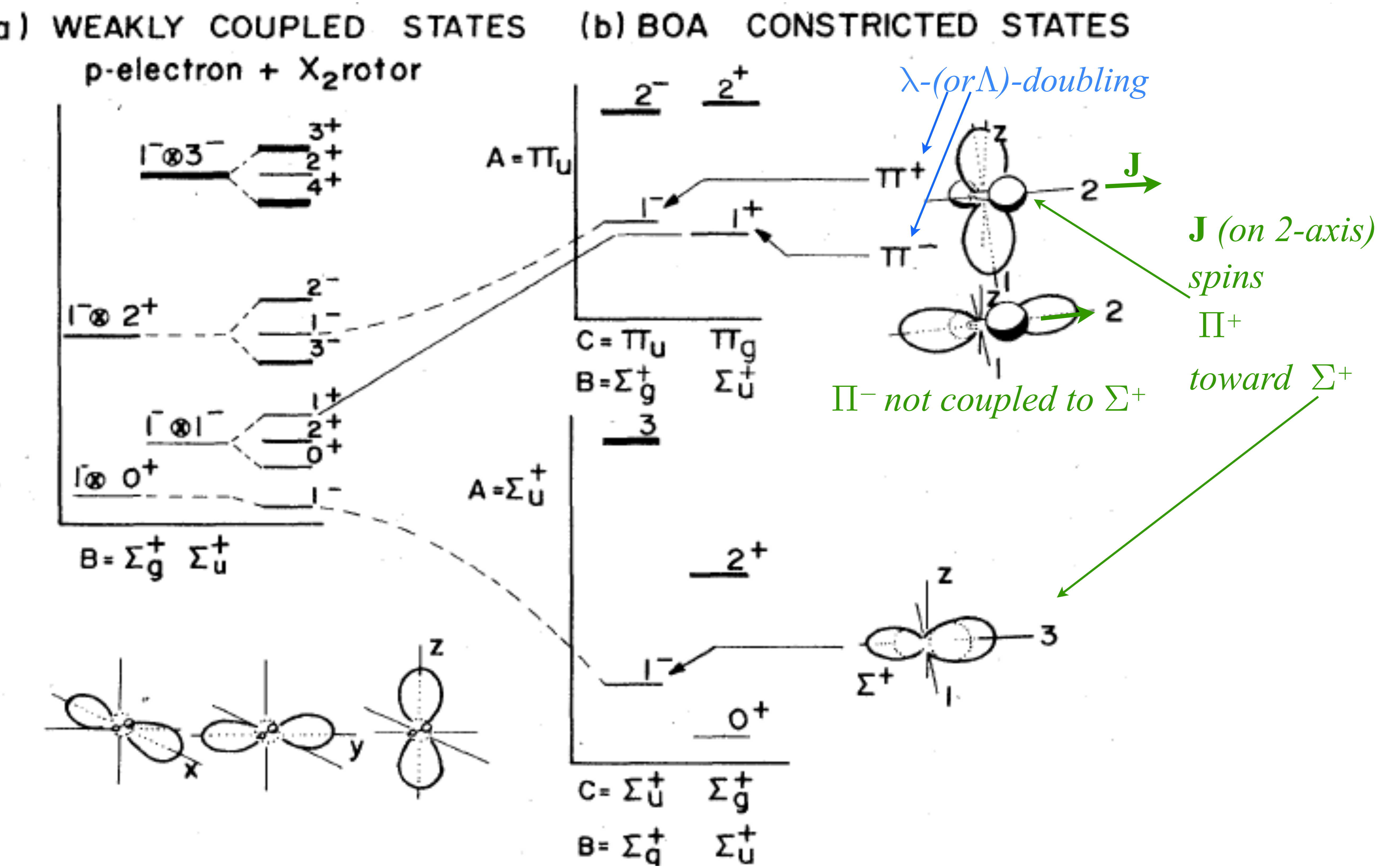
Rev. Mod. Phys. 50,1,1 (1978)[pdf p.19.](#)

Diatomic or linear molecule: Coriolis and λ-doubling levels

$$\mathbf{H} = \mathbf{H}_e + (\mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{J}_{\bar{x}}\mathbf{L}_{\bar{x}} - 2\mathbf{J}_{\bar{y}}\mathbf{L}_{\bar{y}} - 2\mathbf{J}_{\bar{z}}\mathbf{L}_{\bar{z}})/2I_{\bar{x}\bar{y}}$$

(J =1)-case

$$\begin{array}{cccc} & |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \\ \langle\mathbf{H}\rangle = & \left|\begin{array}{ccc} \epsilon_\Sigma + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_\pi + 2 & 0 \\ 0 & 0 & \epsilon_\pi + 2 \end{array}\right| /2I_{\bar{x}\bar{y}} \end{array}$$



Rev. Mod. Phys. 50,1,1 (1978)[pdf p.19.](#)

Diatomic or linear molecule: Coriolis and λ-doubling levels

$$\langle \mathbf{H} \rangle = \begin{array}{c} \\ \\ \\ \end{array}\begin{array}{ccc} |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \\ \end{array}$$

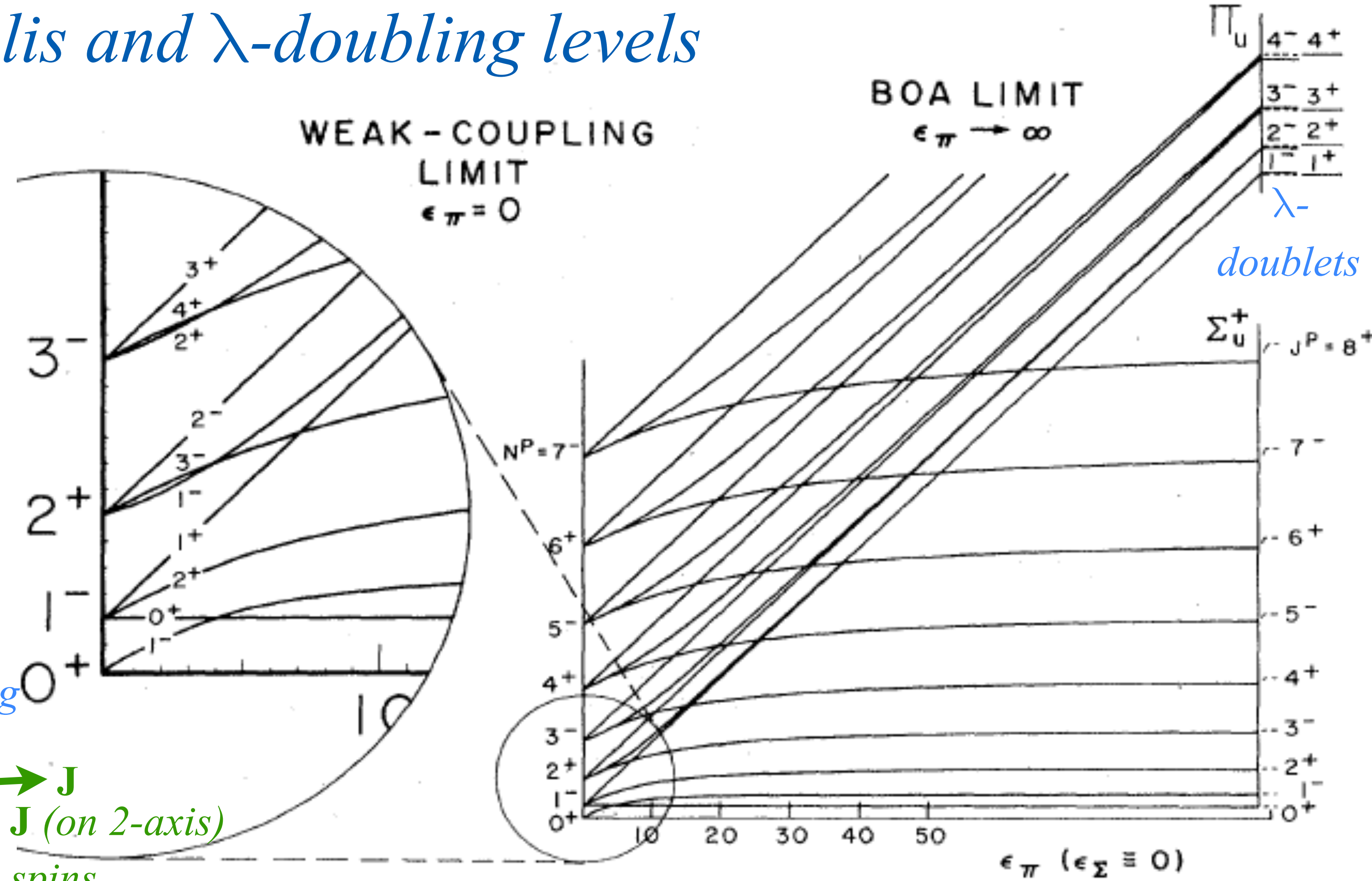
$$\langle \mathbf{H} \rangle = \begin{bmatrix} J(J+1)+2 & -2(J(J+1))^{1/2} & 0 \\ -2(J(J+1))^{1/2} & \epsilon_\pi + J(J+1) & 0 \\ 0 & 0 & \epsilon_\pi + J(J+1) \end{bmatrix}$$

$$\mathbf{H} = \mathbf{H}_e + (\mathbf{J}^2 + \mathbf{L}^2 - 2\mathbf{J}_{\bar{x}}\mathbf{L}_{\bar{x}} - 2\mathbf{J}_{\bar{y}}\mathbf{L}_{\bar{y}} - 2\mathbf{J}_{\bar{z}}\mathbf{L}_{\bar{z}})/2I_{\bar{x}\bar{y}}$$

$$\begin{array}{cccc} & |\Sigma^+\rangle & |\Pi^+\rangle & |\Pi^-\rangle \end{array}$$

$$\langle \mathbf{H} \rangle = \begin{vmatrix} \epsilon_\Sigma + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_\pi + 2 & 0 \\ 0 & 0 & \epsilon_\pi + 2 \end{vmatrix} /2I_{\bar{x}\bar{y}}$$

(J =1)-case



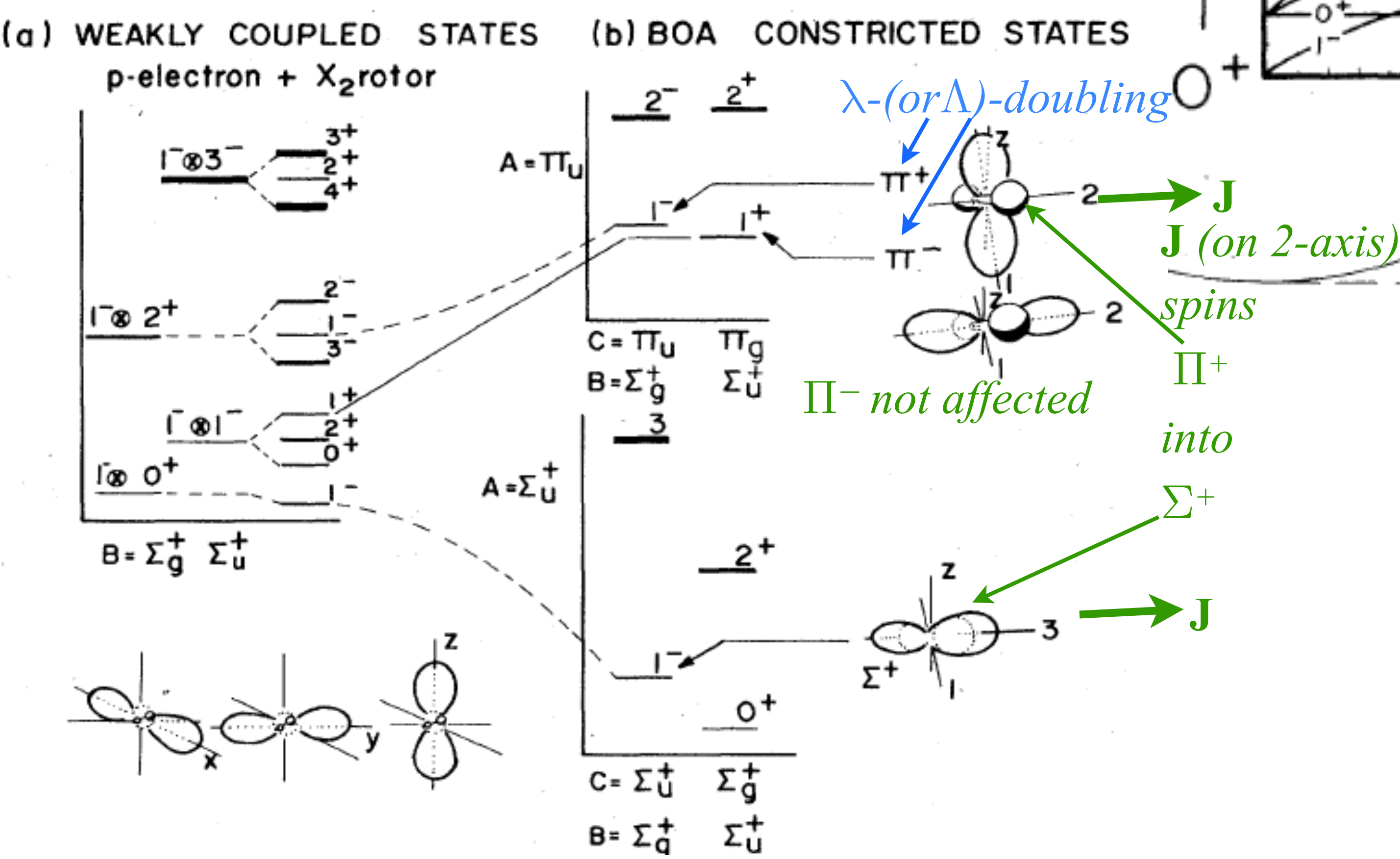


FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an X_2 rotor. (a) Weakly-coupled states. (N^P, B, and J^P are good labels.) (b) BOA-constricted states. (A, B, C, and J^P are good labels.) States with the same $B=\Sigma_g^+$ and $J^P=1^-$ are connected by dotted lines. The $B=\Sigma_u^+$ and $J^P=1^+$ state (solid line) turns out to be the same for either side as long as $l=1$ is unspoiled. Note that $A=\Pi_u$-doublets are represented by standing waves in the body system. The lower doublet is alternatively + and − parity.

FIG. 20. $(n=0)$ J-level plots $(J=0-8)$ for $(l=1:\ \Sigma,\Pi)$ as functions of electronic energy difference (ϵ_π). The right-hand side of the figure shows the separate Π and Σ manifolds that will arise in the BOA limit as $\epsilon_\pi \to \infty$. (In this figure we set $\epsilon_\Sigma = 0$, and let the rotational constant $B_v = 1/I_{\bar{x}\bar{y}}$ be unity.) Splitting or "λ doubling" is seen in the Π manifolds increasing with J. Corresponding downshifts from the pure rotational spectrum $(\sim B_v J(J+1)$ are seen in the Σ manifold. For small values of ϵ_π $(\epsilon_\pi < 5)$ there is a near degeneracy between $J=N\pm1$ levels, particularly for larger values of rotor momentum N. At $\epsilon_\pi = 0$ and $\epsilon_\pi = 4$ the degeneracy is exact, while between these points the $J=N-1$ level lies slightly below the $J=N+1$ level. Pairs of $J=(N\pm1)$ weak-coupling levels are analogous to the Π pairs seen in the BOA limits, only the former are defined with respect to a *laboratory* axis. The weakly coupled $J=N$ state can be thought of as a lab analog of a Σ state.

Rev. Mod. Phys. 50,1,1 (1978)[pdf p.23-24.](pdf p.23-24.)

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

State labels by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

*ZIPP (Zero-Interaction-Potential-`Proximation

Diatomic or linear molecule: Nomograms for dipole-allowed transitions

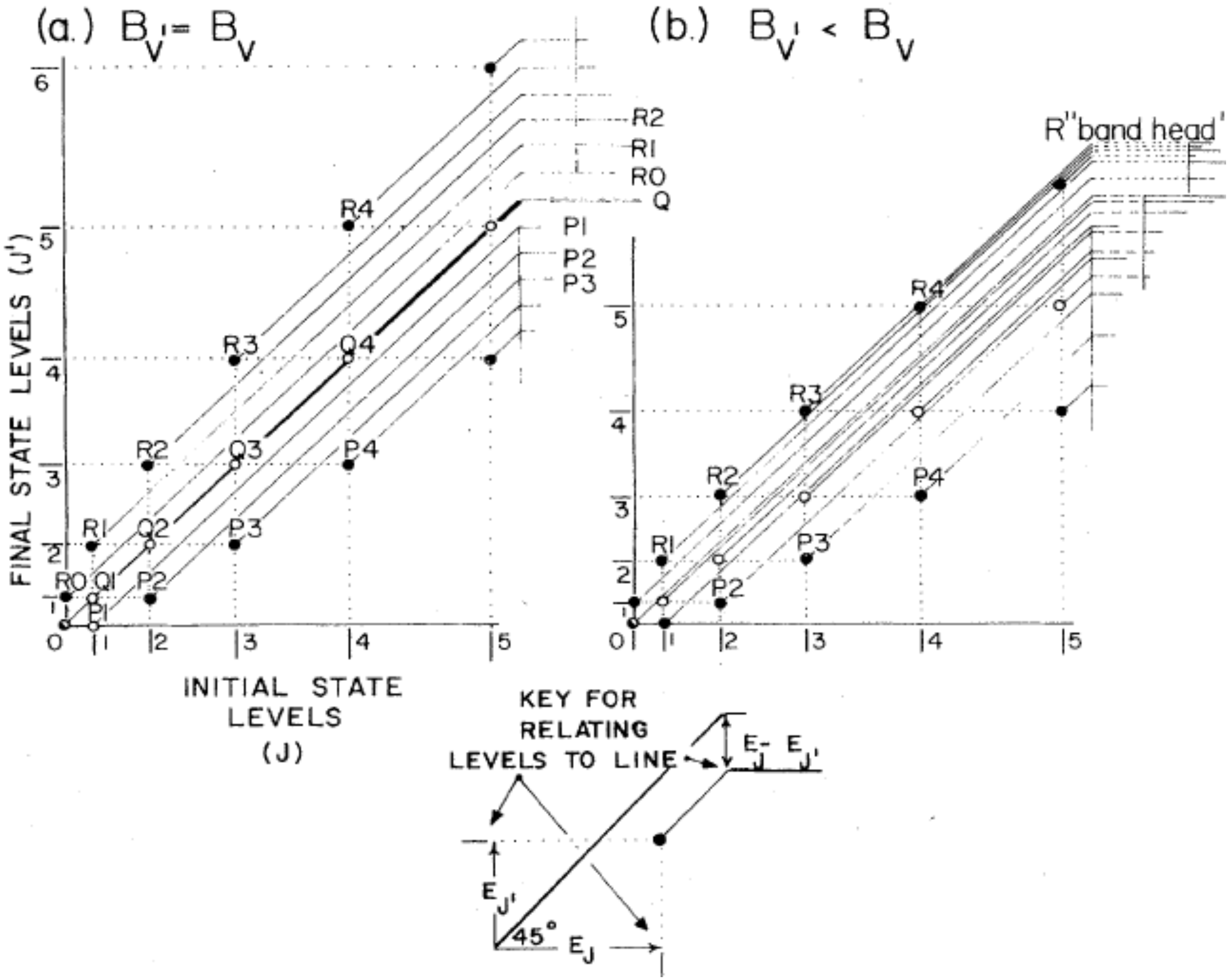


FIG. 30. Demonstrating the use of a rovibronic nomogram for the model Σ → Σ transitions by dipole excitation in a symmetric top molecule.

When excited states have lower B=1/2I (Greater inertia I)

Rev. Mod. Phys. 50,1,1 (1978)[pdf p.32.]

Diatomic or linear molecule: Dipole-allowed transitions

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved)

Central Q-branch missing from $\Sigma \leftrightarrow \Sigma$ spectra of $D_{\infty h}$ molecules

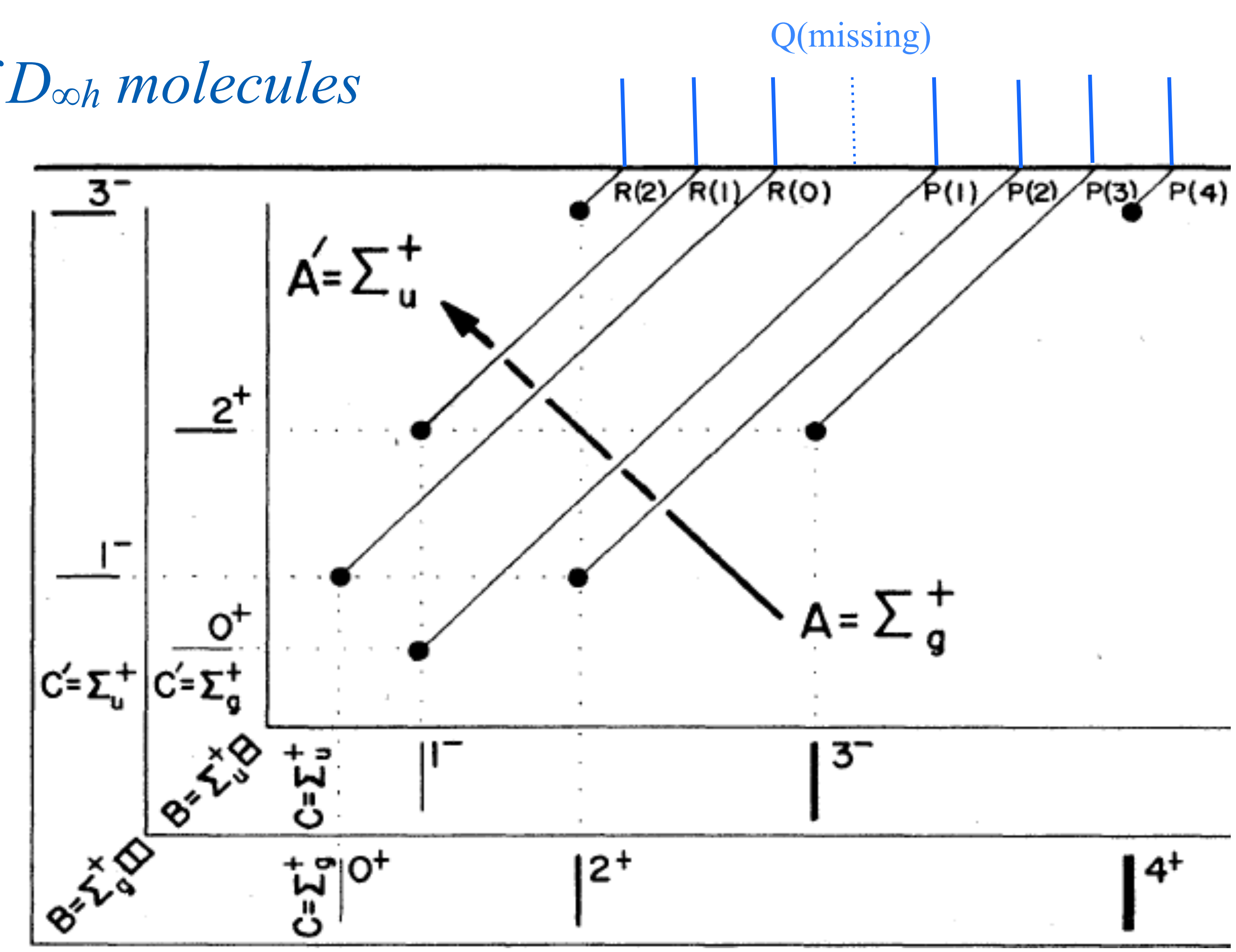
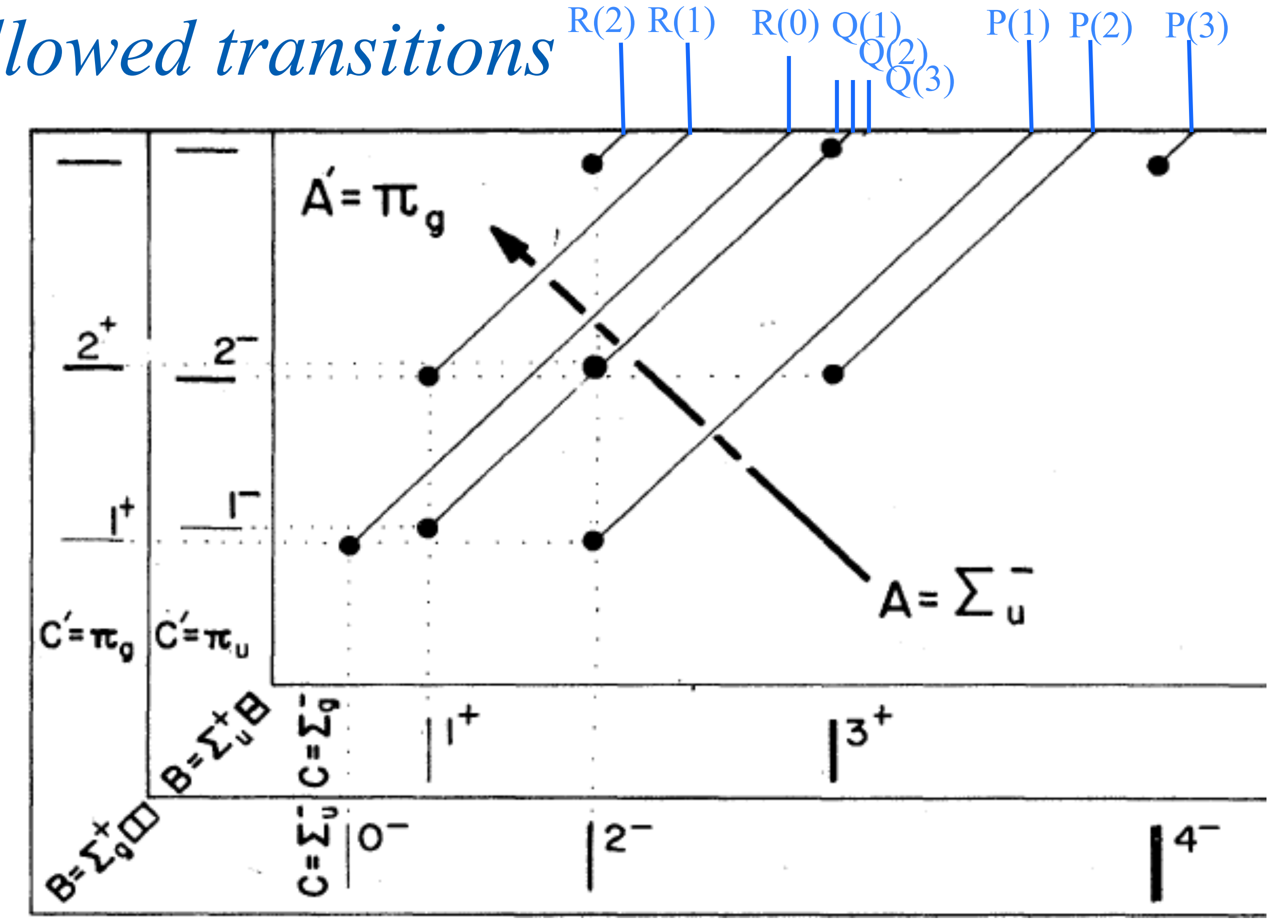


FIG. 31. Electric dipole transitions in linear symmetric (O_{2i}) molecules $X_2, XYX, \ldots$ (a) $\Sigma_g^+ \to \Sigma_u^+$. (b) $\Sigma_u^- \to \Pi_g$. Transitions are only allowed between levels lying in the same B corridor. Note that the $(\Sigma_u^- \to \Pi_g)$ Q branch is not Λ doubled since the upper Π doublet is always involved in a $J \to J$ transition.

Rev. Mod. Phys. 50,1,1 (1978)pdf p.32.

Diatomic or linear molecule: Dipole-allowed transitions

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved)



Central Q-branch missing from Σ↔Σ spectra of $D_{\infty h}$ molecules

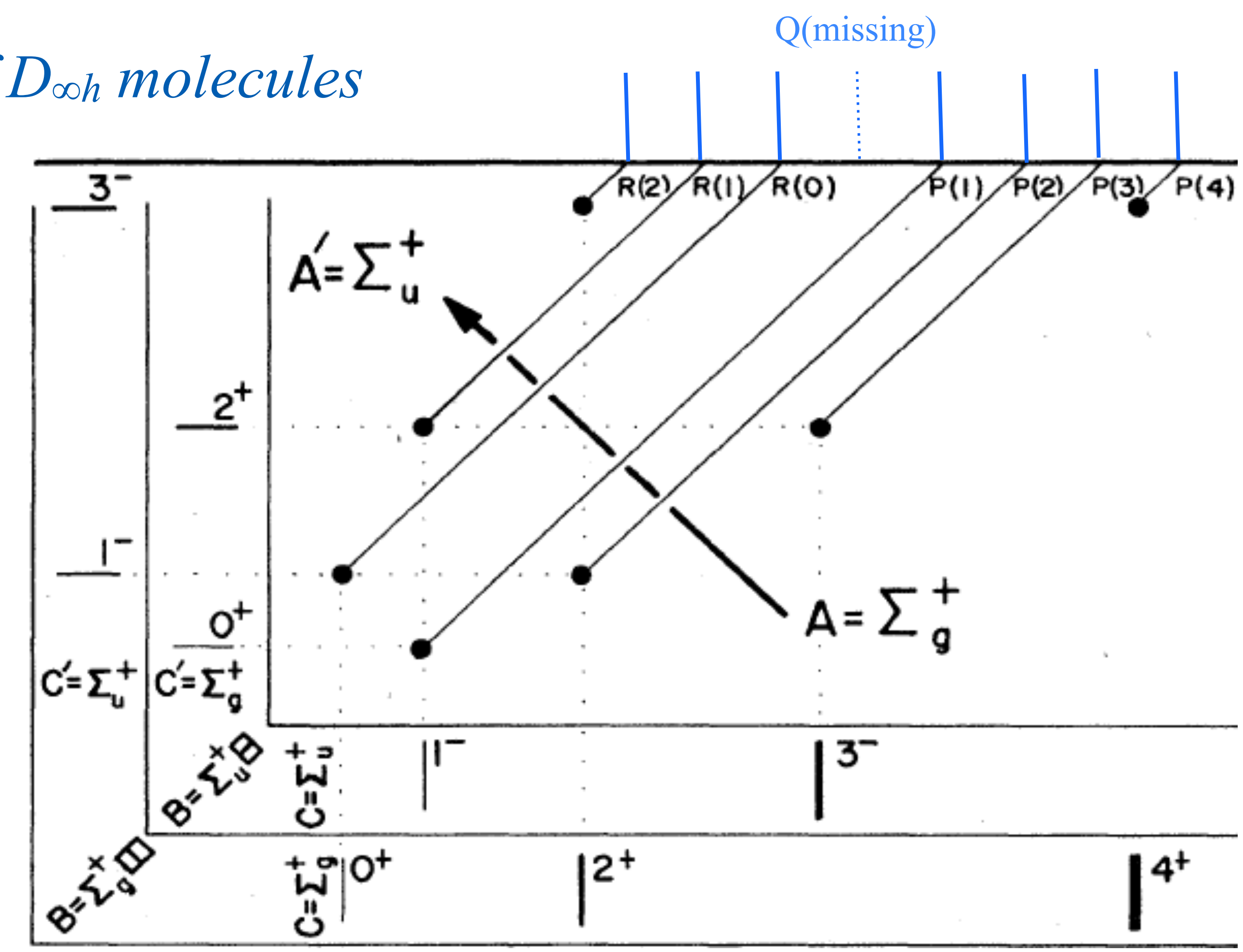


FIG. 31. Electric dipole transitions in linear symmetric (O_{2i}) molecules X_2, XYX, ... (a) $\Sigma_g^+ \to \Sigma_u^+$. (b) $\Sigma_u^- \to \Pi_g$. Transitions are only allowed between levels lying in the same B corridor. Note that the ($\Sigma_u^- \to \Pi_g$) Q branch is not Λ doubled since the upper Π doublet is always involved in a $J \to J$ transition.

Rev. Mod. Phys. 50,1,1 (1978)[pdf p.34.](#)

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$
State labels by symmetry $O(3)\supset D_{\infty h}$
Coriolis and λ-doubling levels
Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
Tableau dimension formulae for X_4 and XY_4 molecules
CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)
REES for high-J Coriolis spectra in SF_6
REES for high-J Coriolis spectra in υ_3 CF_4
. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

X_n and XY_n molecules: S_3-S_6 tableau-characters

Permutation group S_n is equivalent to Point group $\mathscr{G}$

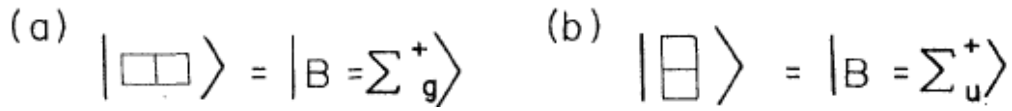
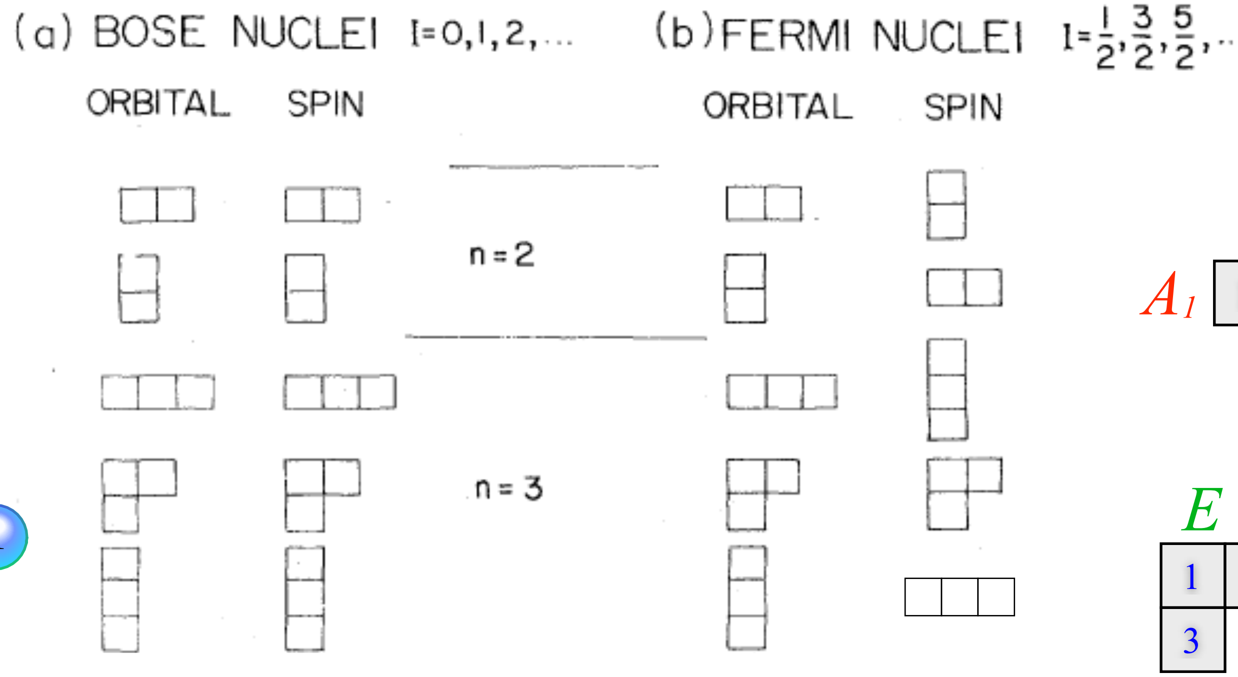
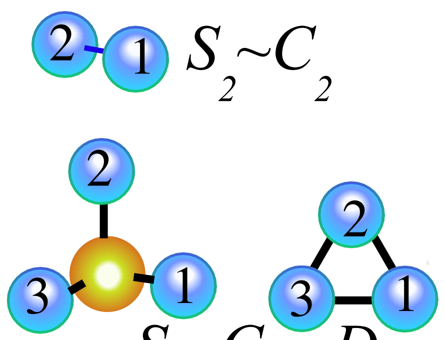


FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n=2,3,4,\ldots$).

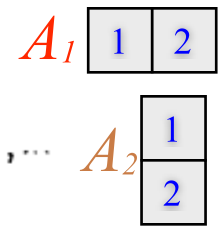




$S_2 \sim C_2$

$S_3 \sim C_{3v} \sim D_3$

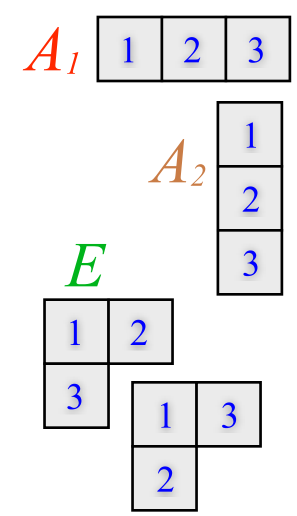
S_2



	(1)(2)	(12)
A_1	1	1
A_2	1	-1

C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

S_3



	(1)(2)(3)	(123) (132)	(12) (13) (23)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

C_{3v}	**1**	$\mathbf{r}^1$ $\mathbf{r}^2$	$\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2$ $\boldsymbol{\sigma}_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

X_n and XY_n molecules: S_3-S_6 tableau-characters

Permutation group S_n is equivalent to Point group $\mathscr{G}$

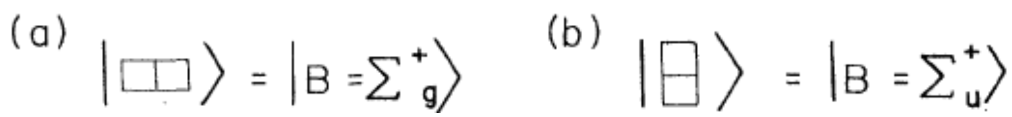
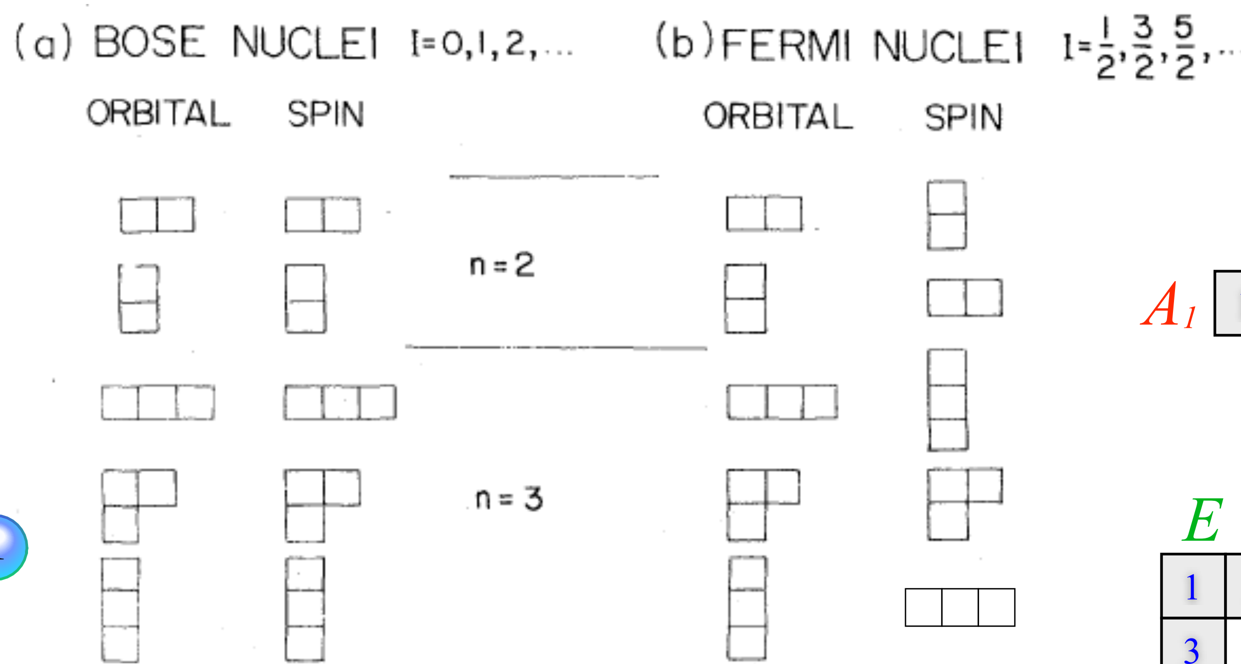
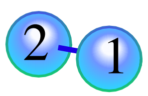


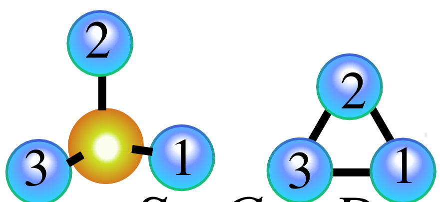
FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2, 3, 4, \ldots$).



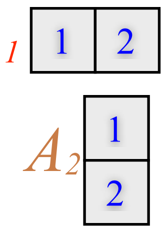


$S_2 \sim C_2$



$S_3 \sim C_{3v} \sim D_3$

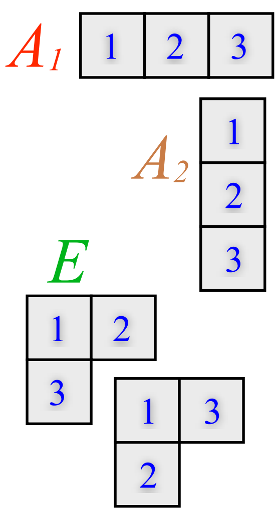
S_2



S_2	(1)(2)	(12)
A_1	1	1
A_2	1	-1

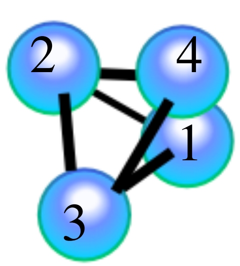
C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

S_3



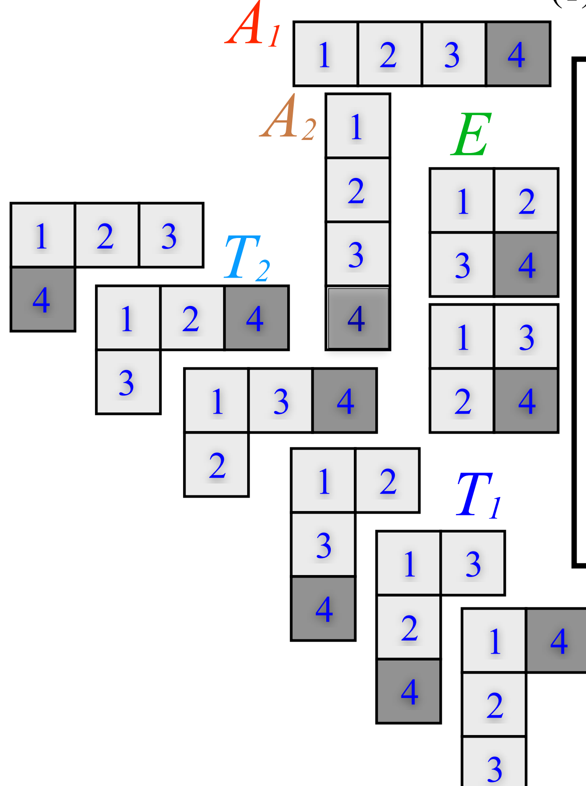
S_3	(1)(2)(3)	(123) (132)	(12) (13) (23)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

C_{3v}	**1**	$\mathbf{r}^1$ $\mathbf{r}^2$	$\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2 \boldsymbol{\sigma}_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0



$S_4 \sim T_d$

S_4



S_4	(1)(2)(3)(4)	(123)(4)	(12)(34)	(1234)	(12)(3)(4)
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_2	3	0	-1	1	-1
T_1	3	0	-1	-1	1

Tetrahedral: $\mathscr{G} = T_d$

T_d	**1**	$\mathbf{r}_{1\ldots4}$	180° $\boldsymbol{\rho}_{xyz}$	$\mathbf{I}\cdot 90°$ $\mathbf{R}_{xyz}$	$\mathbf{I}\cdot 180°$ $\boldsymbol{\sigma}_{1\ldots6}$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_2	3	0	-1	-1	1
T_1	3	0	-1	1	-1

X_n and XY_n molecules: S_3-S_6 tableau-characters

Permutation group S_n is equivalent to Point group $\mathscr{G}$

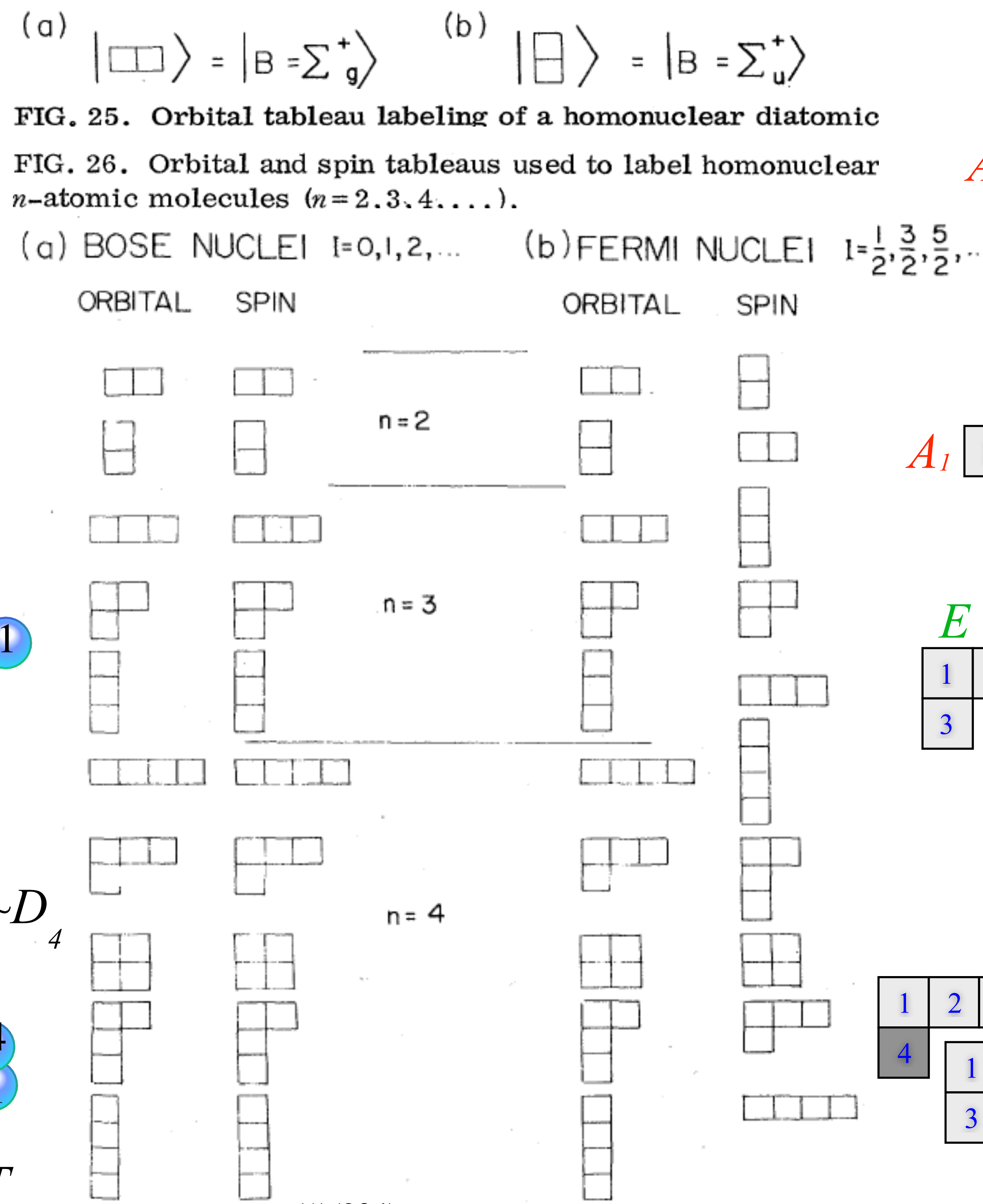

(a) $|\square\square\rangle = |B=\Sigma_g^+\rangle$ (b) $|\,\boxminus\,\rangle = |B=\Sigma_u^+\rangle$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n=2,3,4,\ldots$).

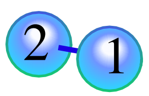
(a) BOSE NUCLEI $I=0,1,2,\ldots$ (b) FERMI NUCLEI $I=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$

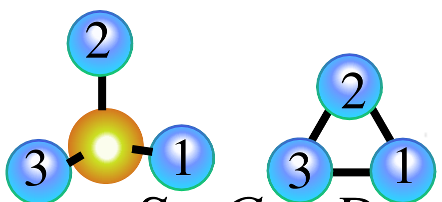
ORBITAL SPIN ORBITAL SPIN

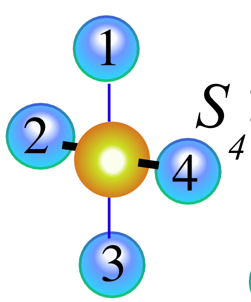
n = 2

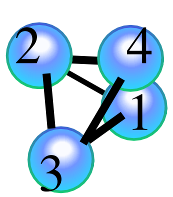
n = 3

n = 4


$S_2 \sim C_2$

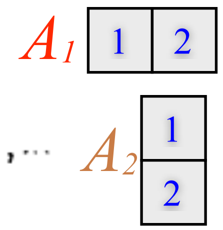

$S_3 \sim C_{3v} \sim D_3$


$S_4 > C_{4v} \sim D_4$


$S_4 \sim T_d$

(1)(2)(3)(4)	(1)(234)	(13)(24)	(1432)	(14)(3)(2)
	(2)(143)	(14)(23)	(1243)	(23)(1)(4)
	(3)(124)	(13)(24)	(1324)	(23)(1)(4)
	(4)(132)		(1234)	(12)(3)(4)
	(1)(243)		(1423)	(24)(1)(3)
	(2)(134)		(1342)	(13)(2)(4)
	(3)(142)			
	(4)(123)			

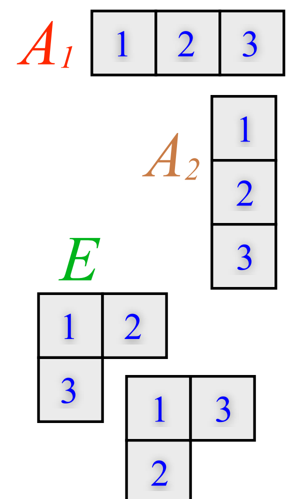
S_2



S_2	(1)(2)	(12)
A_1	1	1
A_2	1	-1

C_2	**1**	**σ**
A_1	1	1
A_2	1	-1

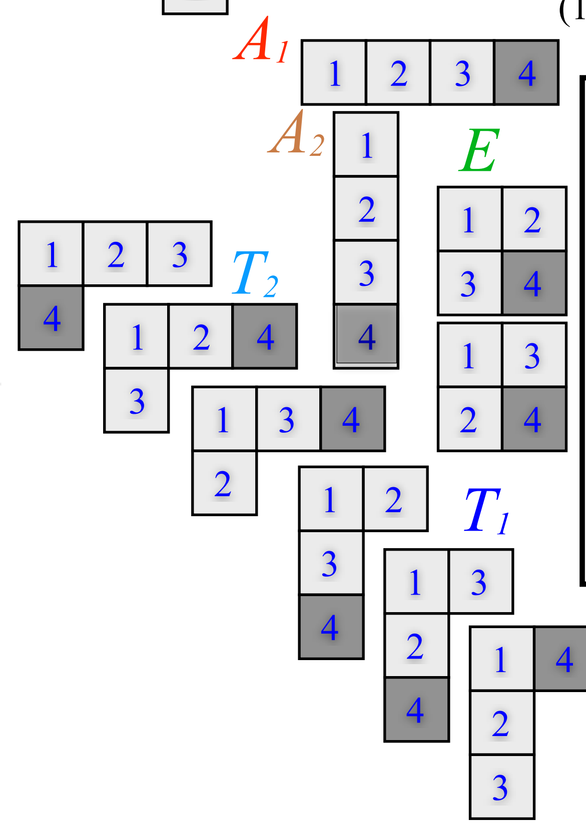
S_3



S_3	(1)(2)(3)	(123) (132)	(12) (13) (23)
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

C_{3v}	**1**	$\mathbf{r}^1$ $\mathbf{r}^2$	$\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2 \boldsymbol{\sigma}_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

S_4



(1)(2)(3)(4)	(123)(4)	(12)(34)	(1234)	(12)(3)(4)
1	1	1	1	1
1	1	1	-1	-1
2	-1	2	0	0
3	0	-1	1	-1
3	0	-1	-1	1

Rev. Mod. Phys. 50,1,1 (1978)

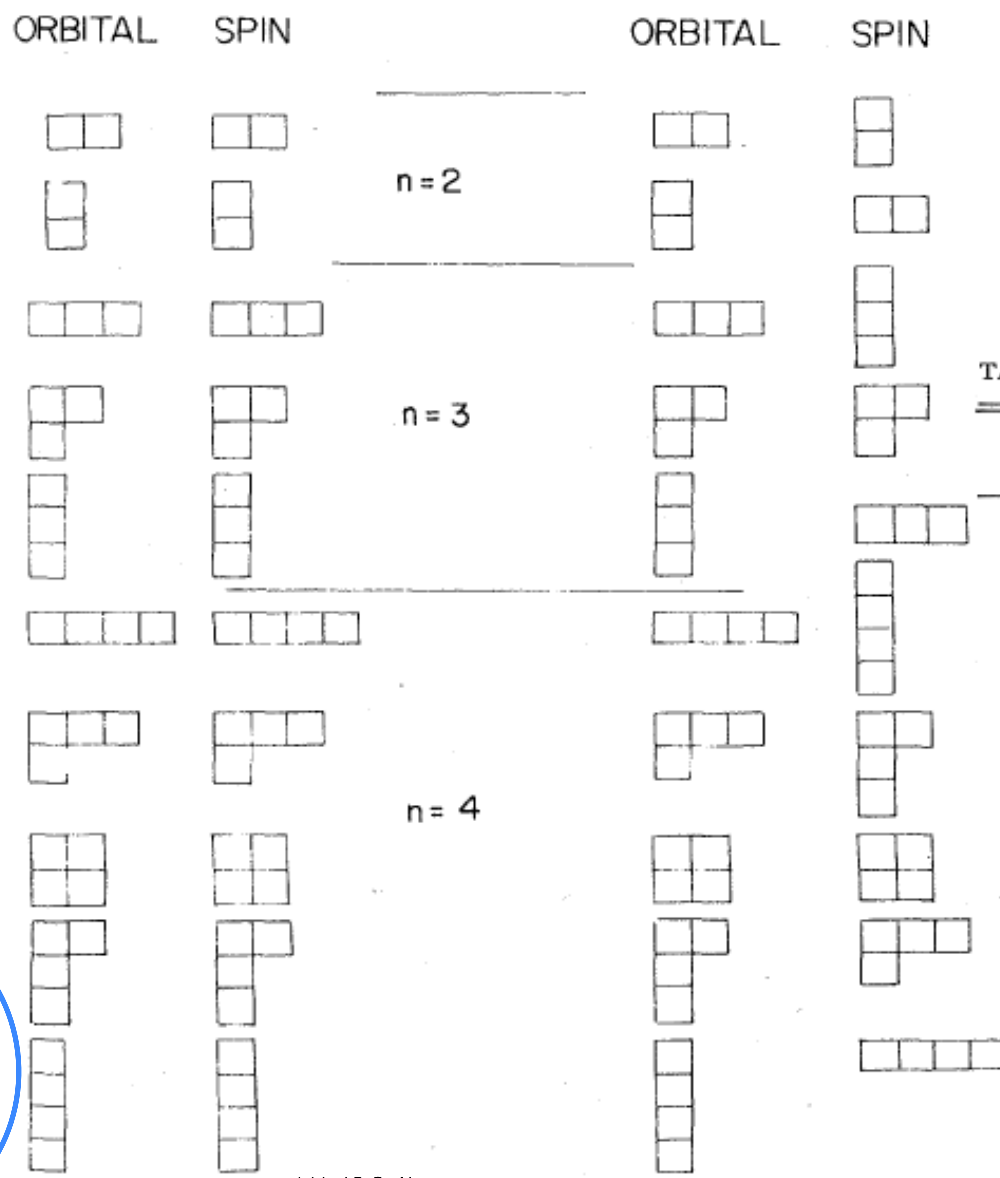
X_n and XY_n molecules: S_3-S_6 tableau-characters

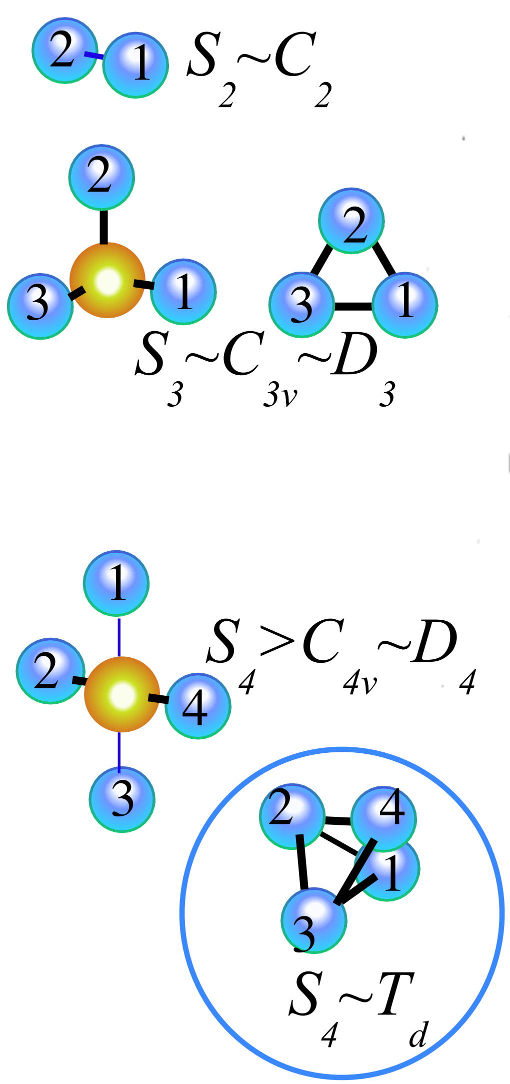
(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\,\substack{\square\\\square}\,\rangle = |B = \Sigma_u^+\rangle$

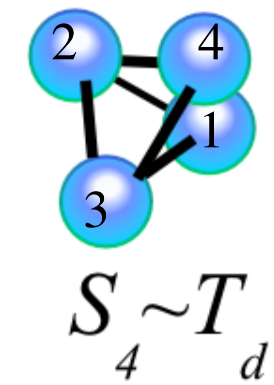
FIG. 25. Orbital tableau labeling of a homonuclear diatomic

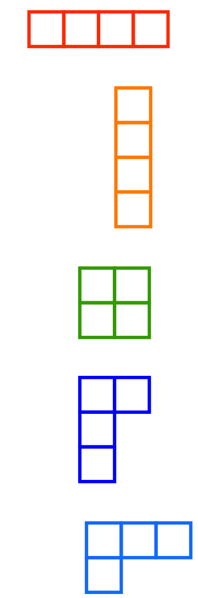
FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2, 3, 4, \ldots$).

(a) BOSE NUCLEI $I = 0, 1, 2, \ldots$ (b) FERMI NUCLEI $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$









Methane-like:XY_4

TABLE XIII. T_d characters and symmetry.

T_d	1	$R\left(\frac{2\pi}{3}\right)$	$R(\pi 00)$	$IR\left(\frac{\pi}{2}00\right)$	$IR\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$	Boson $\{\mu_s\}$	Fermion $\{\mu_s\}$
A_1	1	1	1	1	1	$\{4\}$	$\{1\}\{1\}\{1\}\{1\}$
A_2	1	1	1	-1	-1	$\{1\}\{1\}\{1\}\{1\}$	$\{4\}$
E	2	-1	2	0	0	$\{2\}\{2\}$	$\{2\}\{2\}$
$(L_xL_yL_z)\,F_1$	3	0	-1	1	-1	$\{2\}\{1\}\{1\}$	$\{3\}\{1\}$
$(xyz)\,F_2$	3	0	-1	-1	1	$\{3\}\{1\}$	$\{2\}\{1\}\{1\}\{1\}$

TABLE XIV. $O_3 \downarrow T_d$ correlation.

	A_1	A_2	E	F_1	F_2		A_2	A_1	E	F_2	F_1
$J^p = 0^+$	1	...	...	...	...	0^-	1	...	...	...	...
1^+	...	...	...	1	...	1^-	...	...	...	1	...
2^+	...	...	1	...	1	2^-	...	...	1	...	1
3^+	...	1	...	1	1	3^-	...	1	...	1	1
4^+	1	...	1	1	1	4^-	1	...	1	1	1
5^+	...	...	1	2	1	5^-	...	...	1	2	1
6^+	1	1	1	1	2	6^-	1	1	1	1	2
7^+	...	1	1	2	2	7^-	...	1	1	2	2

(1)(2)(3)(4)

(1)(234)
(2)(143)
(3)(124)
(4)(132)
(1)(243)
(2)(134)
(3)(142)
(4)(123)

(13)(24)
(14)(23)
(13)(24)

(1432)
(1243)
(1324)
(1234)
(1423)
(1342)

(14)(3)(2)
(23)(1)(4)
(23)(1)(4)
(12)(3)(4)
(24)(1)(3)
(13)(2)(4)

Rev. Mod. Phys. 50,1,1 (1978)pdf p.39.

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

S_n Young Tableaus and spin-symmetry for X_4 and XY_4 molecules

Reviewing tableau dimension formulae

$$\ell^{[\mu_s]}(S_n) = \frac{\text{Dimension of } S_n \text{ Tableau } [\mu_1][\mu_2]\cdots[\mu_n]}{} = \frac{n! = n\cdot(n-1)\cdot(n-2)\cdots 3\cdot 2\cdot 1}{\text{hook-length product } \begin{array}{|c|c|c|c|c|}\hline \bullet 8 & \bullet 6 & \bullet 4 & \bullet 2 & \bullet 1 \\ \hline \bullet 5 & \bullet 3 & \bullet 1 \\ \cline{1-3} \bullet 3 & \bullet 1 \\ \cline{1-2} \bullet 1 \\ \cline{1-1} \end{array}}$$

Examples:

$$\ell^{A_1} = \ell^{[3,0,0]}(S_3) = \frac{3\cdot 2\cdot 1}{\begin{array}{|c|c|c|}\hline 3 & 2 & 1 \\ \hline \end{array}} = 1$$

$$\ell^{A_2} = \ell^{[1,1,1]}(S_3) = \frac{3\cdot 2\cdot 1}{\begin{array}{|c|}\hline 3 \\ \hline 2 \\ \hline 1 \\ \hline \end{array}} = 1$$

$$\ell^{E} = \ell^{[2,1,0]}(S_3) = \frac{3\cdot 2\cdot 1}{\begin{array}{|c|c|}\hline 3 & 1 \\ \hline 1 \\ \cline{1-1} \end{array}} = 2$$

S_3 (1)(2)(3)

A_1 $\begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline \end{array}$

A_2 $\begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline 3 \\ \hline \end{array}$

E $\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1} \end{array}$ $\begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1} \end{array}$

1
1
2

FIG. 28. Robinson formula for statistical weights. The "hook-length" of a box in the tableau is the number of boxes in a "hook" which includes that box and all boxes in the line to the right and in the column below it.

$$\ell^{[\mu_s]}(U_m) = \frac{\text{Dimension of } S_n{*}U_m \text{ Tableau } [\mu_1][\mu_2]\cdots[\mu_m]}{} = \frac{m\text{-dimension product } \begin{array}{|c|c|c|c|c|}\hline m & m+1 & m+2 & m+3 & m+4 \\ \hline m-1 & m & m+1 \\ \cline{1-3} m-2 & m-1 \\ \cline{1-2} m-3 \\ \cline{1-1} \end{array}}{\text{hook-length product } \begin{array}{|c|c|c|c|c|}\hline \bullet 8 & \bullet 6 & \bullet 4 & \bullet 2 & \bullet 1 \\ \hline \bullet 5 & \bullet 3 & \bullet 1 \\ \cline{1-3} \bullet 3 & \bullet 1 \\ \cline{1-2} \bullet 1 \\ \cline{1-1} \end{array}}$$

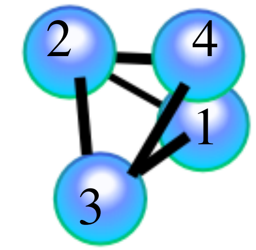
Examples:

$$\ell^{[2,1,0]}(S_3{*}U(3)) = \frac{\begin{array}{|c|c|}\hline 3 & 4 \\ \hline 2 \\ \cline{1-1} \end{array}}{\begin{array}{|c|c|}\hline 3 & 1 \\ \hline 1 \\ \cline{1-1} \end{array}} = 8$$

$$\ell^{[3,0,0]}(S_3{*}U(3)) = \frac{\begin{array}{|c|c|c|}\hline 3 & 4 & 5 \\ \hline \end{array}}{\begin{array}{|c|c|c|}\hline 3 & 2 & 1 \\ \hline \end{array}} = 10$$

S_4 and spin-symmetry for XY_4 molecules (Reviewing tableau formulae)

CH_4 and DH_4 (J=7)



$S_4 \sim T_d$

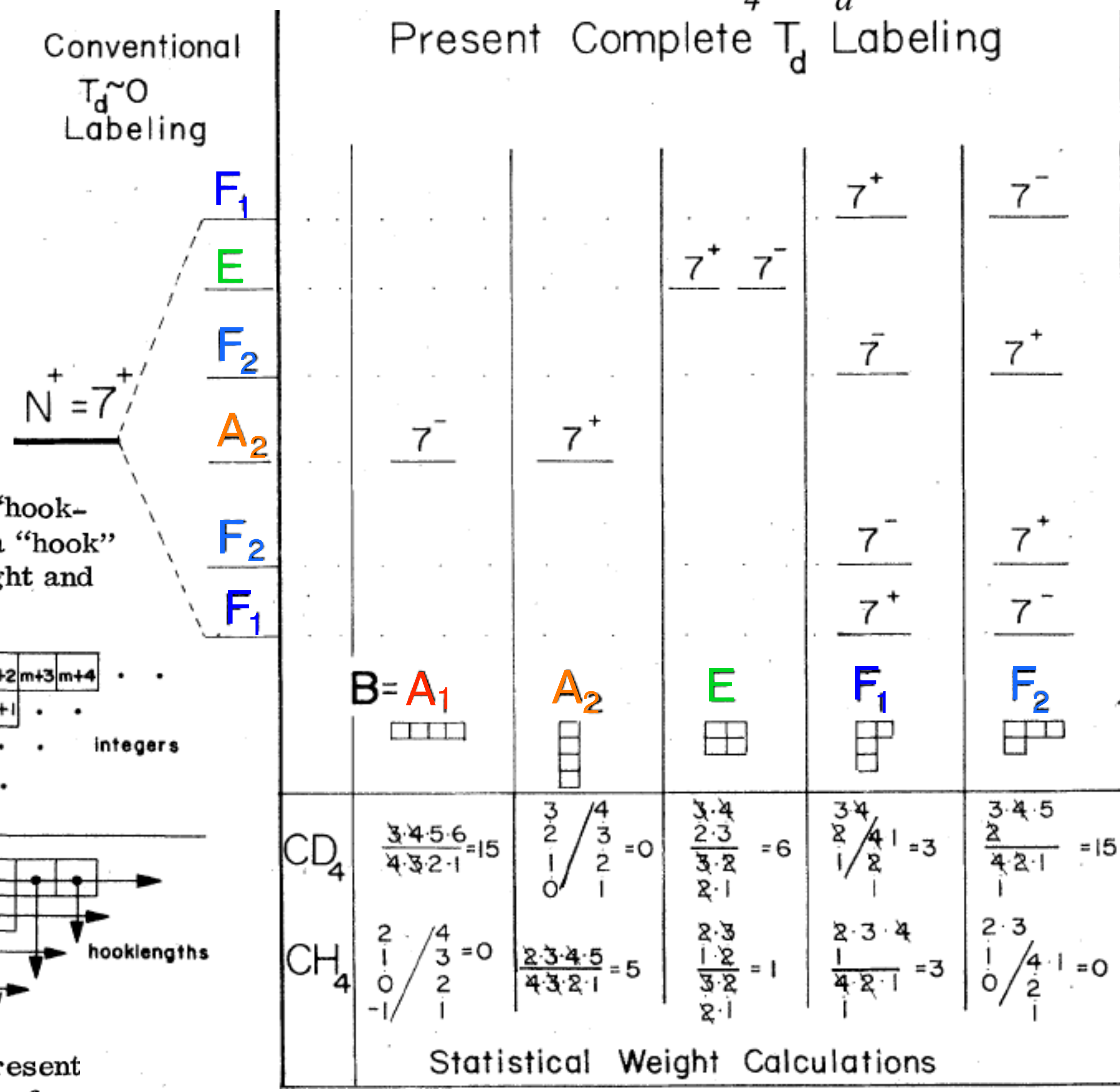
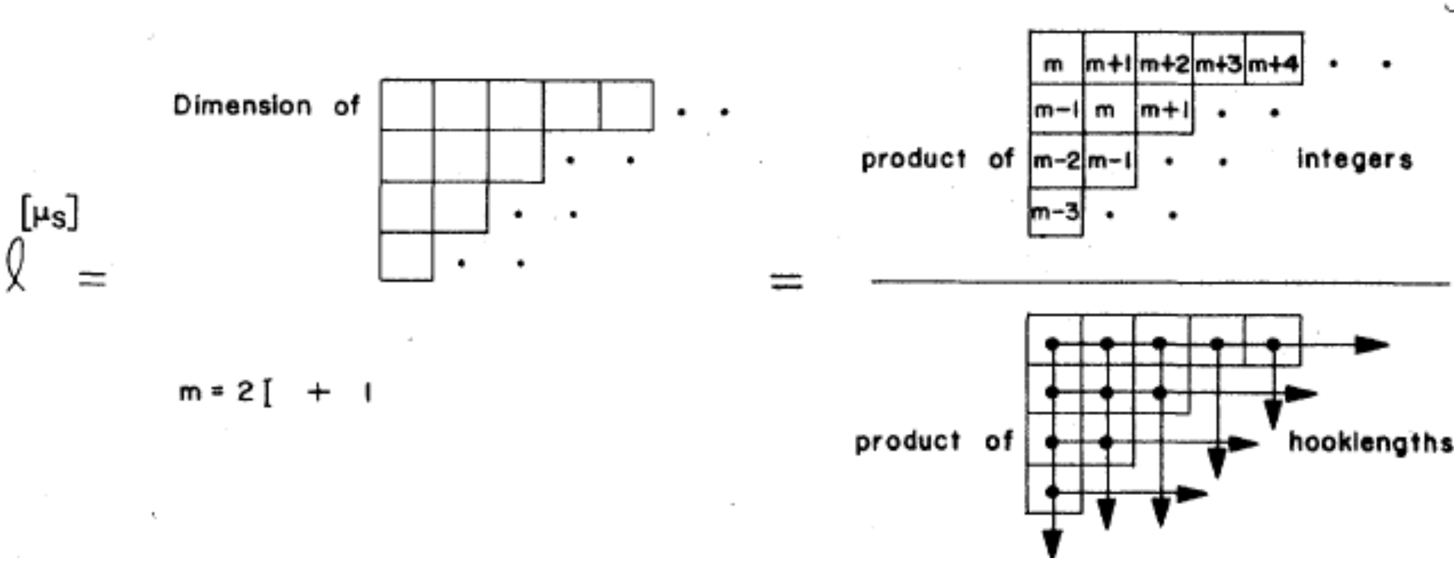


FIG. 36. Comparison of conventional CH_4 labeling with present labeling. The latter shows clearly the "hidden" structure of inversion doublets which has a structure very much like that of NH_3. For CH_4, however, only the E levels are actually double according to the statistical weight calculations.

FIG. 28. Robinson formula for statistical weights. The "hook-length" of a box in the tableau is the number of boxes in a "hook" which includes that box and all boxes in the line to the right and in the column below it.



AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6 **ZIPP (Zero-Interaction-Potential-`Proximation*

REES for high-J Coriolis spectra in υ_3 CF_4

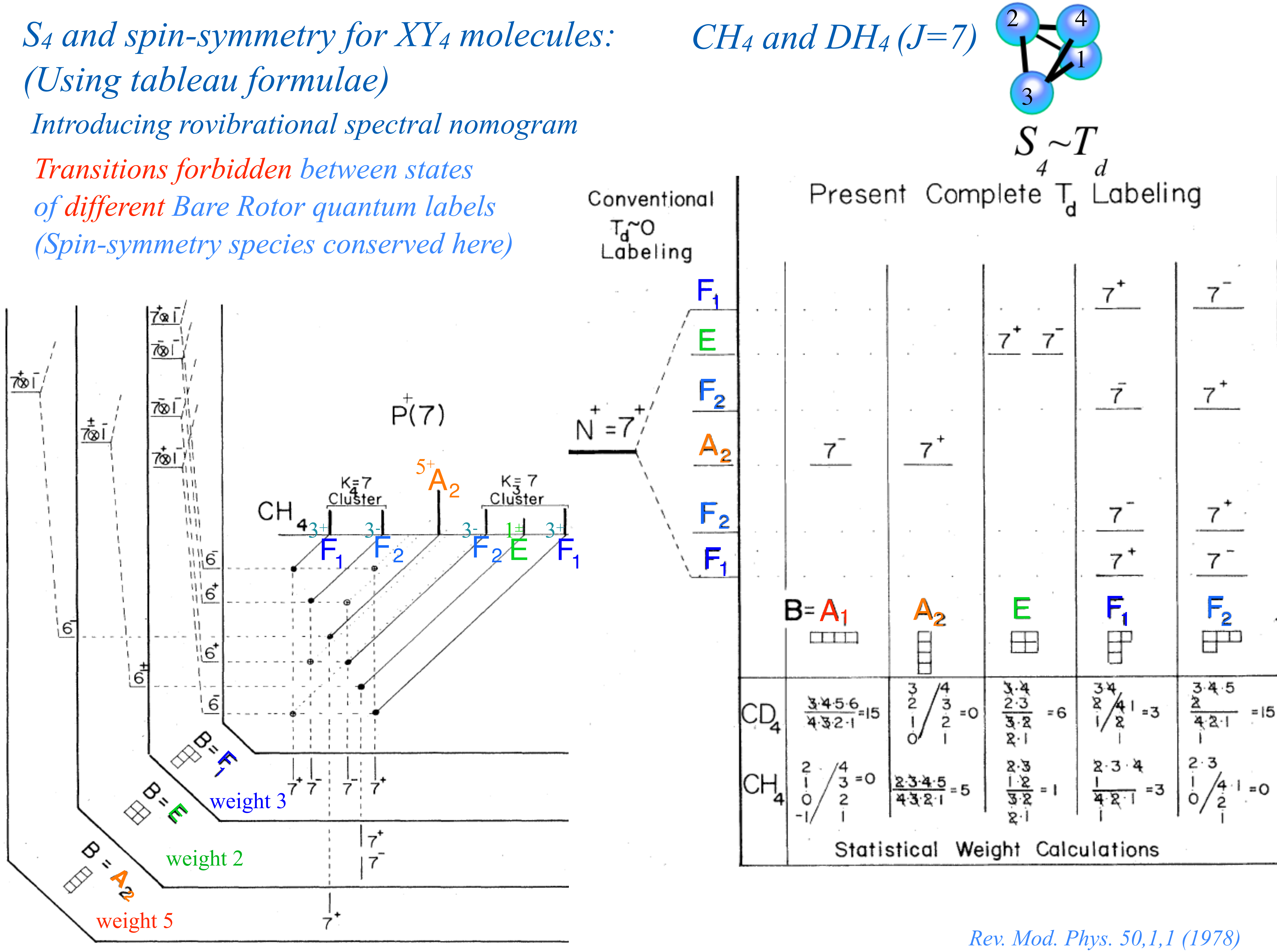
. REES for high-J and high-υ rovibration polyads

S_4 and spin-symmetry for XY_4 molecules: (Using tableau formulae)

CH_4 and DH_4 (J=7)

Introducing rovibrational spectral nomogram

Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved here)



Rev. Mod. Phys. 50,1,1 (1978)

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

State labels by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

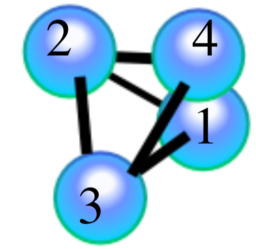
REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

S_4 and spin-symmetry for XY_4 molecules (Reviewing tableau formulae)

CH_4 and DH_4 $(J=7)$



$S_4 \sim T_d$

SiF_4 $(J=30)$

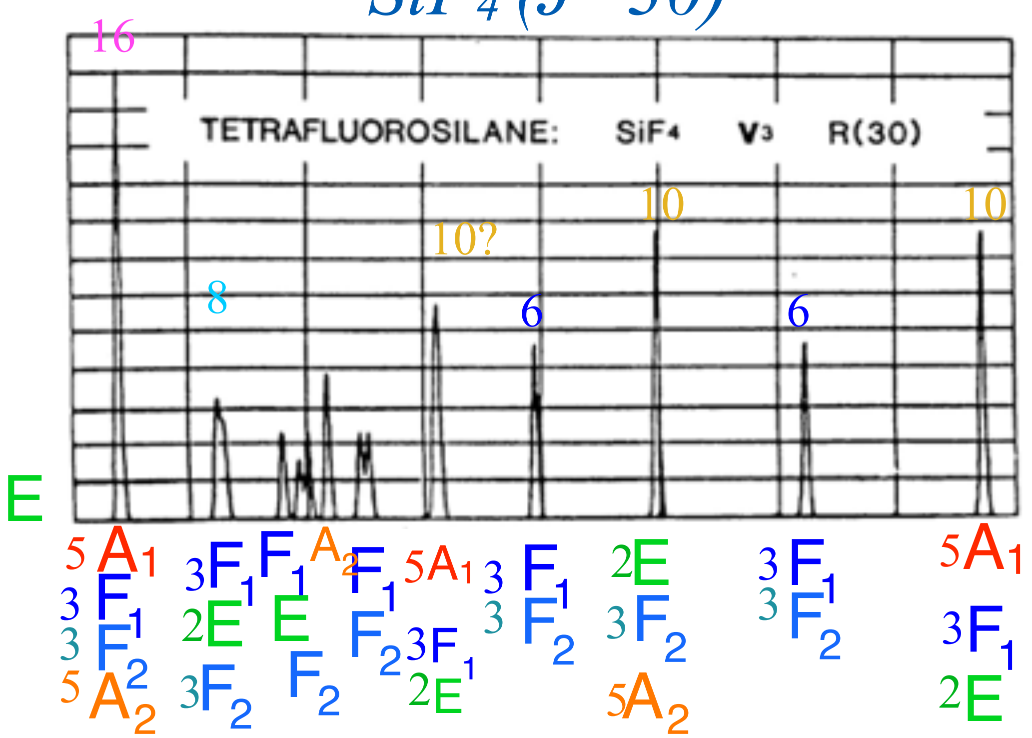
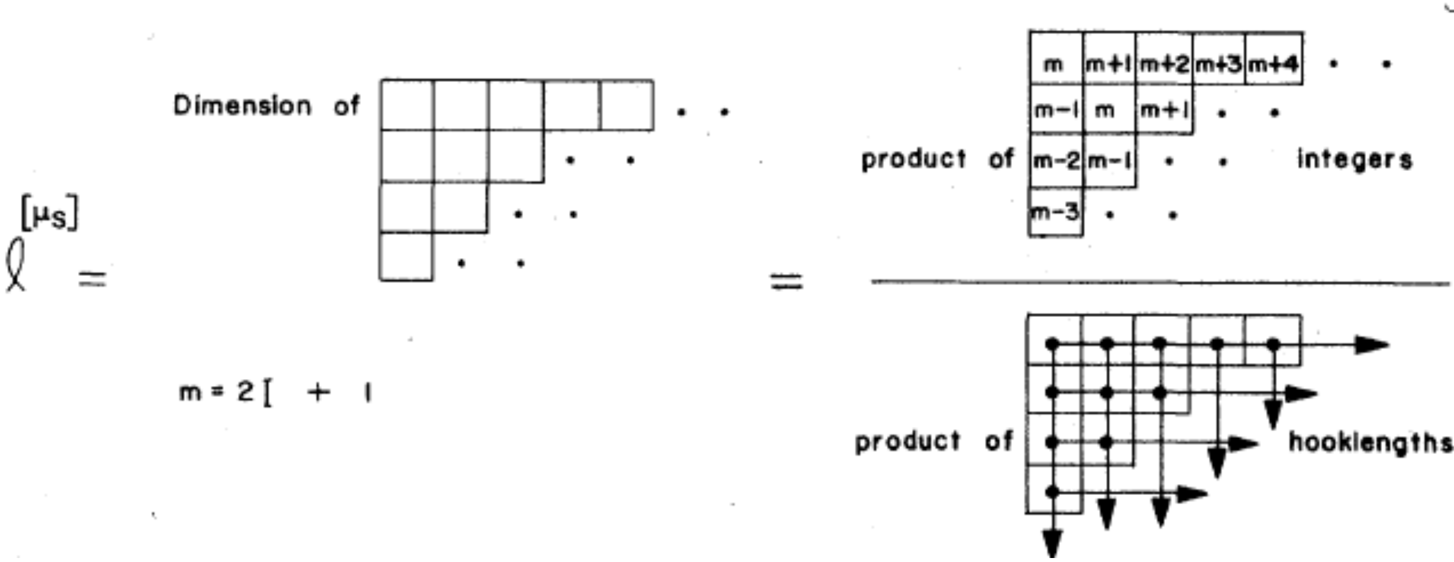


FIG. 28. Robinson formula for statistical weights. The "hook-length" of a box in the tableau is the number of boxes in a "hook" which includes that box and all boxes in the line to the right and in the column below it.



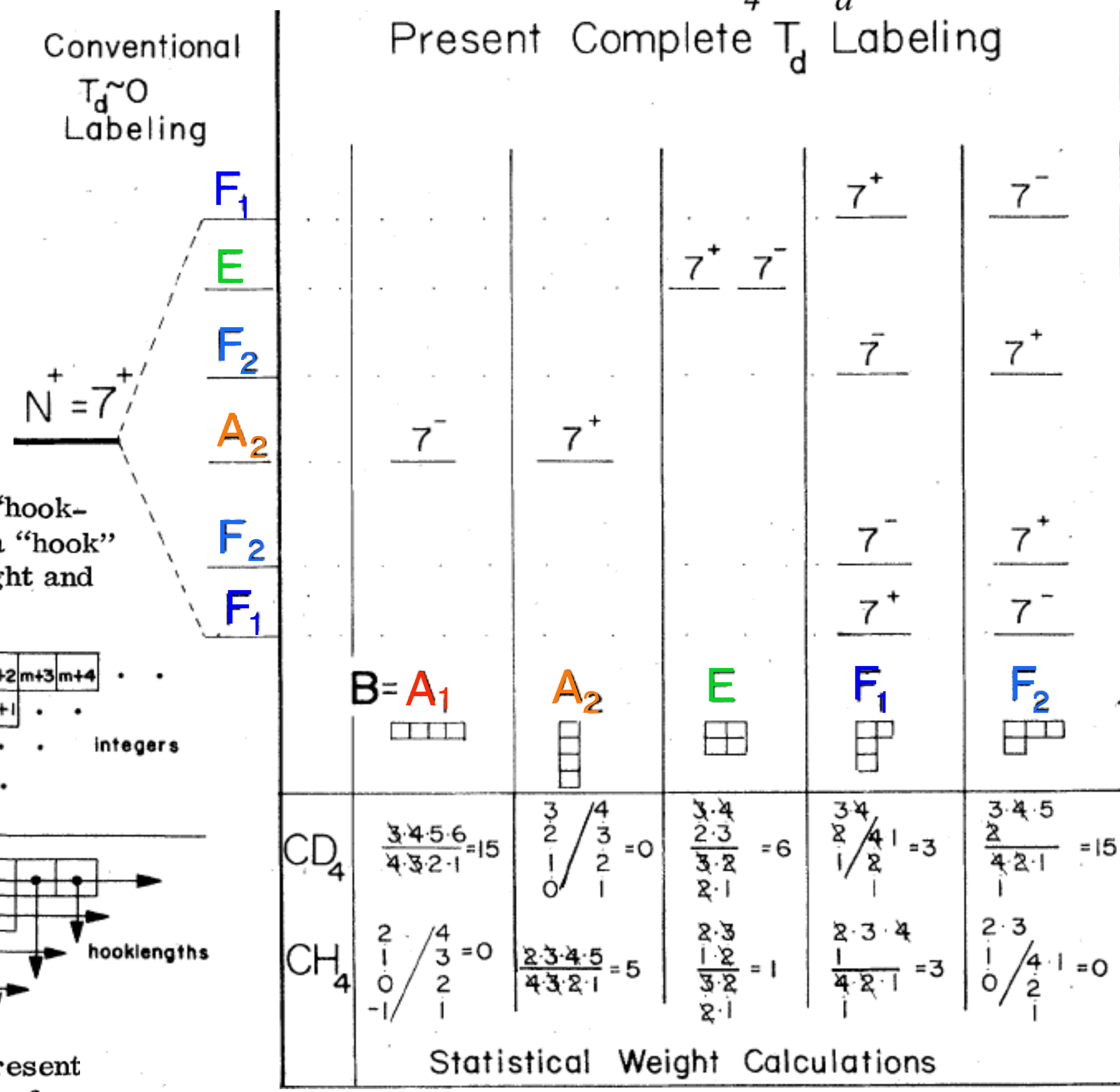


FIG. 36. Comparison of conventional CH_4 labeling with present labeling. The latter shows clearly the "hidden" structure of inversion doublets which has a structure very much like that of NH_3. For CH_4, however, only the E levels are actually double according to the statistical weight calculations.

Rev. Mod. Phys. 50,1,1 (1978)

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

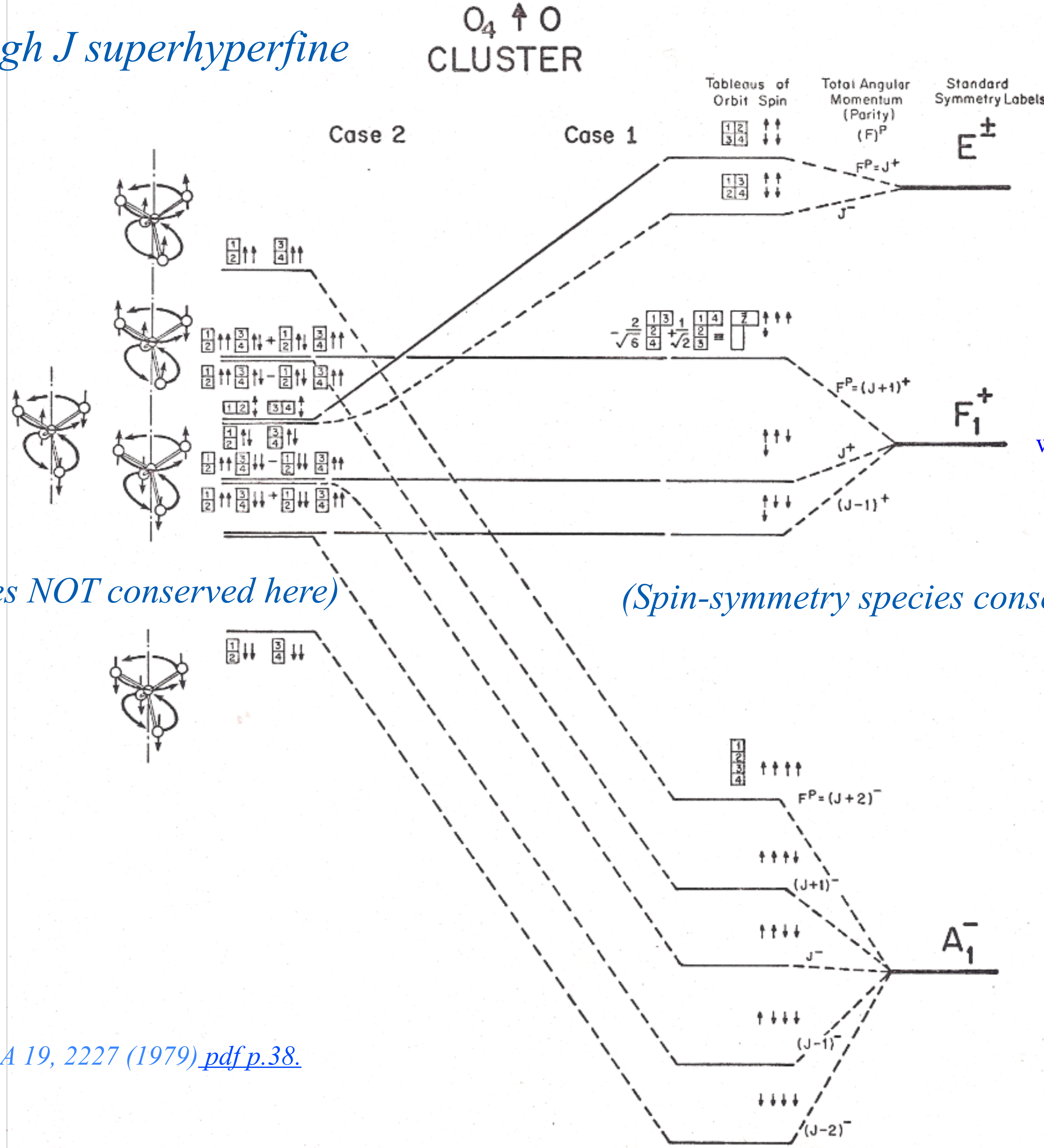
William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$
State labels by symmetry $O(3)\supset D_{\infty h}$
Coriolis and λ-doubling levels
Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
Tableau dimension formulae for X_4 and XY_4 molecules
CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)
REES for high-J Coriolis spectra in SF_6
REES for high-J Coriolis spectra in υ_3 CF_4
. REES for high-J and high-υ rovibration polyads

*ZIPP (Zero-Interaction-Potential-`Proximation

Possible SiF_4 High J superhyperfine



weight 2

weight 3

weight 5

(Spin-symmetry species NOT conserved here)

(Spin-symmetry species conserved here)

Harter-Patterson, PRA 19, 2227 (1979) pdf p.38.

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$
State labels by symmetry $O(3)\supset D_{\infty h}$
Coriolis and λ-doubling levels
Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
Tableau dimension formulae for X_4 and XY_4 molecules
CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 **SF_6 levels&spectra**
Born-Oppenheimer Approximation (BOA) for RES
Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)
REES for high-J Coriolis spectra in SF_6
REES for high-J Coriolis spectra in υ_3 CF_4
. REES for high-J and high-υ rovibration polyads

*ZIPP (Zero-Interaction-Potential-`Proximation

APPENDIX C. S_n CHARACTER FORMULA

We give a formula (Coleman, 1966) for S_n characters $\chi^{[\mu_1\cdots\mu_p]}_{1^\alpha 2^\beta 3^\gamma}$. Here the S_n IR is labeled by a tableau symbol $[\mu_1\cdots\mu_p]$ wherein μ_j means that row j has μ_j boxes. The S_n classes are labeled by the notation $1^\alpha 2^\beta 3^\gamma \cdots n$ wherein α, β, γ, ... are the number of permutation 1-cycles, 2-cycles, 3-cycles, ... respectively. For example, the permutation (1)(3)(2, 5)(4, 7, 6, 8) would be in the class $1^2 2^1 3^0 4^1 5^0 6^0 7^0 8^0$ of S_8. The character then is given by the following formula and definitions. Note that th formula starts with a column of numbers that are the hooklengths of the first column of the tableau. Then the definitions are used to whittle it down to a sum of sequentially numbered columns which each contribute unit according to Def. 2.

$$\chi^{[\mu_1\cdots\mu_p]}_{1^\alpha 2^\beta 3^\gamma\cdots} = \partial_1^\alpha \partial_2^\beta \partial_3^\gamma \cdots \left| \begin{array}{c} \mu_1 + p - 1 \\ \cdot \\ \cdot \\ \cdot \\ \mu_{p-2} + 2 \\ \mu_{p-1} + 1 \\ \mu_p \end{array} \right| ;$$

For example, here is the character of the [56, 13] IR of class 2, 11, 56 of S_{69}:

$$\chi^{[56,13]}_{2,11,56} = \partial_2 \partial_{11} \partial_{56} \left| \begin{array}{c} 57 \\ 13 \end{array} \right| = \partial_2 \partial_{11} \left| \begin{array}{c} 1 \\ 13 \end{array} \right|$$

$$= \partial_2 \left| \begin{array}{c} 1 \\ 2 \end{array} \right| = \left| \begin{array}{c} 1 \\ 0 \end{array} \right| = 1 .$$

Def. 1:

$$\partial_m \left| \begin{array}{c} a \\ b \\ c \\ \cdot \\ \cdot \\ \cdot \end{array} \right| = \left| \begin{array}{c} a-m \\ b \\ c \\ \cdot \\ \cdot \\ \cdot \end{array} \right| + \left| \begin{array}{c} a \\ b-m \\ c \\ \cdot \\ \cdot \\ \cdot \end{array} \right| + \left| \begin{array}{c} a \\ b \\ c-m \\ \cdot \\ \cdot \\ \cdot \end{array} \right| + \cdots ;$$

Def. 2:

$$\left| \begin{array}{c} p-1 \\ \cdot \\ \cdot \\ \cdot \\ 2 \\ 1 \\ 0 \end{array} \right| = 1 ;$$

Def. 3:

$$\left| \begin{array}{c} a \\ b \\ c \\ \cdot \\ \cdot \\ \cdot \end{array} \right| = 0$$ if any two numbers in the column are equal, or if any number is less than zero;

Def. 4:

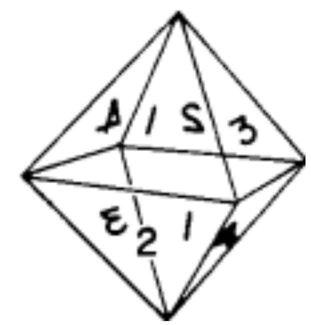
$$\left| \begin{array}{c} a \\ b \\ c \\ \cdot \\ \cdot \\ \cdot \end{array} \right| = - \left| \begin{array}{c} b \\ a \\ c \\ \cdot \\ \cdot \\ \cdot \end{array} \right|$$ interchanging any two numbers gives a change of sign.

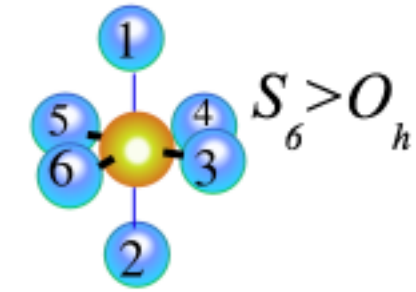
Calculating SF_6 correlations of symmetry O_h to S_6

TABLE XV. Characters of permutation group (S_6) and octahedral (O_h) subgroup.

	1^6	3^2	2^2	4^1	2^3	2^3	6^1	2^1	$2^1 4^1$	$2^2 = S_6$ Class
$\{\mu\}=\{6\}$	1	1	1	1	1	1	1	1	1	1
$\{5,1\}$	5	−1	1	1	−1	−1	−1	3	−1	1
$\{4,2\}$	9	0	1	−1	3	3	0	3	1	1
$\{4,1,1\}$	10	1	−2	0	−2	−2	1	2	0	−2
$\{3,3\}$	5	2	1	−1	−3	−3	0	1	−1	1
$\{3,2,1\}$	16	−2	0	0	0	0	0	0	0	0
$\{2,2,2\}$	5	2	1	1	3	3	0	−1	−1	1
$\{3,1,1,1\}$	10	1	−2	0	2	2	−1	−2	0	−2
$\{2,2,1,1\}$	9	0	1	1	−3	−3	0	−3	1	1
$\{2,1,1,1,1\}$	5	−1	1	−1	1	1	1	−3	−1	1
$\{1,1,1,1,1,1\}$	1	1	1	−1	−1	−1	−1	−1	1	1
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
E_g	2	−1	2	0	0	2	−1	2	0	0
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
E_u	2	−1	2	0	0	−2	1	−2	0	0
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1
	1	120° Class	180° Class	90° Class	180° Class	I				

RevModPhys(1978)
pdf page 45





Phys Rev. A24(1981)
pdf page 13

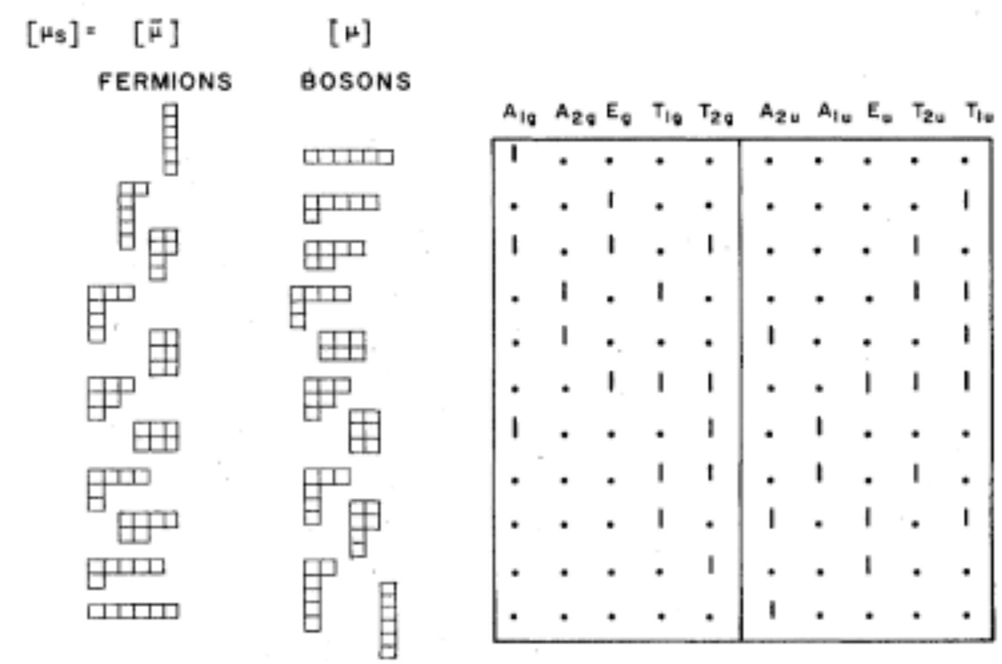


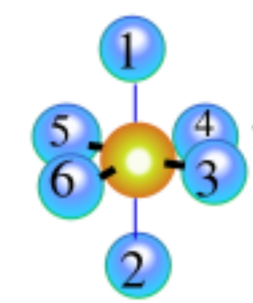
FIG. 27. Spin tableau-(B) correlation for octahedral XY_6 molecule (see Appendix D).

Calculating SF_6 correlations of symmetry O_h to S_6

TABLE I. Permutational - octahedral correlation table $S_6 + O_h$. Only the last four rows are relevant for spin-$\frac{1}{2}$ nuclei.

Fermi nuclei	Bose nuclei	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_g	E_u	T_{1g}	T_{1u}	T_{2g}	T_{2u}	
$[1^6]$	$[6]$	1	·	·	·	·	·	·	·	·	·	
$[2,1^4]$	$[5,1]$	·	·	·	·	1	·	·	1	·	·	
$[2,2,1,1]$	$[4,2]$	1	·		·	1	·	·	·	1	1	
$[3,1^3]$	$[4,1,1]$	·	·	1	·	·	·	1	1	·	1	
$[2,2,2]$	$[3,3]$	·	·	1	1	·	·	·	1	·	·	
$[3,2,1]$	$[3,2,1]$	·	·	·	·	1	1	1	1	1	1	
$[4,1,1]$	$[3,1^3]$	·	1	·	·	·	·	1	·	1	1	
$[3,3]$	$[2,2,2]$	1	1	·	·	·	·	·	·	1	·	$I=0$
$[4,2]$	$[2,2,1,1]$	·	·	·	1	·	1	1	1	·	·	$I=1$ Spin-$\frac{1}{2}$ nuclei
$[5,1]$	$[2,1^4]$	·	·	·	·	·	1	·	·	1	·	$I=2$ Spin-$\frac{1}{2}$ nuclei
$[6]$	$[1^6]$	·	·	·	1	·	·	·	·	·	·	$I=3$ Spin-$\frac{1}{2}$ nuclei

Phys Rev. A24(1981)
pdf page 13



$S_6 > O_h$

Calculating SF_6 correlations of symmetry O_h to S_6

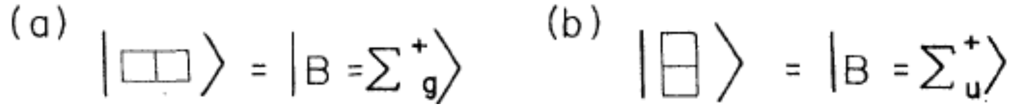
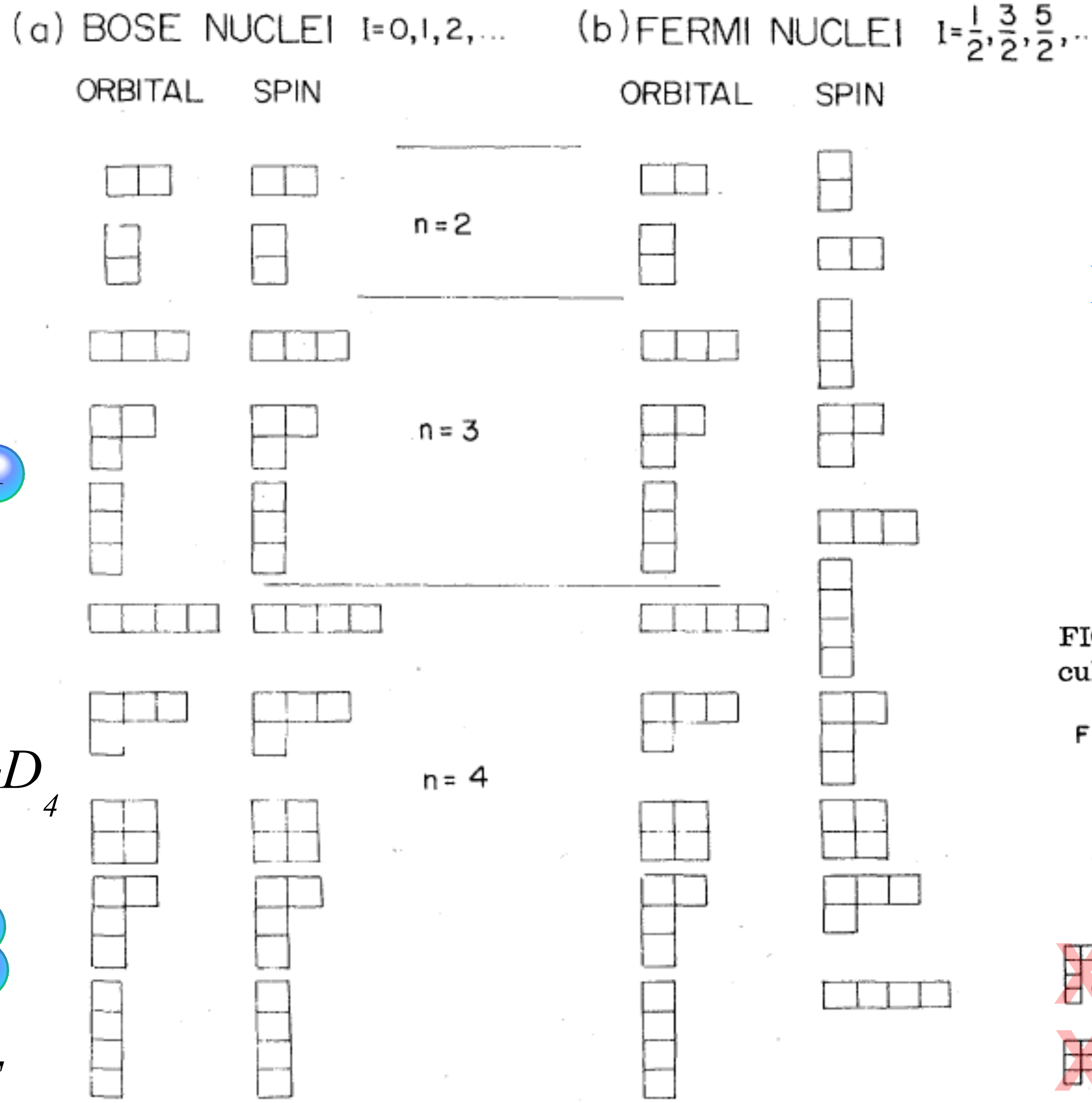
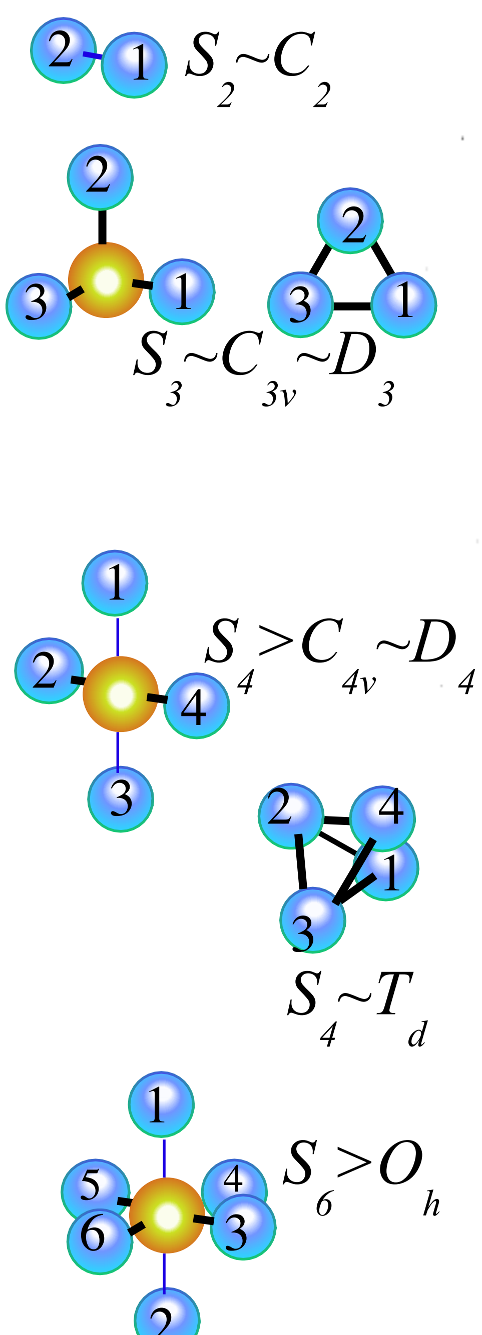
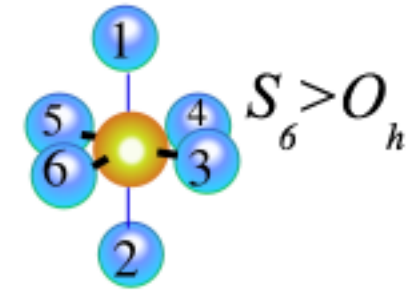


FIG. 25. Orbital tableau labeling of a homonuclear diatomic

FIG. 26. Orbital and spin tableaus used to label homonuclear n-atomic molecules ($n = 2.3.4. \ldots$).







Hexa-flouride-like:XY_6

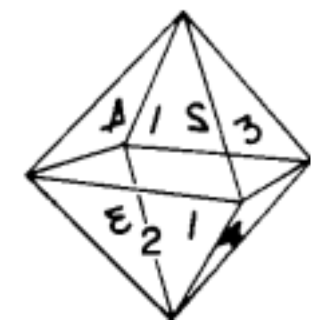
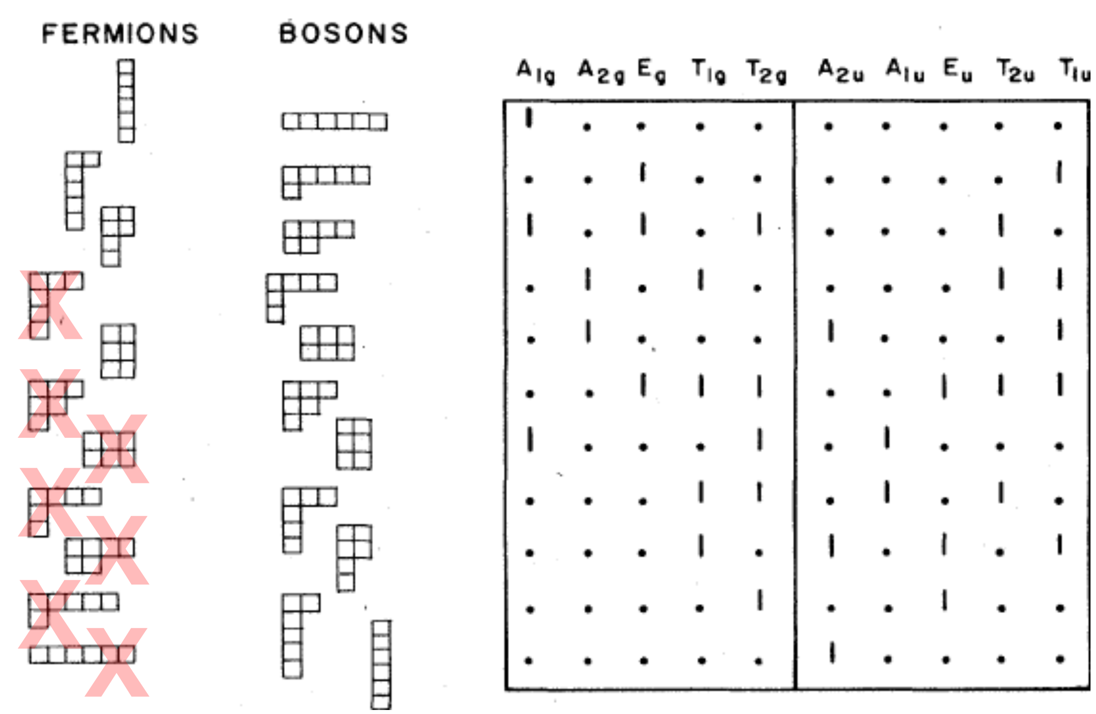


FIG. 27. Spin tableau-(B) correlation for octahedral XY_6 molecule (see Appendix D).



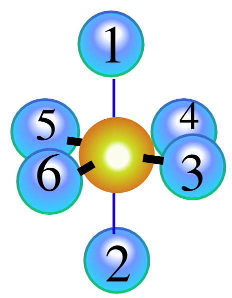
Compare to spin-½ case of $S_6 > O_h$ table that follows where orbit-tableau with more than 2 columns are *forbidden*

Rev. Mod. Phys. 50,1,1 (1978)

SF_6 *Entanglement!*

How F-nuclei become entangled total-spin-I-symmetry O_h species in SF_6.

With rotation all six nuclei are equivalent



C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E_1	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

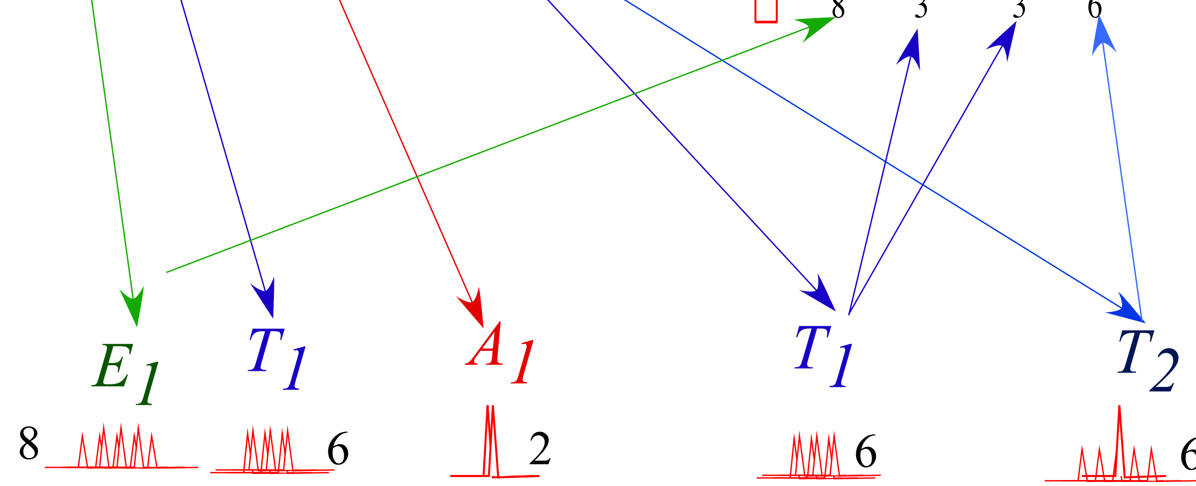
Spin-Permutation to Octahedral Correlations $S_6 \supset O_h$

	E_u	T_{1g}	T_{1u}	T_{2g}	A_{1g}	A_{1u}	A_{2u}
I=0	.	.	.	1	1	1	.
I=1	1	1	1	.	.	.	1
I=2	1	.	.	1	.	.	.
I=3	.	.	.	.	.	.	1
Species Spin Weights	8	3	3	6	1	1	10

Forbidden SF_6 species: E_g, T_{2u}, A_{2g}

0 0 0

Compare to complete $S_6 > O_h$ table on p.86

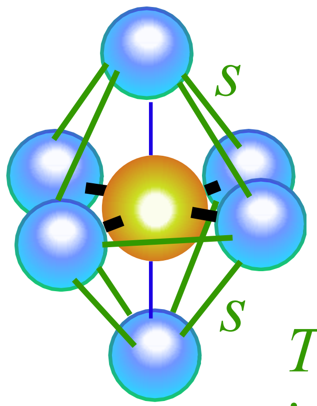


Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde´, C. Saloman, and Oliver Pfister (Pfister did SiF_4, too.)

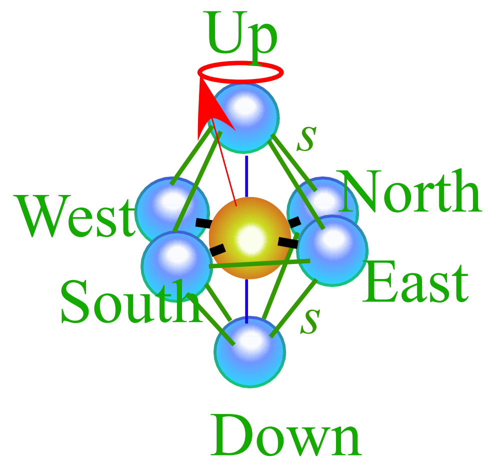
See SF_6 spectra with A_2 T_2 E level cluster that follows

SF_6 cluster $0_4 \uparrow O_h$

*Internal **J** gets "stuck" on RES axes*
Must "tunnel" axis-to-axis at rate s



Tunneling s=-S
is negative here



|U>|D>|E>|W>|N>|S>

$$\begin{pmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{pmatrix}$$

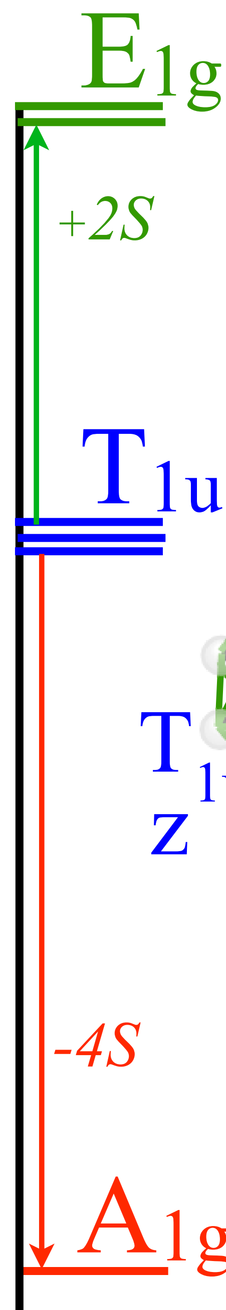
Review O(0_4)⊃C_4 cluster:

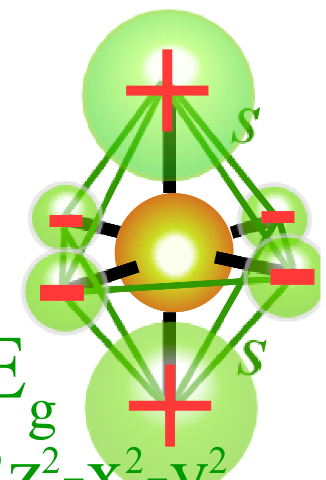
0_4 cluster splitting

$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}} = (H-2s) \begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}}$$

$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}} = (H+0) \begin{vmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}}$$

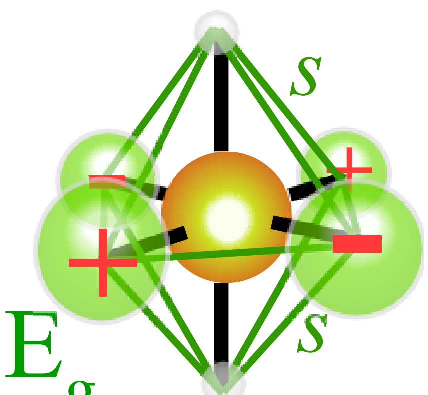
$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}} = (H+4s) \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}}$$





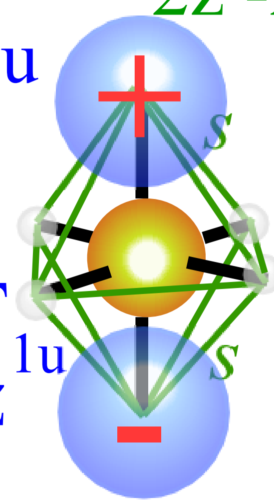
E_g $2z^2-x^2-y^2$

$$\begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}}$$



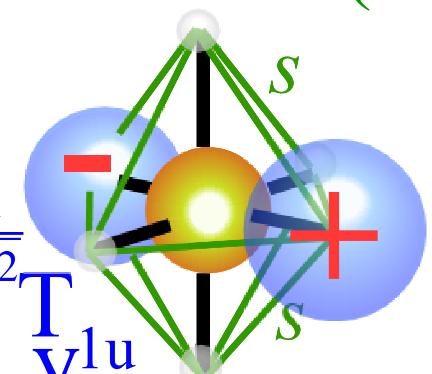
E_g $(x^2-y^2)\sqrt{3}$

$$\begin{vmatrix} 0 \\ 0 \\ -1 \\ -1 \\ +1 \\ +1 \end{vmatrix} \frac{1}{2}$$

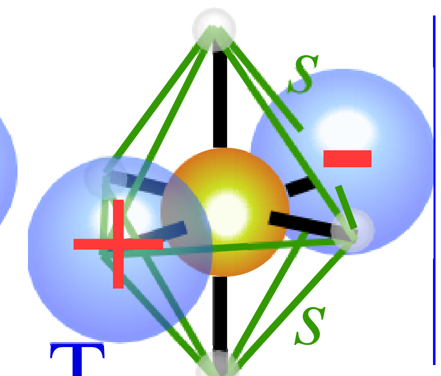


T_{1u} z

$$\begin{vmatrix} 0 \\ 0 \\ +1 \\ -1 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}}$$

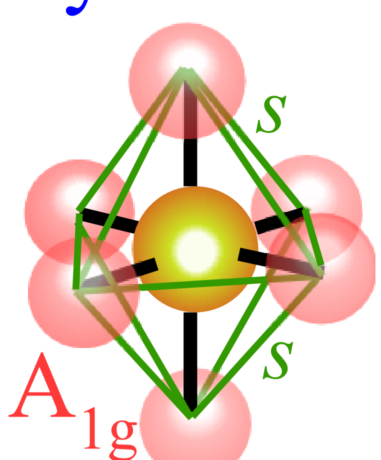


T_{1u} y



$$\begin{vmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ +1 \end{vmatrix} \frac{1}{\sqrt{2}}$$

T_{1u} x



A_{1g}

$$\begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}}$$

SF_6 DISentanglement!

How F-nuclei become distinguished
(but not distinguishable)
in SF_6.

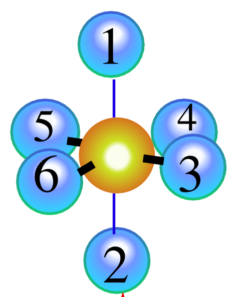
C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E_1	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

Spin-Permutation to Octahedral Correlations $S_6 \supset O_h$

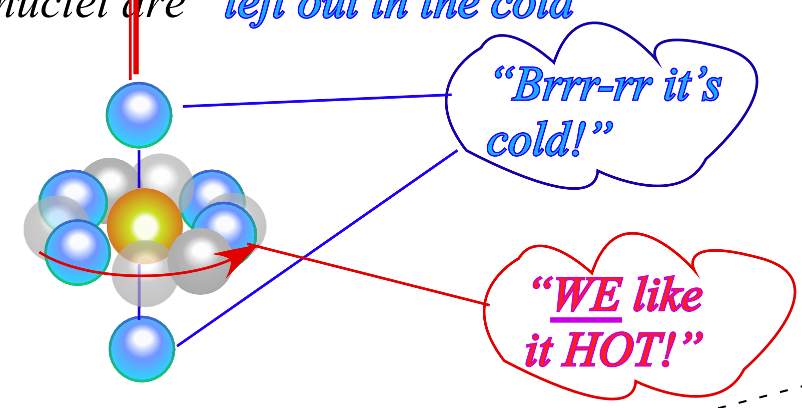
Spin	E_u	T_{1g}	T_{1u}	T_{2g}	A_{1g}	A_{1u}	A_{2u}
weight 1, I=0	.	.	.	1	1	1	.
weight 3, I=1	1	1	1	.	.	.	1
weight 5, I=2	1	.	.	1	.	.	.
weight 7, I=3	.	.	.	.	.	.	1
Species Spin Weights	8	3	3	6	1	1	10

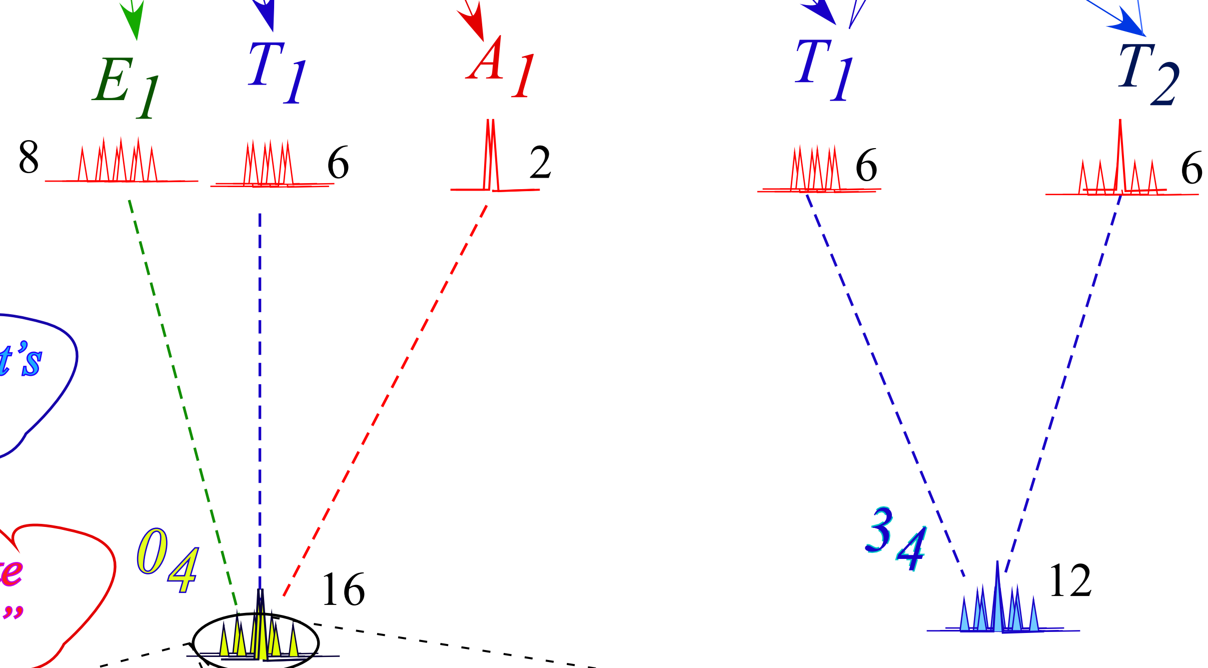
Forbidden SF_6 species: E_g, T_{2u}, A_{2g}

Without rotation being stuck on C_4 axis all six nuclei are equivalent



*With rotation stuck on C_4 axis polar nuclei are "**left out in the cold**"*

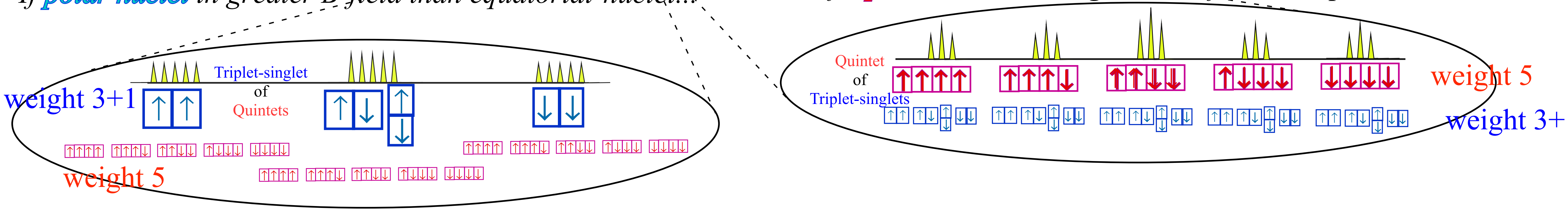




Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde´, C. Saloman, and Oliver Pfister (Pfister did SiF_4, too.)

*If **polar nuclei** in greater B-field than equatorial-nuclei...*

*If **equatorial nuclei** in greater B-field than polar-nuclei...*



AMOP reference links on pages 2-4

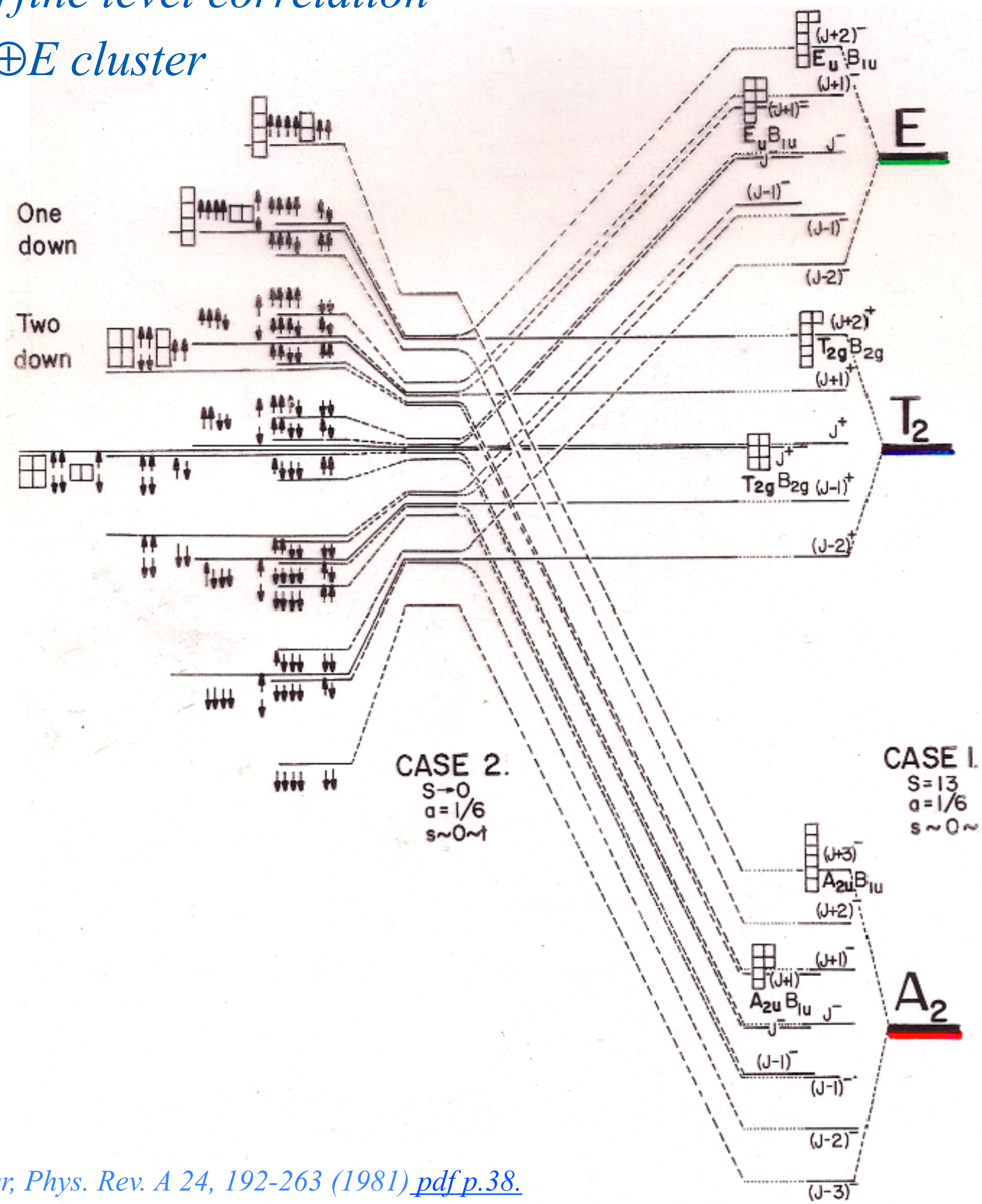
5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

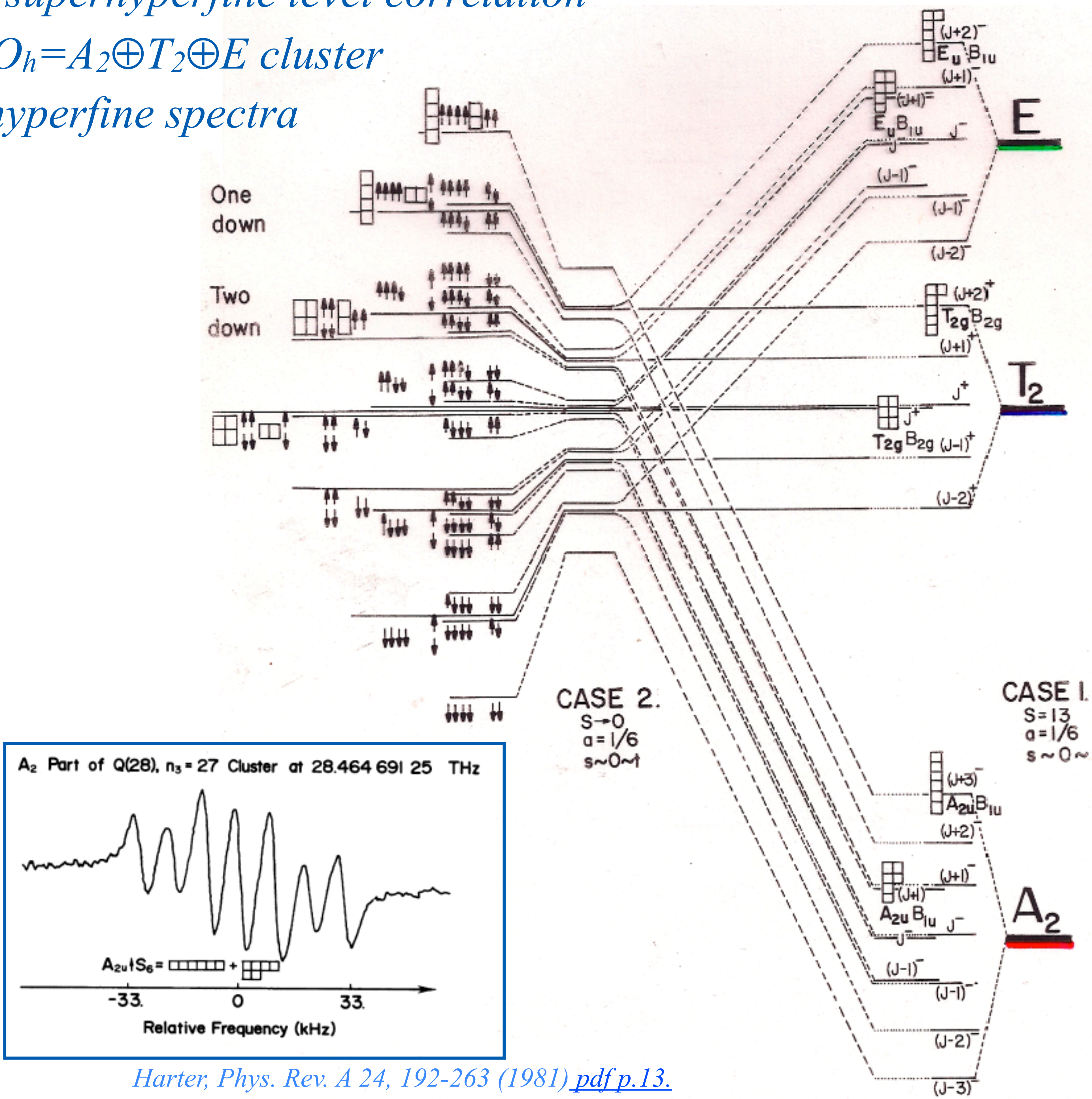
Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$
    State labels by symmetry $O(3)\supset D_{\infty h}$
        Coriolis and λ-doubling levels
    Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
    Tableau dimension formulae for X_4 and XY_4 molecules
        CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
    Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 → SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
    Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
    Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
    Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES)   (UnZIPPed)
    REES for high-J Coriolis spectra in SF_6 **ZIPP (Zero-Interaction-Potential-`Proximation*
    REES for high-J Coriolis spectra in υ_3 CF_4
.   REES for high-J and high-υ rovibration polyads

SF_6 superhyperfine level correlation
$2_4\uparrow O_h = A_2 \oplus T_2 \oplus E$ cluster



Harter, Phys. Rev. A 24, 192-263 (1981) pdf p.38.

SF_6 superhyperfine level correlation
$2_4\uparrow O_h = A_2 \oplus T_2 \oplus E$ cluster
A_2 hyperfine spectra



weight 8=5+3

weight 6=5+1

weight 10=7+3

Harter, Phys. Rev. A 24, 192-263 (1981) pdf p.13.

Typical hyperfine Slater-to-tableau assembly matrix

TABLE V. *(Continued.)*

(c)

	↑↑↑ ↓↓↓					↑↑↑↓ ↓↓									↑↑↑↓↓ ↓					↑↑↑↓↓↓
1 2 3 4 5 6	T_{2g} E_g B_{1g}	B_{2g}	B_{2g} A_{2g}	A_{1u} A_{1u} A_{1u}	A_{1g} A_{1g} A_{1g}	T_{1u} E_u B_{1u}	B_{2u}	A_{2u} A_{2u}	T_{1g} E_g B_{1g}	B_{2g}	A_{2g} A_{2g}	E_u A_{1u} A_{1u}	A_{1u} A_{1u}	A_{2u} B_{1u} A_{1u}	T_{2g} E_g B_{1g}	B_{2g}	B_{2g} A_{2g}	E_u A_{1u} A_{1u}	B_{1u} A_{1u}	A_{2u} B_{1u} A_{1u}
∣ ∣ ∣ ↓ ↓ ↓	0	2	0	−1	0	0	0	0	0	1	0	−1	1	2	0	−1	0	1	1	1
∣ ∣ ↓ ∣ ↓ ↓	−2	0	0	1	0	0	0	0	−1	0	0	1	1	2	1	0	0	−1	1	1
∣ ∣ ↓ ↓ ∣ ↓	1	−1	1	0	1	−1	−1	−1	0	0	0	0	0	−3	1	−1	1	0	0	1
∣ ∣ ↓ ↓ ↓ ∣	1	−1	−1	0	−1	1	1	−1	0	0	0	0	0	−3	1	−1	−1	0	0	1
∣ ↓ ∣ ∣ ↓ ↓	0	−2	0	−1	0	0	0	0	0	−1	0	−1	1	2	0	1	0	1	1	1
∣ ↓ ∣ ↓ ∣ ↓	0	0	−2	1	0	0	0	0	0	0	−1	0	−2	2	0	0	1	2	0	1
∣ ↓ ∣ ↓ ↓ ∣	0	0	2	1	0	0	0	0	0	0	1	0	−2	2	0	0	−1	2	0	1
∣ ↓ ↓ ∣ ∣ ↓	1	1	1	0	−1	1	−1	1	0	0	0	0	0	−3	1	1	1	0	0	1
∣ ↓ ↓ ∣ ↓ ∣	1	1	−1	0	1	−1	1	1	0	0	0	0	0	−3	1	1	−1	0	0	1
∣ ↓ ↓ ↓ ∣ ∣	−2	0	0	−1	0	0	0	0	1	0	0	1	1	2	1	0	0	1	−1	1
↓ ∣ ∣ ∣ ↓ ↓	2	0	0	1	0	0	0	0	1	0	0	1	1	2	−1	0	0	−1	1	1
↓ ∣ ∣ ↓ ∣ ↓	−1	−1	1	0	−1	−1	1	1	0	0	0	0	0	−3	−1	−1	1	0	0	1
↓ ∣ ∣ ↓ ↓ ∣	−1	−1	−1	0	1	1	−1	1	0	0	0	0	0	−3	−1	−1	−1	0	0	1
↓ ∣ ↓ ∣ ∣ ∣	0	0	−2	−1	0	0	0	0	0	0	1	0	−2	2	0	0	1	−2	0	1
↓ ∣ ↓ ∣ ↓ ∣	0	0	2	−1	0	0	0	0	0	0	−1	0	−2	2	0	0	−1	−2	0	1
↓ ∣ ↓ ↓ ∣ ∣	0	2	0	1	0	0	0	0	0	−1	0	−1	1	2	0	−1	0	−1	−1	1
↓ ↓ ∣ ∣ ∣ ↓	−1	1	1	0	1	1	1	−1	0	0	0	0	0	−3	−1	1	1	0	0	1
↓ ↓ ∣ ∣ ↓ ∣	−1	1	−1	0	−1	−1	−1	−1	0	0	0	0	0	−3	−1	1	−1	0	0	1
↓ ↓ ∣ ↓ ∣ ∣	2	0	0	−1	0	0	0	0	−1	0	0	1	1	2	−1	0	0	1	−1	1
↓ ↓ ↓ ∣ ∣ ∣	0	−2	0	1	0	0	0	0	0	1	0	−1	1	2	0	1	0	−1	−1	1
	$1/2\sqrt{6}$	$1/2\sqrt{6}$	$1/2\sqrt{6}$	$1/2\sqrt{3}$	$1/2\sqrt{2}$	$1/2\sqrt{2}$	$1/2\sqrt{2}$	$1/2\sqrt{2}$	$1/2$	$1/2$	$1/2$	$1/2\sqrt{2}$	$1/2\sqrt{6}$	$1/2\sqrt{30}$	$1/2\sqrt{3}$	$1/2\sqrt{3}$	$1/2\sqrt{3}$	$1/2\sqrt{6}$	$1/2\sqrt{2}$	$1/2\sqrt{5}$

Harter, Phys. Rev. A 24, 192-263 (1981) pdf p.26.

SF_6 superhyperfine level correlation
$1_4\uparrow O_h = T_1 \oplus T_2$ cluster
$T_1 \oplus T_2$ hyperfine spectra

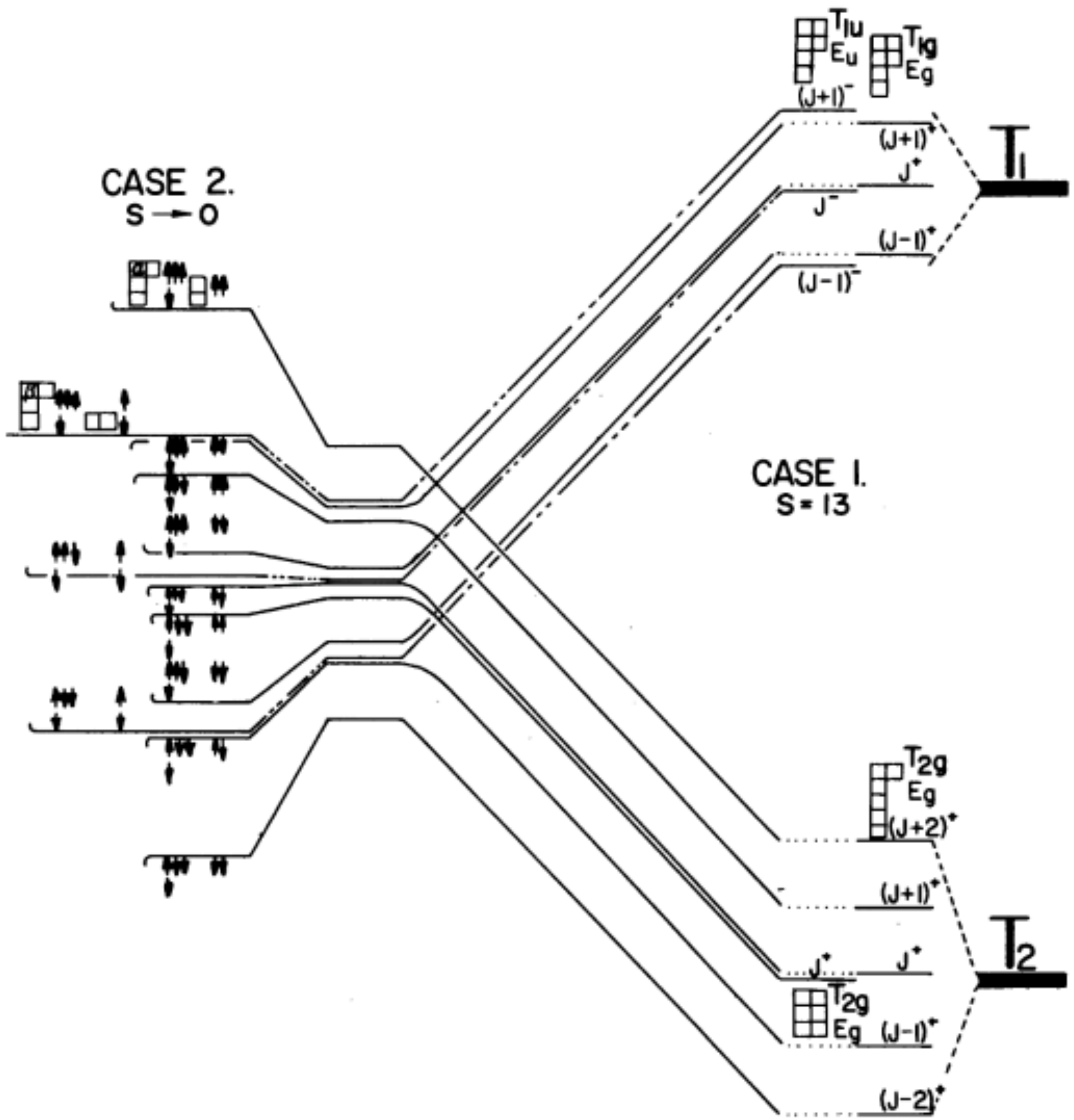
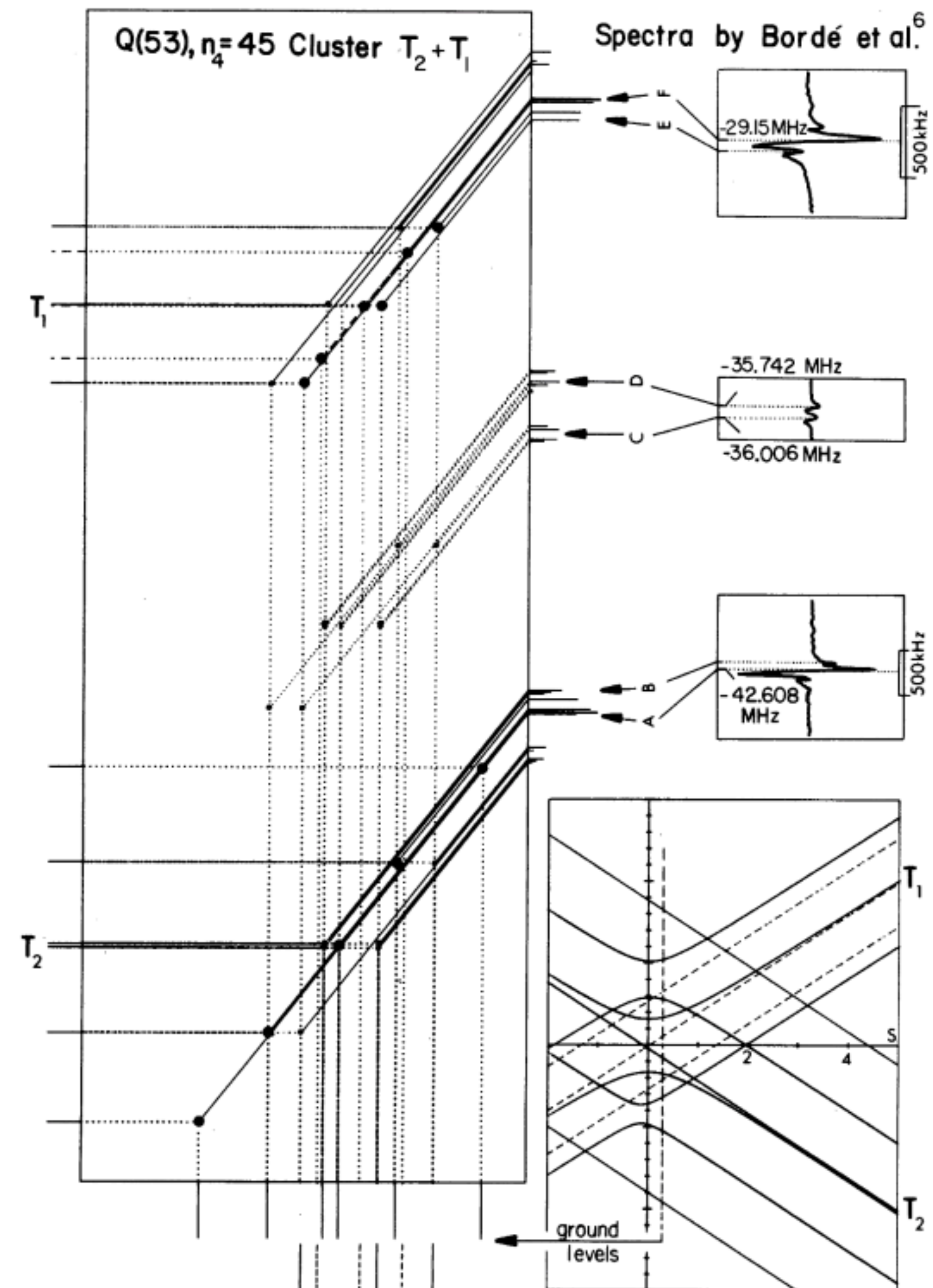


FIG. 17. Superhyperfine level correlations for the E-type tetragonal clusters ($\pm 1_4 \uparrow O = T_1 + T_2$).



Harter, Phys. Rev. A 24, 192-263 (1981) pdf p.46.

Harter, Phys. Rev. A 24, 192-263 (1981) pdf p.48.

T₁⊕T₂ hyperfine spectra and nomograms

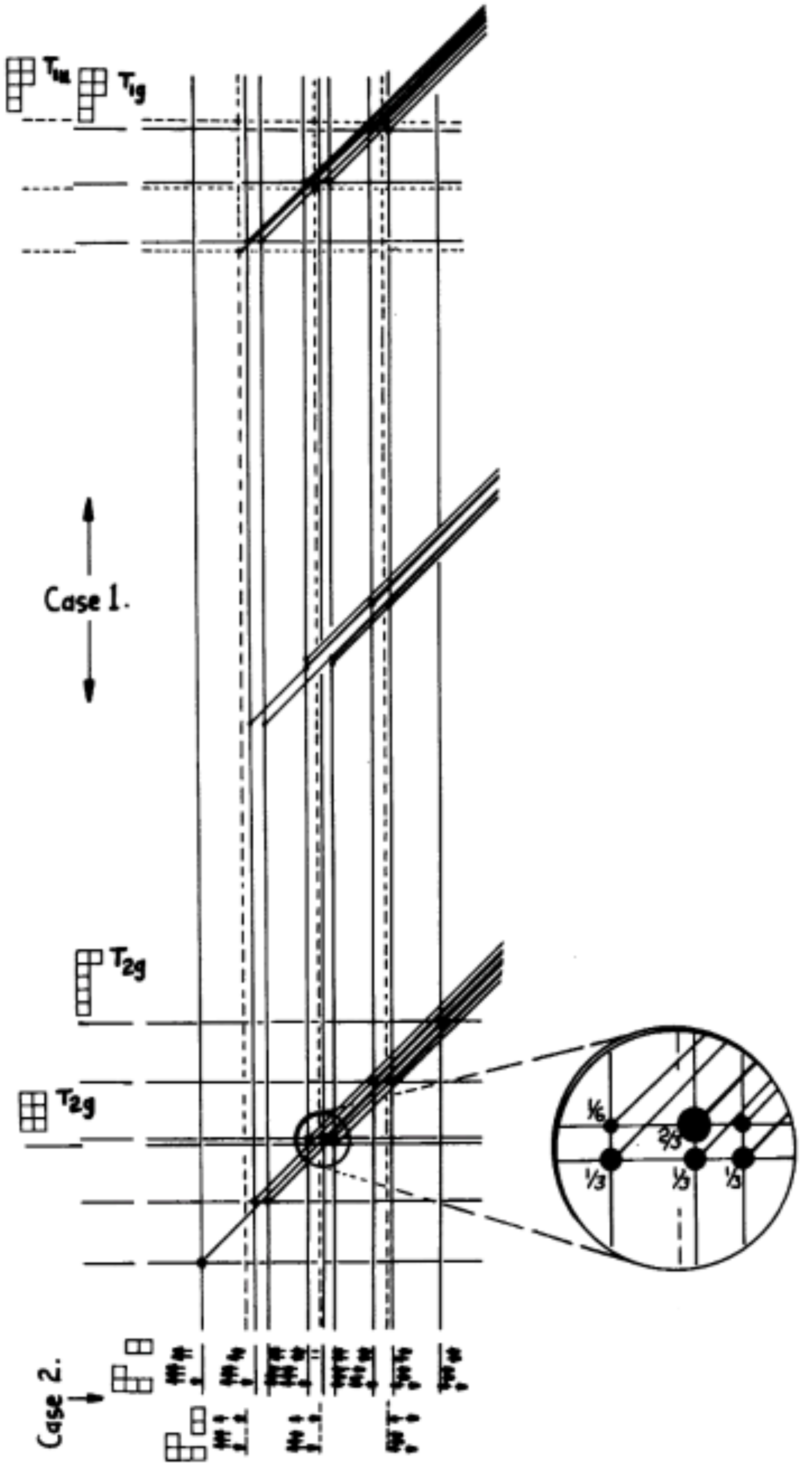


FIG. 18. Transition nomogram for transitions between a strong case-2 and a case-1 E-type (T_1, T_2) cluster. The relative transition rates are taken from Table VII(c) and indicated on the figure.

Harter, PRA 24,(1981) [pdf p.47.]

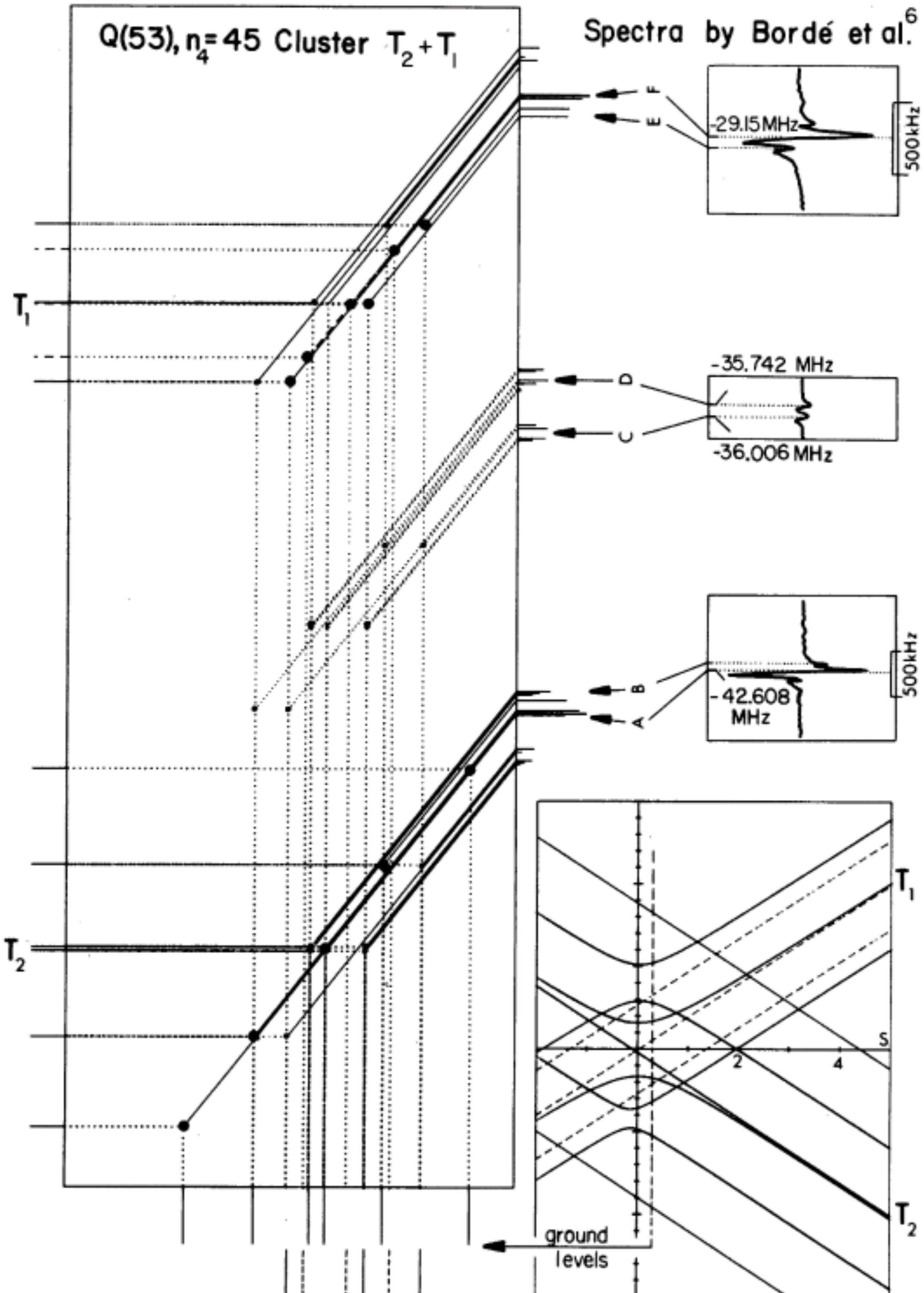
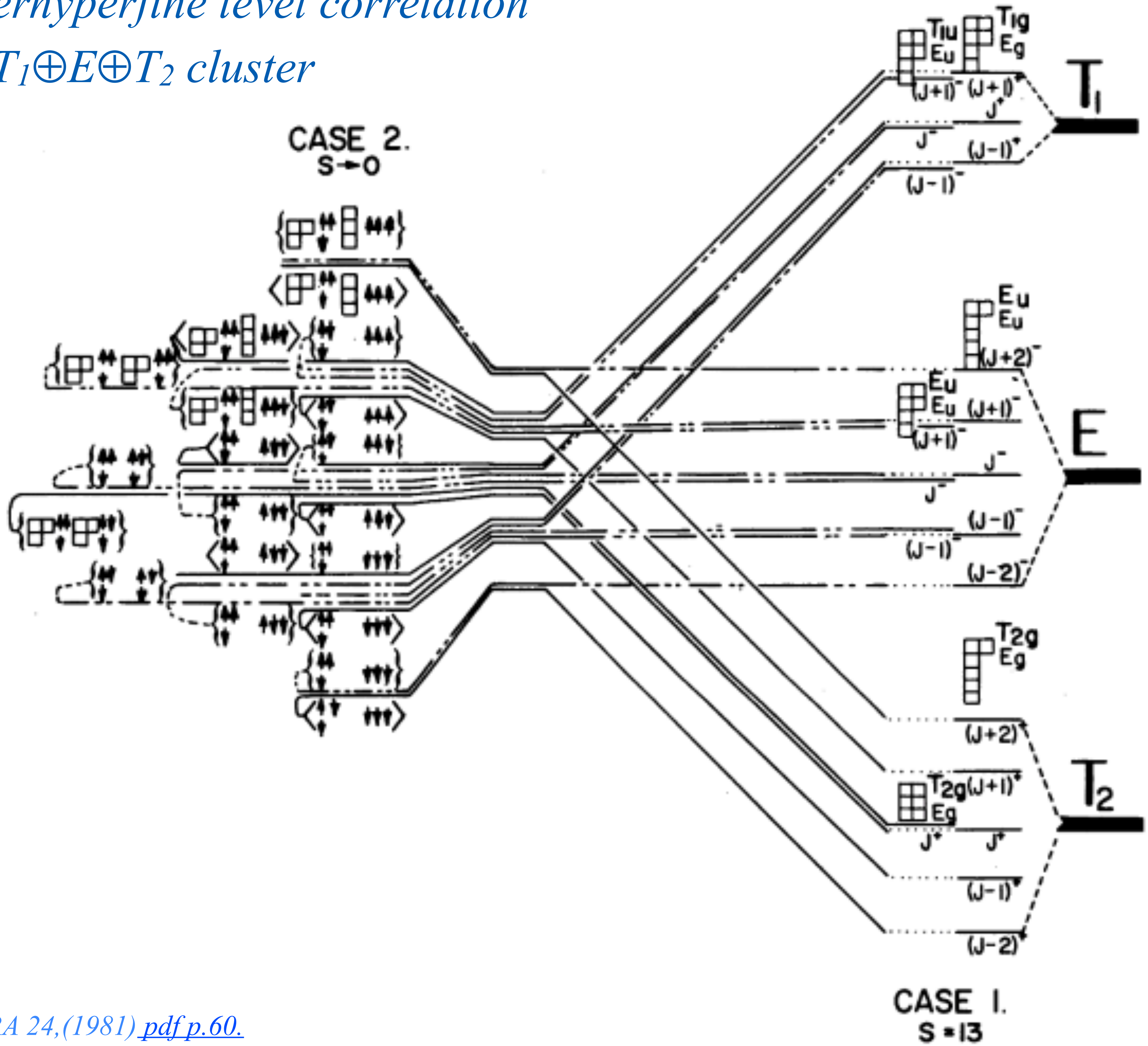


FIG. 19. Transition nomogram for transitions between a weak case-2 and a case-1 E-type (T_1, T_2) cluster. Fram transformation and diagonalization yield the level correlations shown in the lower right-hand inset. Spectra produce by Bordé *et al.*[4,6] are compared with the resulting spectral nomogram and intensities. The theoretical ground level were obtained using constants $S = 0.3$, $\tau = 6.2$, and $a = -0.2$ in Table XI(c) with all other constants set equal to zero.

SF_6 superhyperfine level correlation

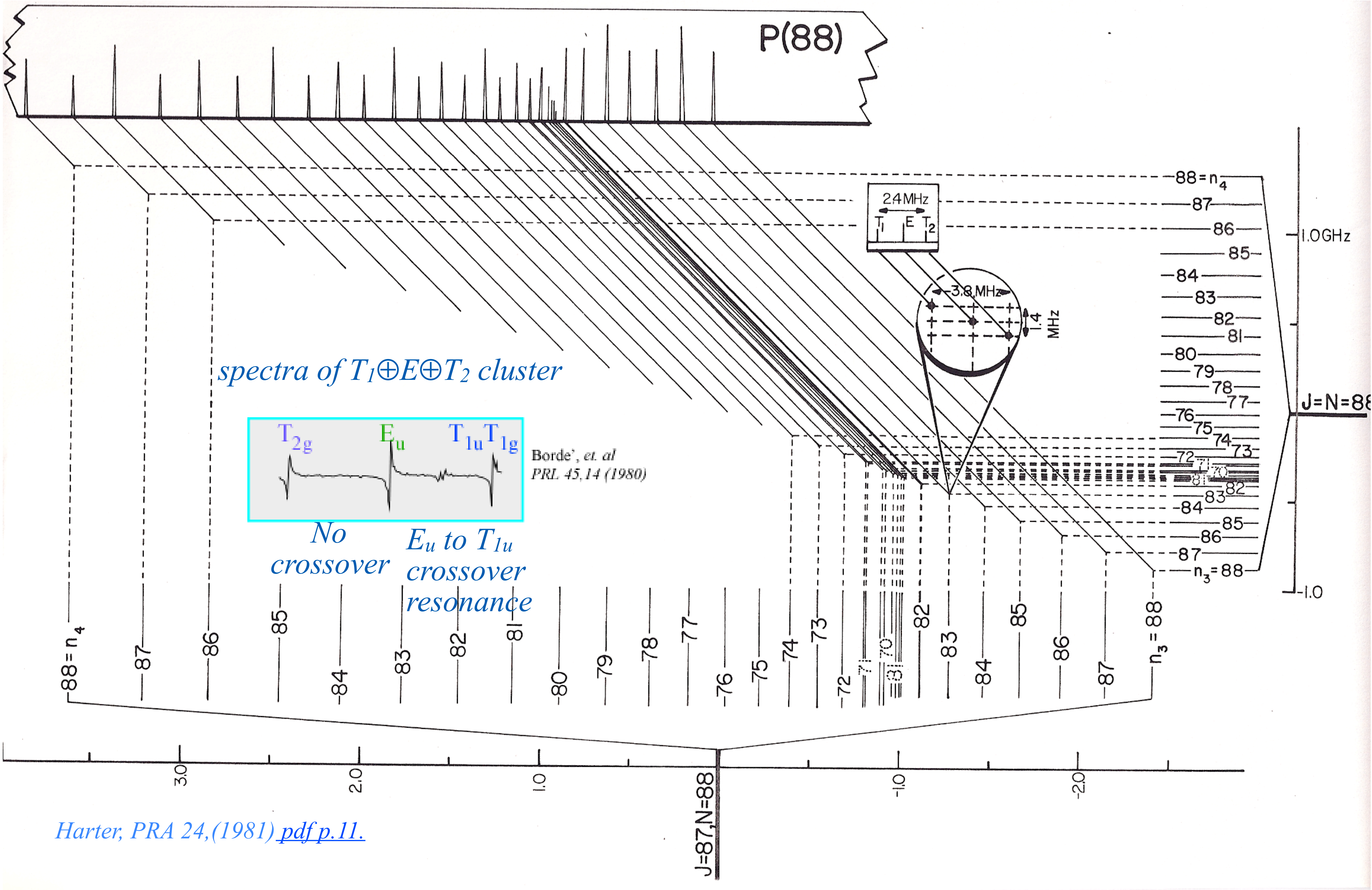
$1_3\uparrow O_h=T_1\oplus E\oplus T_2$ cluster



Harter, PRA 24,(1981) pdf p.60.

FIG. 22. Superhyperfine level correlations for the E-type trigonal clusters ($\pm 1_3 \uparrow O = T_1 + E + T_2$).

Nomogram of SF_6 ν_4 P(88) fine, superfine, and hyperfine structure



Harter, PRA 24,(1981) pdf p.11.

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

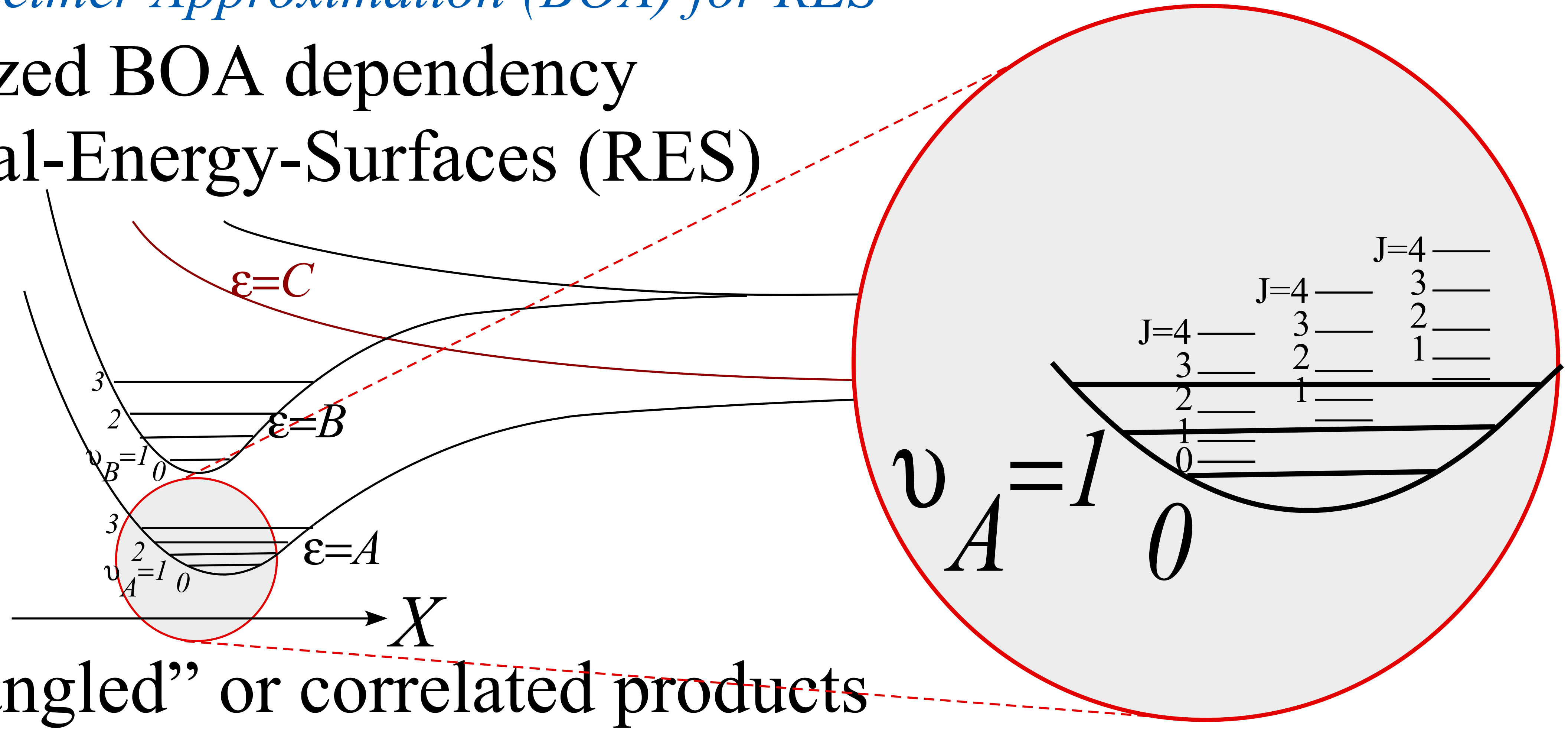
Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$
State labels by symmetry $O(3) \supset D_{\infty h}$
Coriolis and λ-doubling levels
Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
Tableau dimension formulae for X_4 and XY_4 molecules
CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)
REES for high-J Coriolis spectra in SF_6
REES for high-J Coriolis spectra in υ_3 CF_4
. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

Born-Oppenheimer Approximation (BOA) for RES

Generalized BOA dependency

Rotational-Energy-Surfaces (RES)



BOA-"Entangled" or correlated products

"FAST" "SLOW" "SLOWER"

$$\Phi_{J[\upsilon(\varepsilon)]}(x^{elect.}\ldots.Q^{vib.}\ldots\Theta^{rotate}) = \psi_\varepsilon(x_{(Q(\Theta)\ldots)}\ldots)\cdot\eta_{\upsilon(\varepsilon)}(Q_{(\Theta)}\ldots)\cdot\rho_{J[\upsilon(\varepsilon)]}(\Theta)$$

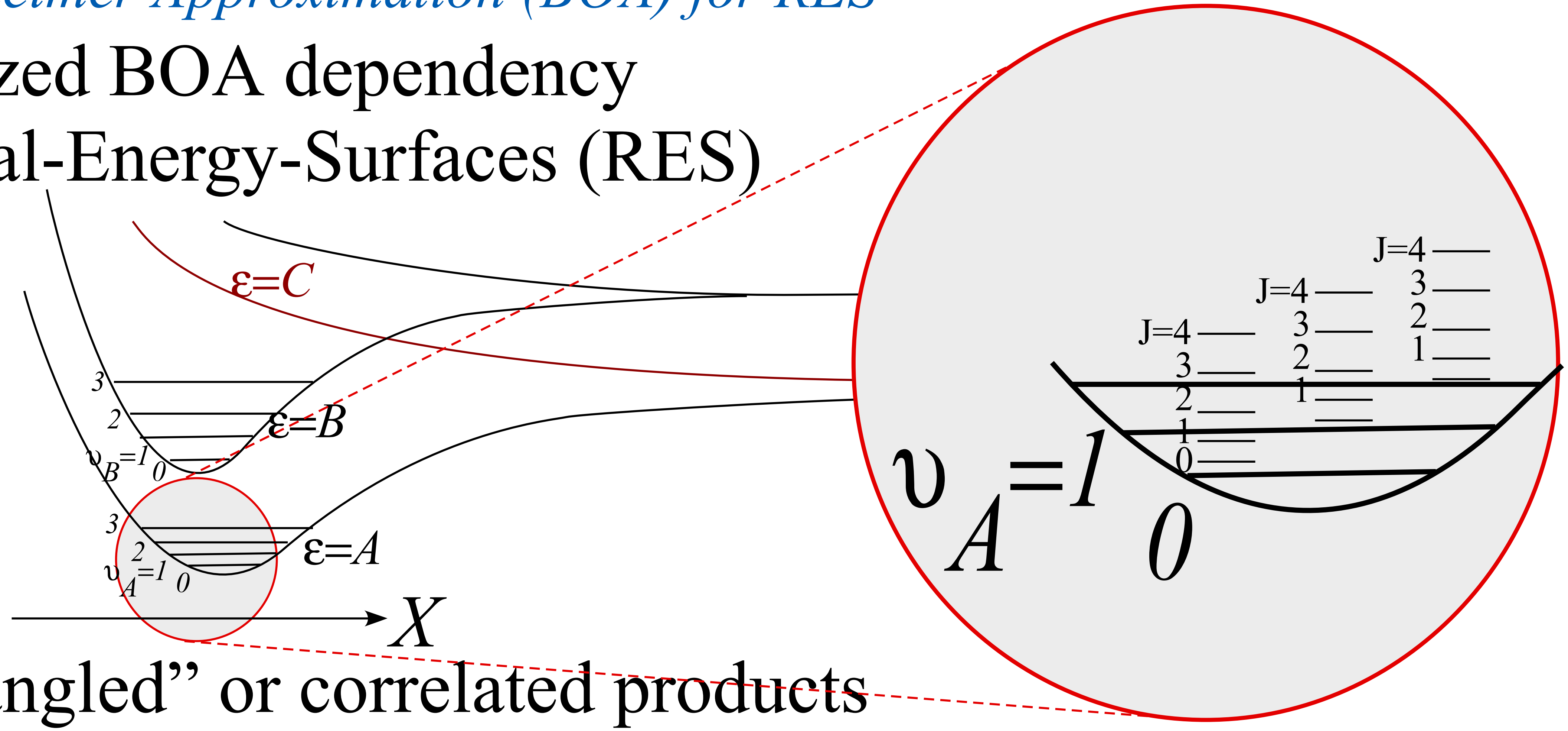
BOA issues discussed in:
Rev. Mod. Phys. 50,1,[37(1978)p.19]

BOA issues discussed in:
Int. J. Mol. Sci. 14,[714(2013)p.4]

Born-Oppenheimer Approximation (BOA) for RES

Generalized BOA dependency

Rotational-Energy-Surfaces (RES)



BOA-"Entangled" or correlated products

"FAST" "SLOW" "SLOWER"

$$\Phi_{J[\upsilon(\varepsilon)]}(x^{elect.}\ldots Q^{vib.}\ldots\Theta^{rotate}) = \psi_{\varepsilon}(x_{(Q(\Theta)\ldots)}\ldots)\cdot\eta_{\upsilon(\varepsilon)}(Q_{(\Theta)}\ldots)\cdot\rho_{J[\upsilon(\varepsilon)]}(\Theta)$$

vibe υ(ε)-quanta depend on electron ε-quanta

vibe $Q(\Theta)$-coords depend on rotation Θ-coords

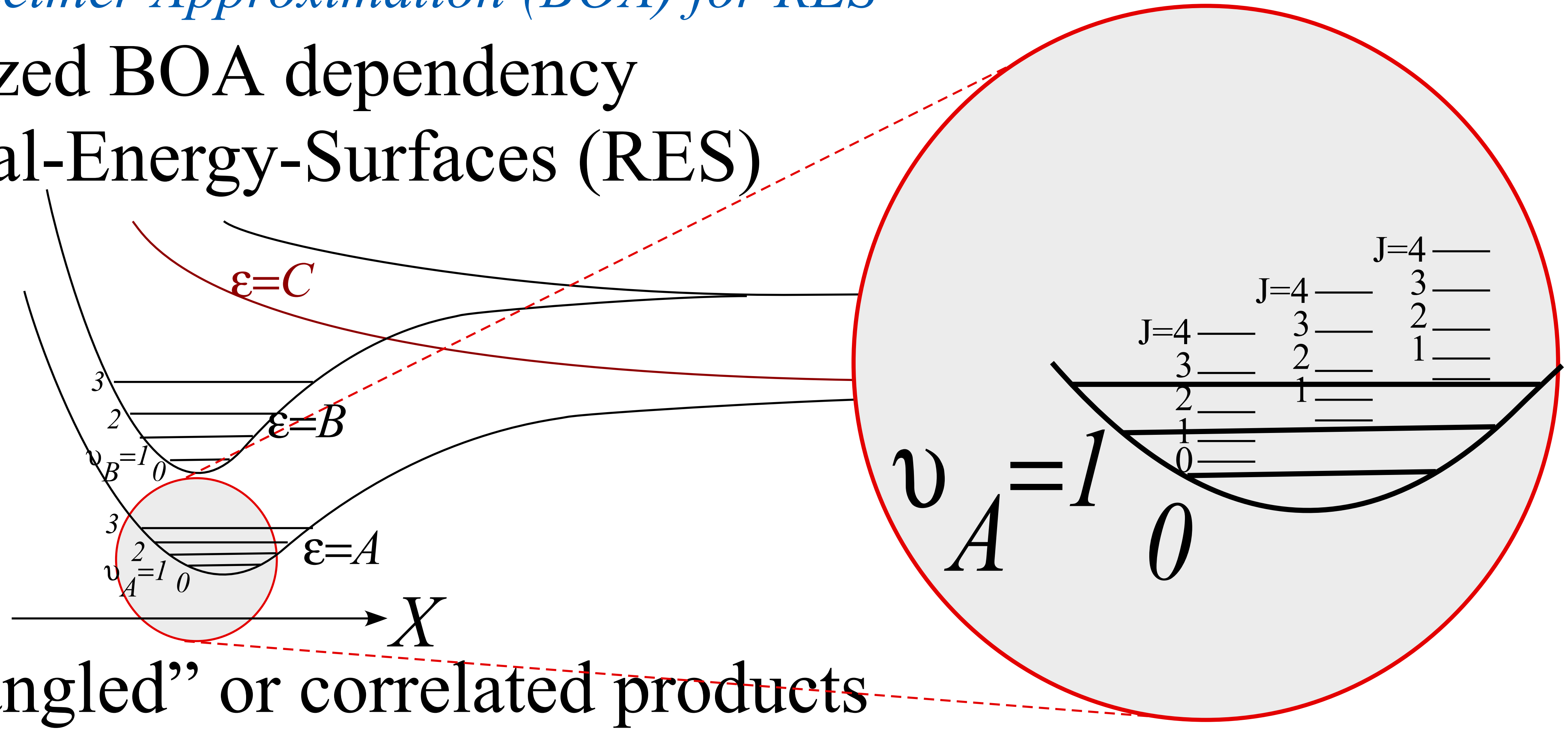
rotation $J[\upsilon(\varepsilon)]$-quanta depend on vibe υ-quanta and electron ε-quanta

BOA issues discussed in:
Rev. Mod. Phys. 50,1,[37(1978)p.19]

BOA issues discussed in:
Int. J. Mol. Sci. 14,[714(2013)p.4]

Born-Oppenheimer Approximation (BOA) for RES

Generalized BOA dependency
Rotational-Energy-Surfaces (RES)



BOA-"Entangled" or correlated products

"FAST" "SLOW" "SLOWER"

$$\Phi_{J[\upsilon(\varepsilon)]}(x^{elect.}....Q^{vib.}...\Theta^{rotate}) = \psi_\varepsilon(x_{(Q(\Theta)...)}...)\cdot\eta_{\upsilon(\varepsilon)}(Q_{(\Theta)}...)\cdot\rho_{J[\upsilon(\varepsilon)]}(\Theta)$$

electron $x_{(Q(\Theta))}$-coords depend on vibration Q-coords and rotation Θ coords

vibe υ(ε)-quanta depend on electron ε-quanta

vibe $Q(\Theta)$-coords depend on rotation Θ-coords

rotation $J[\upsilon(\varepsilon)]$-quanta depend on vibe υ-quanta and electron ε-quanta

BOA issues discussed in:
Rev. Mod. Phys. 50,1,[37(1978)p.19]

BOA issues discussed in:
Int. J. Mol. Sci. 14,[714(2013)p.4]

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

State labels by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

REES for high-J Coriolis spectra in υ_3 CF_4

REES for high-J and high-υ rovibration polyads

*ZIPP (Zero-Interaction-Potential-`Proximation

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

$$\Phi^{BOA}_{J[\upsilon(\varepsilon)]}(x^{vibronic},\Theta^{rotate}) = \psi_\varepsilon(x_{(\Theta)}) \quad \cdot\rho_{J[\varepsilon]}(\Theta)$$

$$= \psi_\varepsilon(x_{(body)})\cdot\rho_{J,M,K}(\alpha,\beta,\gamma)$$

Detailed model of BOA rotor entanglement

Using rotational symmetry analysis

$$= \psi^{\ell}_{\bar{\mu}}(\bar{x}) \qquad \cdot D^{J*}_{M,K=n+\bar{\mu}}(\alpha,\beta,\gamma)\sqrt{[J]}$$

bod-based vibronic factor

BOA issues discussed in:
Rev. Mod. Phys. 50,1,[37(1978)p.19]

BOA issues discussed in:
Int. J. Mol. Sci. 14,[714(2013)p.4]

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

$$\Phi^{BOA}_{J[\upsilon(\varepsilon)]}(x^{vibronic},\Theta^{rotate}) = \psi_\varepsilon(x_{(\Theta)}) \cdot\rho_{J[\varepsilon]}(\Theta)$$

$$= \psi_\varepsilon(x_{(body)})\cdot\rho_{J,M,K}(\alpha,\beta,\gamma)$$

Detailed model of BOA rotor entanglement

Using rotational symmetry analysis

$$= \psi^{\ell}_{\bar{\mu}}(\bar{x}) \cdot D^{J*}_{M,K=n+\bar{\mu}}(\alpha,\beta,\gamma)\sqrt{[J]}$$

bod-based vibronic factor

body-wave from lab-wave

$$\psi^{\ell}_{\bar{\mu}}(\bar{x}) = \psi^{\ell}_{\mu}(x) D^{\ell}_{\bar{\mu},\mu}(\alpha,\beta,\gamma)$$

sum $\mu=-J\ldots+J$

frame rotation

lab-wave from body-wave

$$\psi^{\ell}_{\mu}(x) = \psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell*}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)$$

sum $\bar{\mu}=-J\ldots+J$

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37(1978)p.19

BOA issues discussed in:
Int. J. Mol. Sci. 14,714(2013)p.4

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

$$\Phi^{BOA}_{J[\upsilon(\varepsilon)]}(x^{vibronic},\Theta^{rotate}) = \psi_\varepsilon(x_{(\Theta)}) \cdot \rho_{J[\varepsilon]}(\Theta)$$

$$= \psi_\varepsilon(x_{(body)}) \cdot \rho_{J,\mathrm{M,K}}(\alpha,\beta,\gamma)$$

Detailed model of BOA rotor entanglement

Using rotational symmetry analysis

$$= \psi^{\ell}_{\bar{\mu}}(\bar{x}) \cdot D^{J*}_{\mathrm{M,K=n}+\bar{\mu}}(\alpha,\beta,\gamma)\sqrt{[J]}$$

bod-based vibronic factor

body-wave from lab-wave

$$\psi^{\ell}_{\bar{\mu}}(\bar{x}) = \underbrace{\psi^{\ell}_{\mu}(x) D^{\ell}_{\bar{\mu},\mu}}_{\mathrm{sum}\ \mu=-J\ldots+J}(\alpha,\beta,\gamma)$$

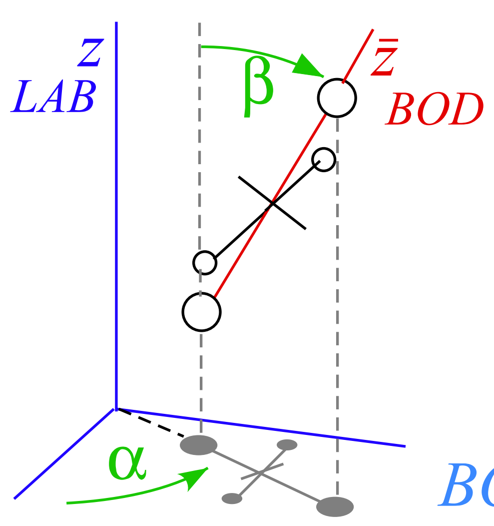
$\xleftrightarrow{\text{frame rotation}}$

lab-wave from body-wave

$$\psi^{\ell}_{\mu}(x) = \underbrace{\psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell *}_{\mu,\bar{\mu}}}_{\mathrm{sum}\ \bar{\mu}=-J\ldots+J}(\alpha,\beta,\gamma)$$

"Hook-up" <u>un</u>entangled lab-based products: $\psi^{\ell}_{\mu}(x) \cdot D^{R*}_{\mathrm{m,n}}(\alpha,\beta,\gamma)\sqrt{[R]}$

(with Clebsch-Gordan $C^{\ell\ R\ J}_{\mu\ m\ M}$)



$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = \underbrace{C^{\ell\ R\ J}_{\mu\ mM}\ \psi^{\ell}_{\mu}}_{\mathrm{sum}\ \mu=-J\ldots+J}\underbrace{(x) \cdot D^{R*}_{\mathrm{m,n}}}_{\mathrm{with}\ m=M-\mu}(\alpha,\beta,\gamma)\sqrt{[R]}$$

BOA issues discussed in:
Rev. Mod. Phys. 50,1,[*37(1978)p.19*]

BOA issues discussed in:
Int. J. Mol. Sci. 14,[*714(2013)p.4*]

AMOP
reference links
on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES)   (UnZIPPed)

REES for high-J Coriolis spectra in SF_6 **ZIPP (Zero-Interaction-Potential-\`Proximation*

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Compare wave Products:

Lab "hook-up" *versus* "BOA-constricted bod"

$$\Phi^{BOA}_{J(\ell\bar{\mu})} = \psi^{\ell}_{\bar{\mu}}(\bar{x})\cdot D^{J*}_{MK}(\alpha,\beta,\gamma)\sqrt{[J]}$$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \overbrace{\psi^{\ell}_{\mu}(x)}\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\mu=-J\ldots+J$ *with* $m=M-\mu$

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37(1978)p.19

BOA issues discussed in:
Int. J. Mol. Sci. 14,714(2013)p.4

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Compare wave Products:

Lab "hook-up" *versus* "BOA-constricted bod"

$$\Phi^{BOA}_{J(\ell\bar{\mu})} = \psi^{\ell}_{\bar{\mu}}(\bar{x}) \cdot D^{J*}_{MK}(\alpha,\beta,\gamma)\sqrt{[J]}$$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \overbrace{\psi^{\ell}_{\mu}(x)}\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\mu=-J...+J$ with $m=M-\mu$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \overbrace{\psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell*}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)\cdot D^{R*}_{m,n}}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\bar{\mu}=-J...+J$

sum $\mu=-J...+J$ with $m=M-\mu$

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37(1978)p.19

BOA issues discussed in:
Int. J. Mol. Sci. 14,714(2013)p.4

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Compare wave Products:

Lab "hook-up" *versus* "BOA-constricted bod"

$$\Phi^{BOA}_{J(\ell\bar{\mu})} = \psi^{\ell}_{\bar{\mu}}(\bar{x})\cdot D^{J*}_{MK}(\alpha,\beta,\gamma)\sqrt{[J]}$$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \overbrace{\psi^{\ell}_{\mu}(x)}\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\mu=-J\ldots+J$ with $m=M-\mu$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \psi^{\ell}_{\bar{\mu}}(\bar{x})D^{\ell*}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\psi^{\ell}_{\bar{\mu}}(x)\cdot D^{J*}_{MK}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\bar{\mu}=-J\ldots+J$

sum $\mu=-J\ldots+J$ with $m=M-\mu$

sum $\bar{\mu}=-J\ldots+J$ with: $K=\bar{\mu}+n$

BOA issues discussed in:
Rev. Mod. Phys. 50,1,[37(1978)p.19]

BOA issues discussed in:
Int. J. Mol. Sci. 14,[714(2013)p.4]

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Compare wave Products:

Lab "hook-up" *versus* "BOA-constricted bod"

$$\Phi^{BOA}_{J(\ell\bar{\mu})} = \psi^{\ell}_{\bar{\mu}}(\bar{x})\cdot D^{J*}_{MK}(\alpha,\beta,\gamma)\sqrt{[J]}$$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \overbrace{\psi^{\ell}_{\mu}(x)}\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\mu=-J\ldots+J$ with $m=M-\mu$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \overbrace{\psi^{\ell}_{\bar{\mu}}(\bar{x})D^{\ell*}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)}\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\psi^{\ell}_{\bar{\mu}}(x)\cdot D^{J*}_{MK}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\bar{\mu}=-J\ldots+J$; sum $\mu=-J\ldots+J$ with $m=M-\mu$; sum $\bar{\mu}=-J\ldots+J$ with: $K=\bar{\mu}+n$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\frac{\sqrt{[R]}}{\sqrt{[J]}}\ \Phi^{BOA}_{J(\ell\bar{\mu})}$$

sum $\bar{\mu}=-J\ldots+J$

This has form:

$$C^{\ell\ R\ J}_{\mu\ mM}\ D^{\ell*}_{\mu\bar{\mu}}(\alpha\beta\gamma)\cdot D^{R*}_{mn}(\alpha\beta\gamma) = C^{\ell\ R\ J}_{\bar{\mu}\ nK}D^{J*}_{MK}(\alpha\beta\gamma)$$

with $m=M-\mu$; sum $\mu=-J\ldots J$; with: $K=\bar{\mu}+n$

...that follows from well known coupling identity.

$$C^{\ell\ R\ J'}_{\mu\ mM}\ D^{\ell*}_{\mu\bar{\mu}}(\alpha\beta\gamma)\cdot D^{R*}_{mn}(\alpha\beta\gamma)C^{\ell\ R\ J}_{\bar{\mu}\ nK} = \delta^{JJ'}D^{J*}_{MK}(\alpha\beta\gamma)$$

with $m=M-\mu$; sum $\mu=-J\ldots+J$; sum $\bar{\mu}=-J\ldots+J$; with $n=K-\bar{\mu}$

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Compare wave Products:

Lab "hook-up" *versus* "BOA-constricted bod"

$$\Phi^{BOA}_{J(\ell\bar{\mu})} = \psi^{\ell}_{\bar{\mu}}(\bar{x})\cdot D^{J*}_{MK}(\alpha,\beta,\gamma)\sqrt{[J]}$$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \psi^{\ell}_{\mu}(x)\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\mu=-J\ldots+J$ *with* $m=M-\mu$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell*}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\psi^{\ell}_{\bar{\mu}}(x)\cdot D^{J*}_{MK}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\bar{\mu}=-J\ldots+J$ *sum* $\mu=-J\ldots+J$ *with* $m=M-\mu$ *sum* $\bar{\mu}=-J\ldots+J$

with: $K=\bar{\mu}+n$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\frac{\sqrt{[R]}}{\sqrt{[J]}}\ \Phi^{BOA}_{J(\ell\bar{\mu})}$$

sum $\bar{\mu}=-J\ldots+J$

This has form:

$$C^{\ell\ R\ J}_{\mu\ mM}\ D^{\ell*}_{\mu\bar{\mu}}(\alpha\beta\gamma)\cdot D^{R*}_{mn}(\alpha\beta\gamma) = C^{\ell\ R\ J}_{\bar{\mu}\ nK} D^{J*}_{MK}(\alpha\beta\gamma)$$

with $m=M-\mu$ *sum* $\mu=-J\ldots J$ *with:* $K=\bar{\mu}+n$

...that follows from well known coupling identity.

$$C^{\ell\ R\ J'}_{\mu\ mM}\ D^{\ell*}_{\mu\bar{\mu}}(\alpha\beta\gamma)\cdot D^{R*}_{mn}(\alpha\beta\gamma) C^{\ell\ R\ J}_{\bar{\mu}\ nK} = \delta^{JJ'} D^{J*}_{MK}(\alpha\beta\gamma)$$

with $m=M-\mu$ *sum* $\mu=-J\ldots+J$ *sum* $\bar{\mu}=-J\ldots+J$ *with* $n=K-\bar{\mu}$

$LAB_{hook\text{-}up}$ state:	BOA_{bod} state:
sharp R	*mixed R*
mixed $\bar{\mu}$	*sharp* $\bar{\mu}$

BOTH HAVE...

sharp n *sharp n*

An elementary "rovibronic species"

"...gyro in a briefcase"

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005
Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$
State labels by symmetry $O(3) \supset D_{\infty h}$
Coriolis and λ-doubling levels
Nomograms for dipole-allowed transitions
XY_n molecules: S_3-S_6 tableau-characters
Tableau dimension formulae for X_4 and XY_4 molecules
CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra
Possible SiF_4 High J superhyperfine levels
Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra
Born-Oppenheimer Approximation (BOA) for RES
Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave
Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions
Semiclassical Rotor-"Gyro"-Spin coupling
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)
REES for high-J Coriolis spectra in SF_6
REES for high-J Coriolis spectra in υ_3 CF_4
. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-\`Proximation*

Graphical approach to rotation-vibration-spin Hamiltonian

$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Nuclear\ Spin}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \ldots$

OUTLINE

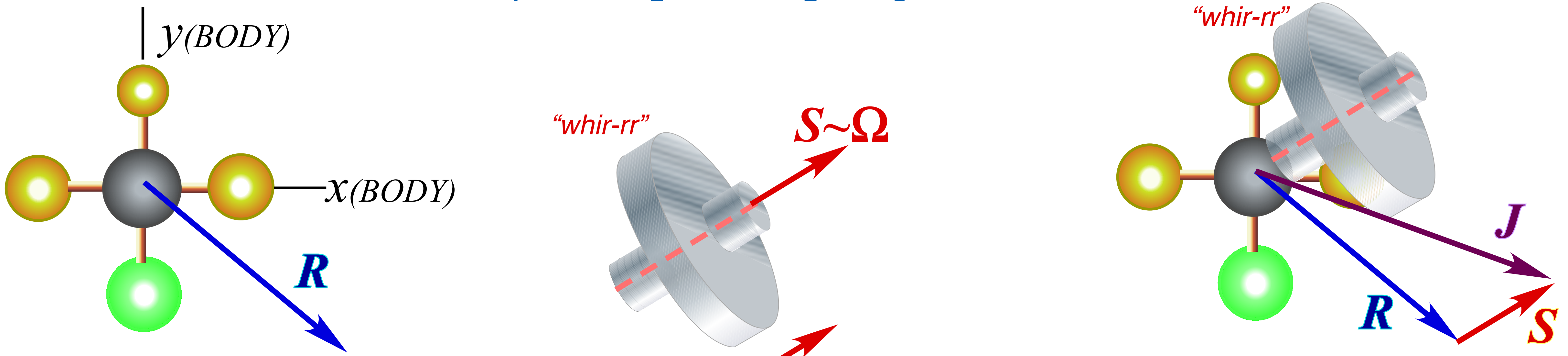
Introductory review

	Example(s)
• *Rovibronic nomograms and PQR structure*	ν_3 and ν_4 SF_6
• *Rotational Energy Surfaces (RES) and θ_K^J-cones*	ν_4 P(88) SF_6
• *Spin symmetry correlation tunneling and entanglement*	SF_6

Recent developments

• *Analogy between PE surface and RES dynamics*	
• *Rotational Energy Eigenvalue Surfaces (REES)*	ν_3 SF_6

Semiclassical Rotor-"Gyro"-Spin coupling



Rotor ***R*** **PLUS** ***"Gyro" Spin*** ***S*** **EQUALS** ***Compound Rotor*** ***J= R+S***

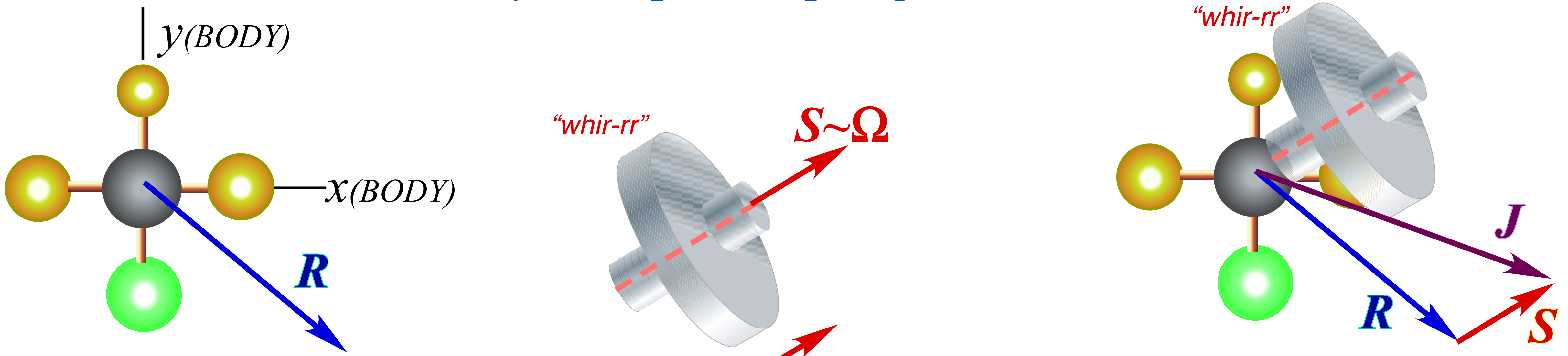
Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

In general, this term is the difficult part...

$$H=AR_x{}^2+BR_y{}^2+CR_z{}^2+\ldots+(\text{coupling or constraint})+\ldots+B_S S\cdot S$$

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)
Spring Handbook of AMOP Ch. 32 (2006)

Semiclassical Rotor-"Gyro"-Spin coupling



Rotor $\boldsymbol{R}$ **PLUS** ***"Gyro" Spin*** $\boldsymbol{S}$ **EQUALS** ***Compound Rotor*** $\boldsymbol{J= R+S}$

Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

In general, this term is the difficult part...

$$H=AR_x{}^2+BR_y{}^2+CR_z{}^2+\ldots+(coupling\ or\ constraint)+\ldots+B_S S\cdot S$$

...but suppose it's zero!

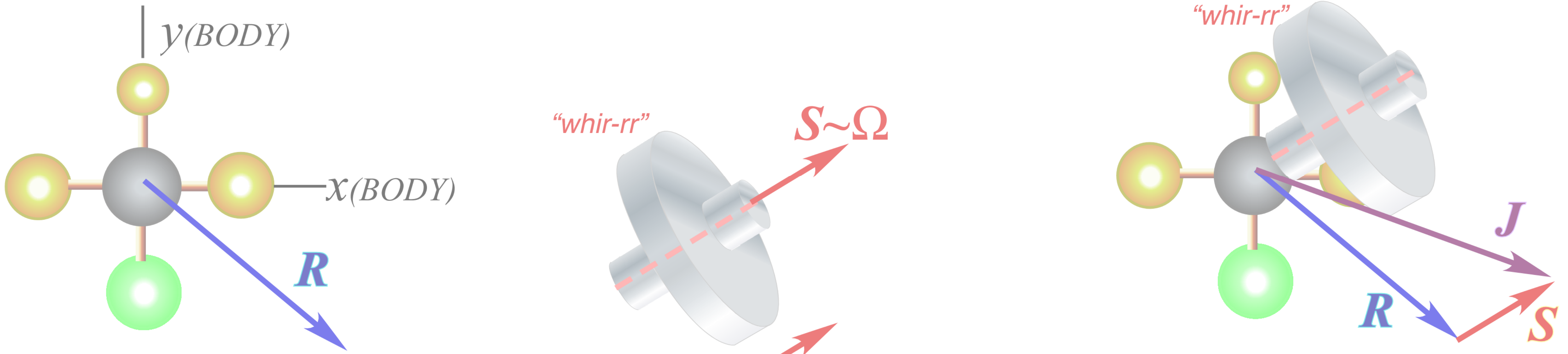
Constraints do no work.

*Zero-Interaction Potential 'Proximation (ZIPP)**

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)
Spring Handbook of AMOP Ch. 32 (2006)

**ZIPP (Zero-Interaction-Potential-`Proximation*

Semiclassical Rotor-"Gyro"-Spin coupling



Rotor $\boldsymbol{R}$ **PLUS *"Gyro" Spin*** $\boldsymbol{S}$ **EQUALS *Compound Rotor*** $\boldsymbol{J= R+S}$

Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

In general, this term is the difficult part...

$H=AR_x{}^2+BR_y{}^2+CR_z{}^2+\ldots+$*(coupling or constraint)*$+\ldots+B_S S\cdot S$

...but suppose it's zero!

*Zero-Interaction Potential 'Proximation (ZIPP)**

Constraints do <u>no</u> <u>work</u>.

(ZIPPed)

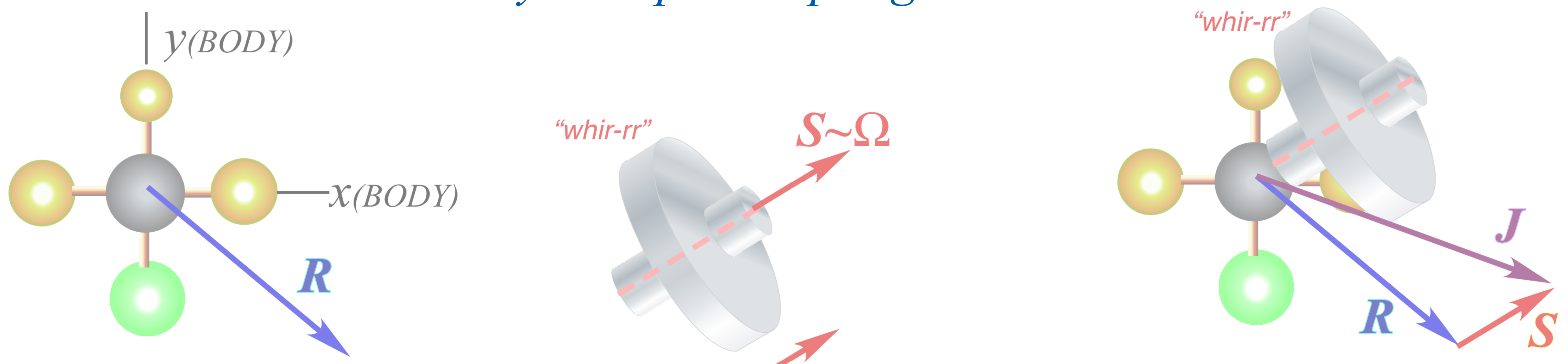
Let: $\boldsymbol{R= J - S}$ *and consider <u>non</u>-constant terms* *(ignore gyro S terms that are constant)*

$H=A(J_x-S_x)^2+B(J_y-S_y)^2+C(J_z-S_z)^2+\ldots+0$ *(for constraint)*$+\ldots+$*(constant BS terms)*

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)
Spring Handbook of AMOP Ch. 32 (2006)

**ZIPP (Zero-Interaction-Potential-`Proximation*

Semiclassical Rotor-"Gyro"-Spin coupling



Rotor $\boldsymbol{R}$ **PLUS "Gyro" Spin** $\boldsymbol{S}$ **EQUALS** **Compound Rotor** $\boldsymbol{J}=\boldsymbol{R}+\boldsymbol{S}$

Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

In general, this term is the difficult part...

$$H=AR_x{}^2+BR_y{}^2+CR_z{}^2+\ldots+(\text{coupling or constraint})+\ldots+B_S S\cdot S$$

...but suppose it's zero!

*Zero-Interaction Potential 'Proximation (ZIPP)**

Constraints do <u>no</u> <u>work</u>.

(ZIPPed)

Let: $\boldsymbol{R}=\boldsymbol{J}-\boldsymbol{S}$ *and consider <u>non</u>-constant terms* *(ignore gyro S terms that are constant)*

$$H=A(J_x-S_x)^2+B(J_y-S_y)^2+C(J_z-S_z)^2+\ldots+0\ (\text{for constraint})+\ldots+(\text{constant BS terms})$$

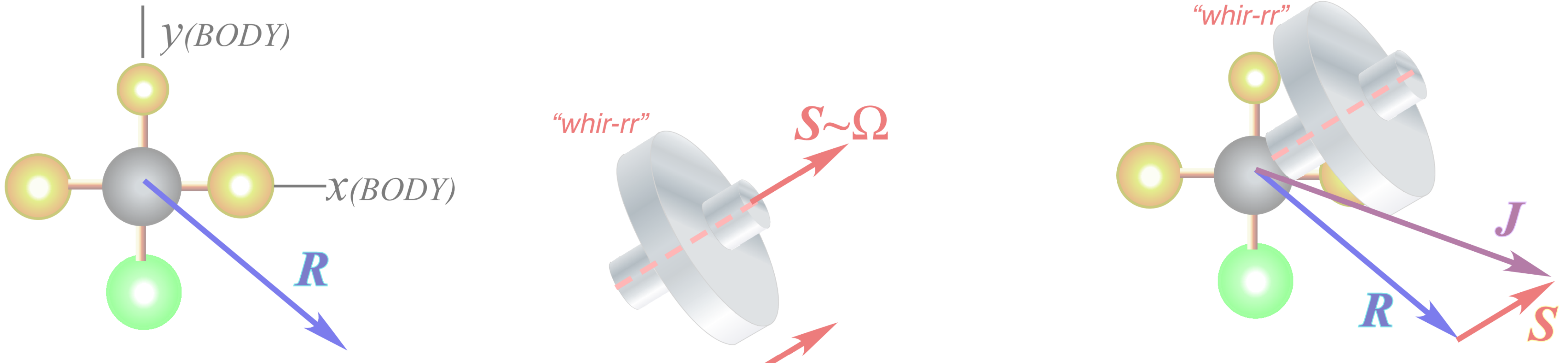
$$H=AJ_x{}^2+BJ_y{}^2+CJ_z{}^2+\ldots-2AJ_xS_x-2BJ_yS_y-2CJ_zS_z+\ldots+(\text{more constant terms})$$

"Coriolis effect" subtracts <u>linear</u> or 1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *terms for gyro-rotor H*

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)
Spring Handbook of AMOP Ch. 32 (2006)

**ZIPP (Zero-Interaction-Potential-`Proximation*

Semiclassical Rotor-"Gyro"-Spin coupling



Rotor $\boldsymbol{R}$ **PLUS "Gyro" Spin** $\boldsymbol{S}$ **EQUALS Compound Rotor** $\boldsymbol{J}=\boldsymbol{R}+\boldsymbol{S}$

Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

In general, this term is the difficult part...

$$H=AR_x^2+BR_y^2+CR_z^2+\ldots+(\text{coupling or constraint})+\ldots+B_S S\cdot S$$

...but suppose it's zero!

*Zero-Interaction Potential 'Proximation (ZIPP)**

Constraints do <u>no</u> <u>work</u>.

(ZIPPed)

Let: $\boldsymbol{R}=\boldsymbol{J}-\boldsymbol{S}$ *and consider <u>non</u>-constant terms* *(ignore gyro S terms that are constant)*

$$H=A(J_x-S_x)^2+B(J_y-S_y)^2+C(J_z-S_z)^2+\ldots+0\ (\text{for constraint})+\ldots+(\text{constant BS terms})$$

$$H=AJ_x^2+BJ_y^2+CJ_z^2+\ldots-2AJ_xS_x-2BJ_yS_y-2CJ_zS_z+\ldots+(\text{more constant terms})$$

"Coriolis effect" subtracts <u>linear</u> or 1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1_m$ *terms for gyro-rotor H*

$B\boldsymbol{R}^2$ *to* $B(\boldsymbol{J}-\boldsymbol{S})^2$ *is analogous to* $\boldsymbol{p}^2/2M$ *to* $(\boldsymbol{p}-e\boldsymbol{A})^2/2M$ *gauge-transformation*

...$\boldsymbol{J}\bullet\boldsymbol{S}$ *is analogous to* $e\boldsymbol{p}\bullet\boldsymbol{A}$

*ZIPP (Zero-Interaction-Potential-`Proximation

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

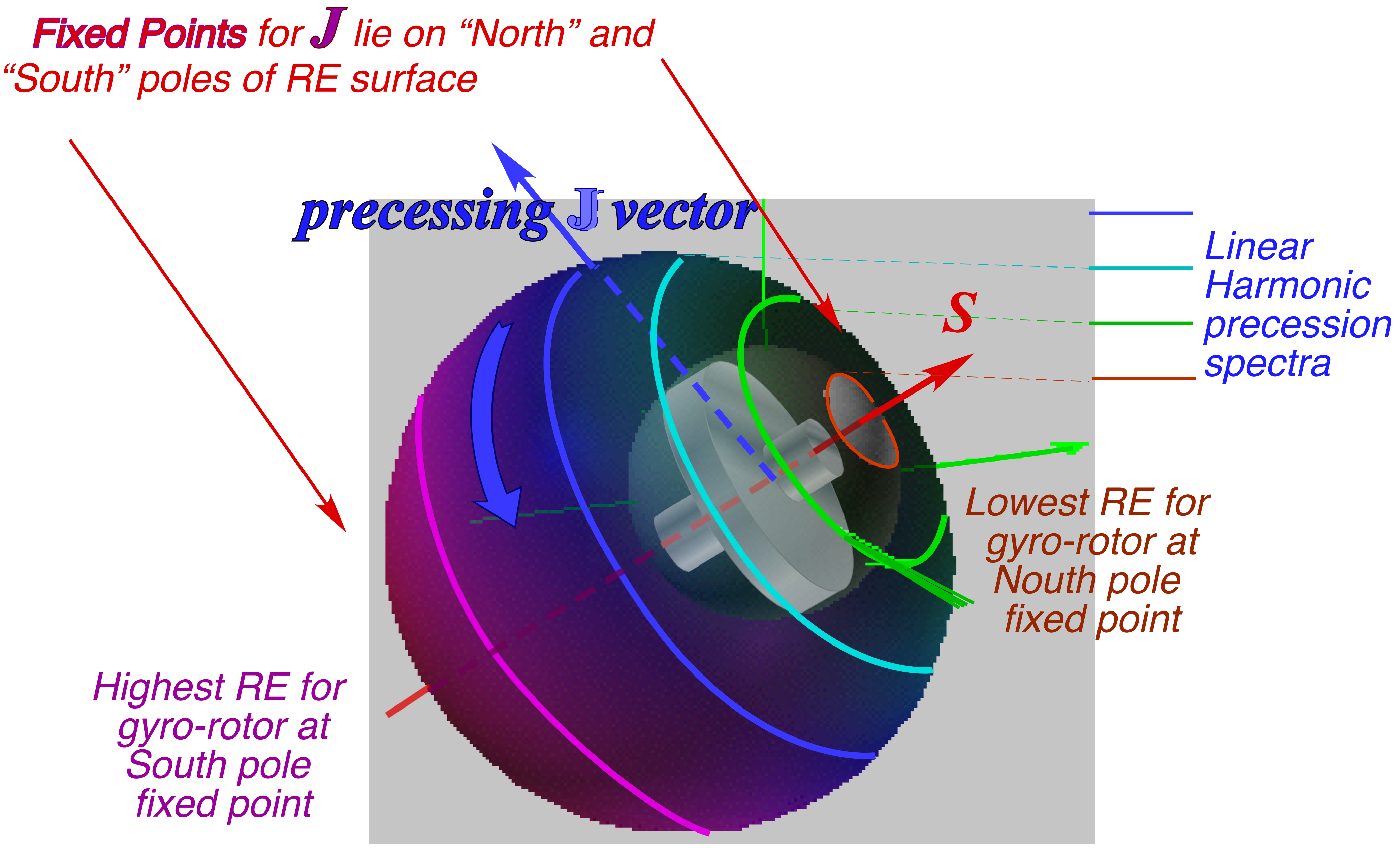
REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

*ZIPP (Zero-Interaction-Potential-`Proximation

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces

RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is a cardioid displaced in J-direction*
Energy sphere intersections are concentric circular precession paths
All paths precess with the same sense around gyro S-vector



Springer DAMOP Handbook 2005 pdf p.20

From Ch. 25 of QTCA Unit 8 pdf p.69

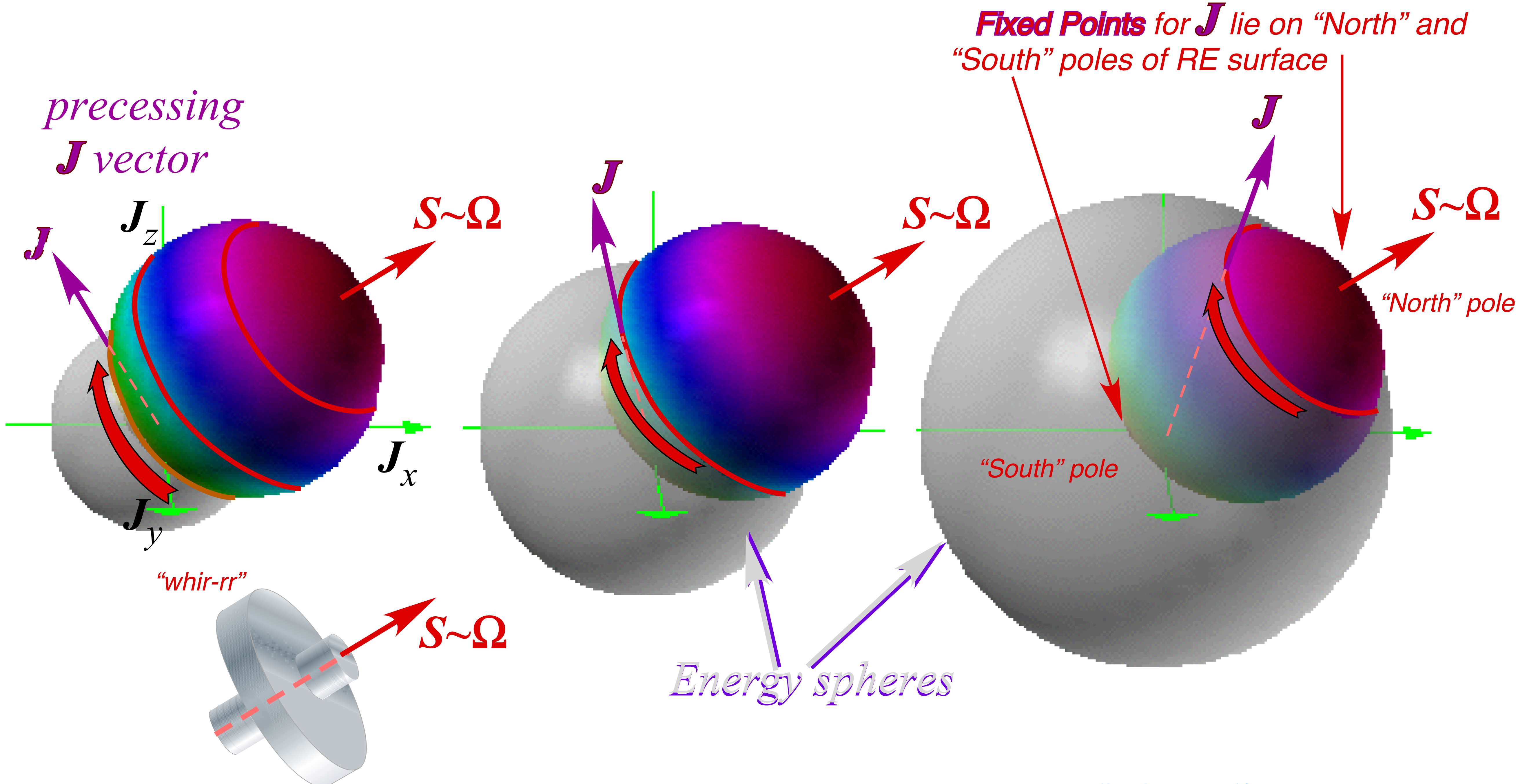
Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces

RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is a quasi-sphere displaced in* **S**-*direction*

Energy sphere intersections are concentric circular precession paths

All paths precess with the same sense around gyro S-vector *(Using left-hand rule here)*

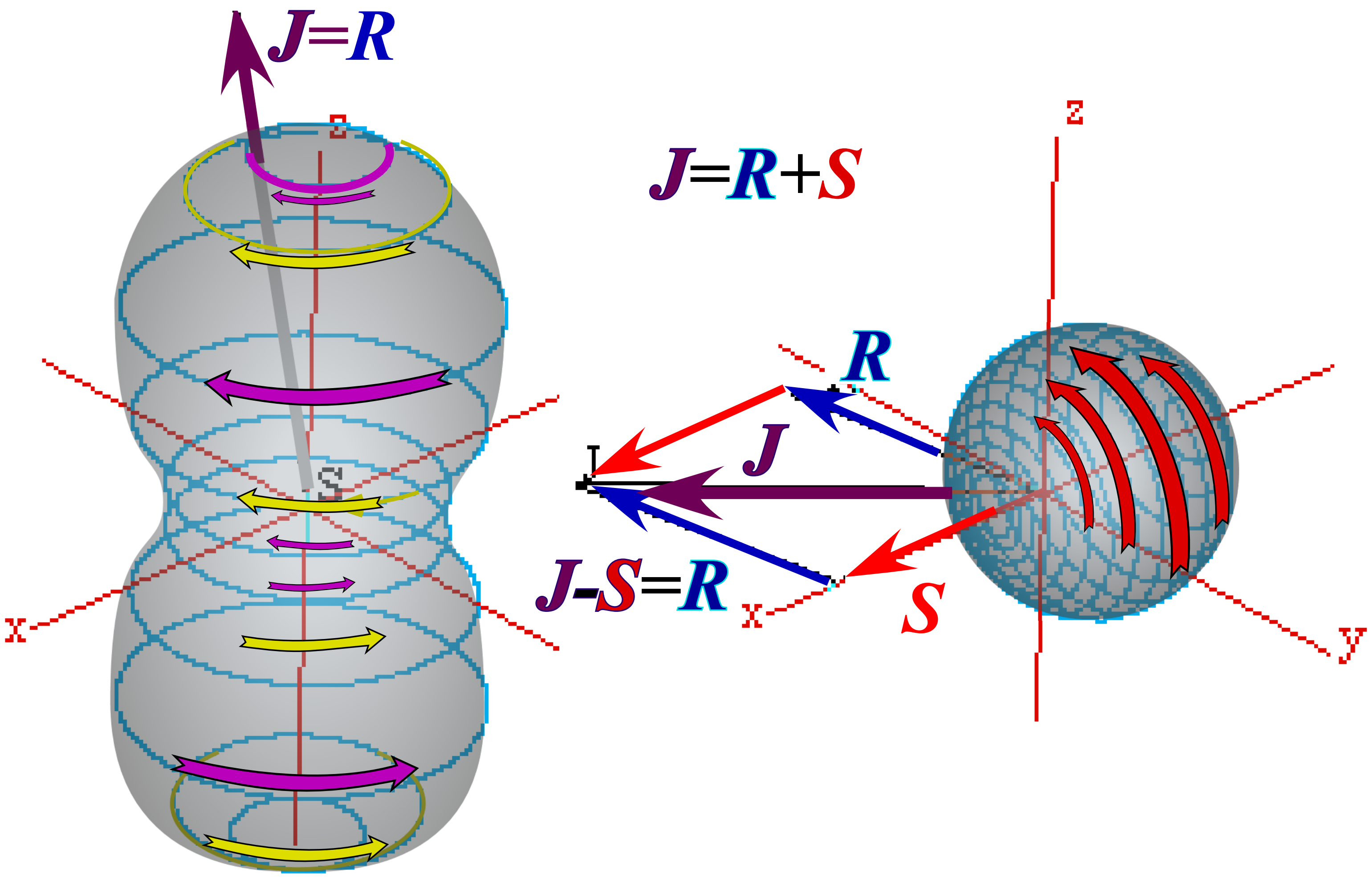


Springer DAMOP Handbook 2005 pdf p.20

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces

Prolate Rotor $\boldsymbol{R}$ **MINUS** *"Gyro" x-Spin* S_x

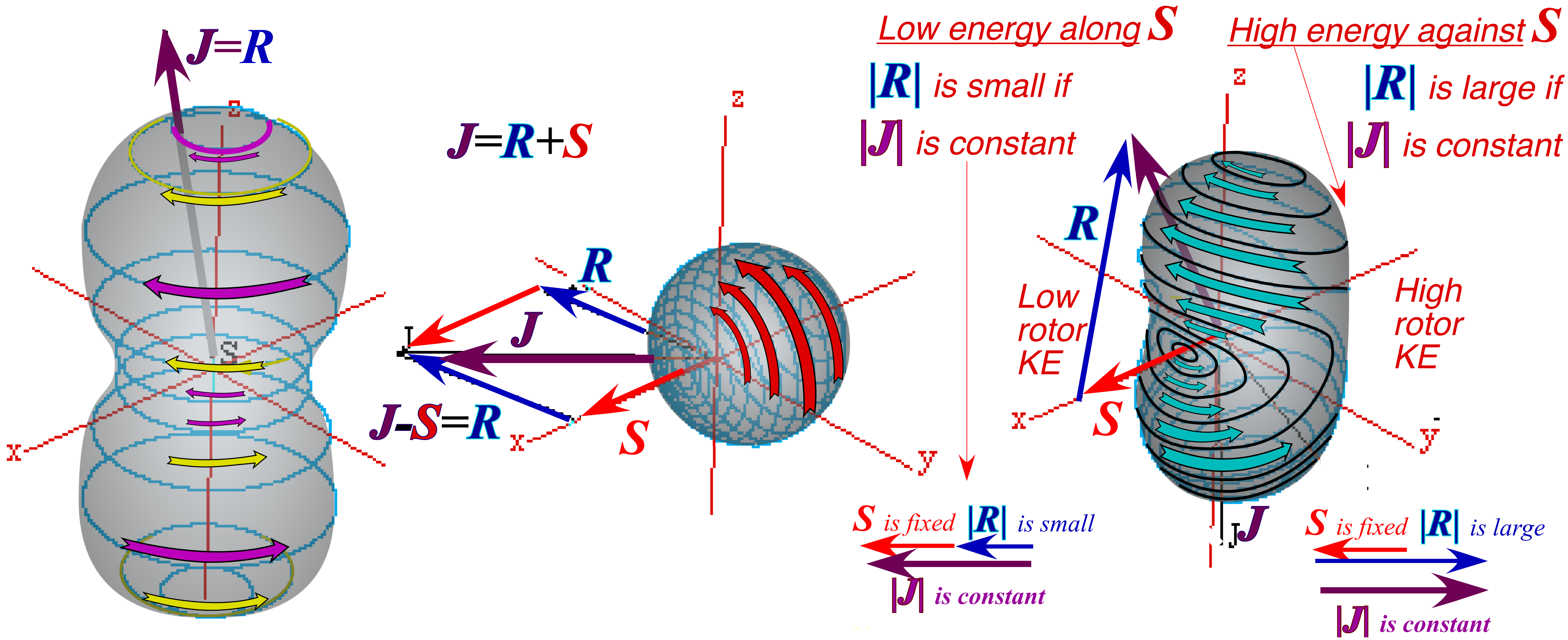


Springer DAMOP Handbook 2005 [pdf p.20]

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces

Prolate Rotor $\boldsymbol{R}$ MINUS *"Gyro" x-Spin* S_x



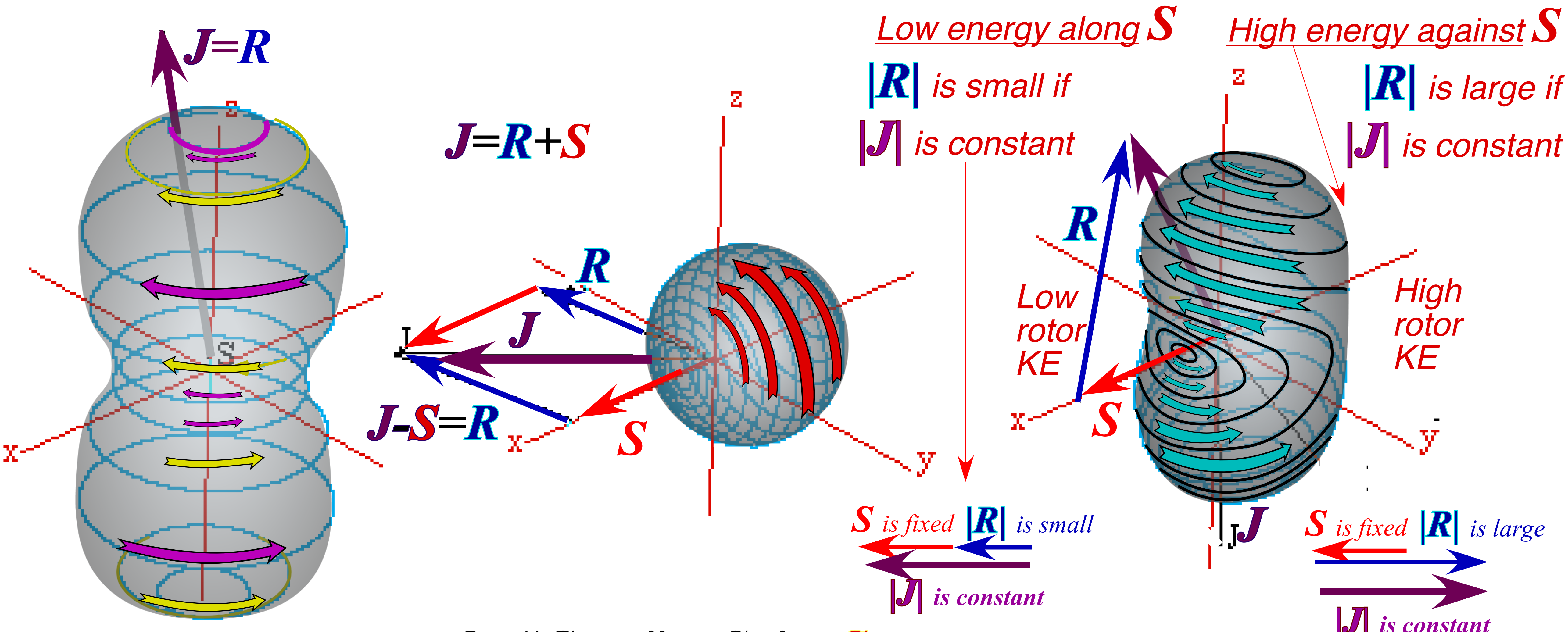
Springer DAMOP Handbook 2005 pdf p.20

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)

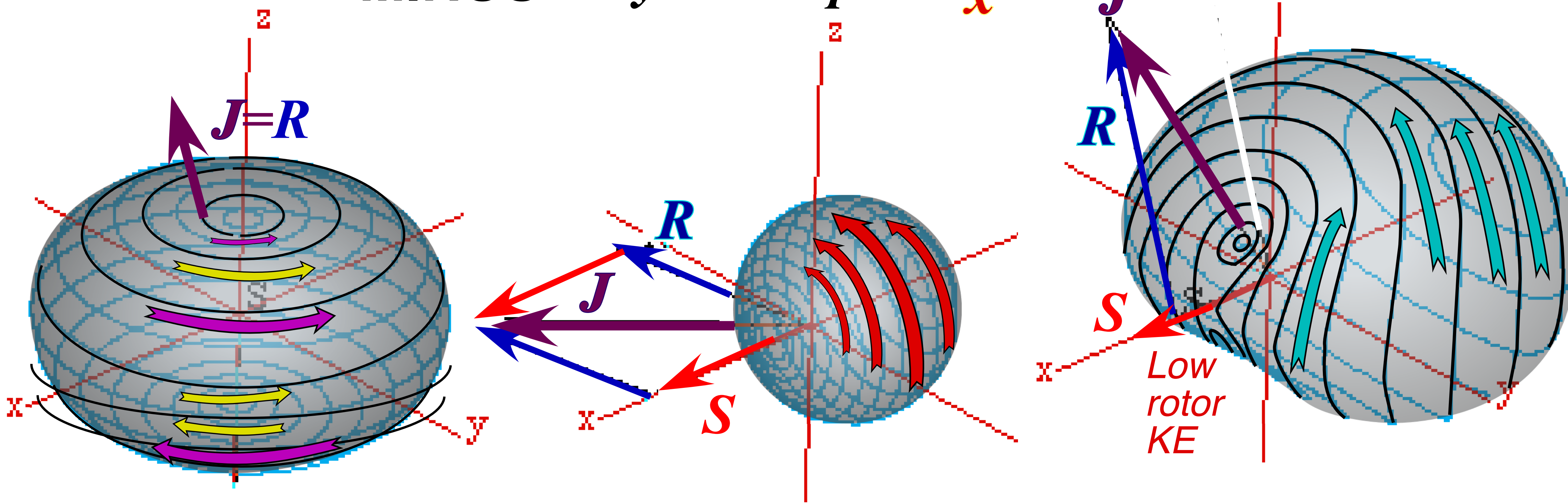
Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces

Prolate Rotor $\boldsymbol{R}$ **MINUS** *"Gyro" x-Spin* S_x

From Ch. 25 of QTCA Unit 8 pdf p.70



Oblate Rotor $\boldsymbol{R}$ **MINUS** *"Gyro" x-Spin* S_x



AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O \supset C_4$ and $O \supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h}$

State labels by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

REES for high-J Coriolis spectra in υ_3 CF_4

. REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

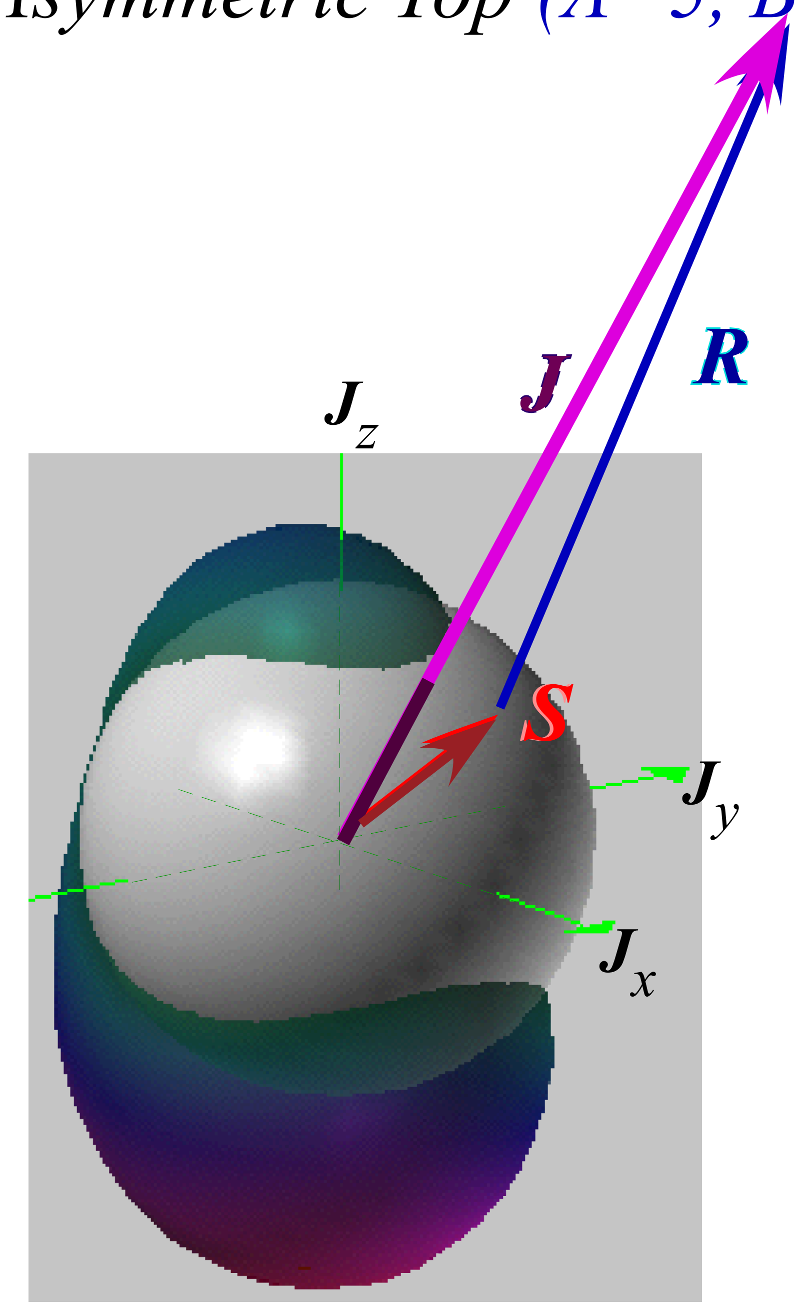
Rotational energy eigenvalue surfaces (REES)

Spin gyro S=(1,1,1) attached (ZIPPed) to Asymmetric Top (A=5, B=10, C=15)

Springer DAMOP Handbook 2005 pdf p.23

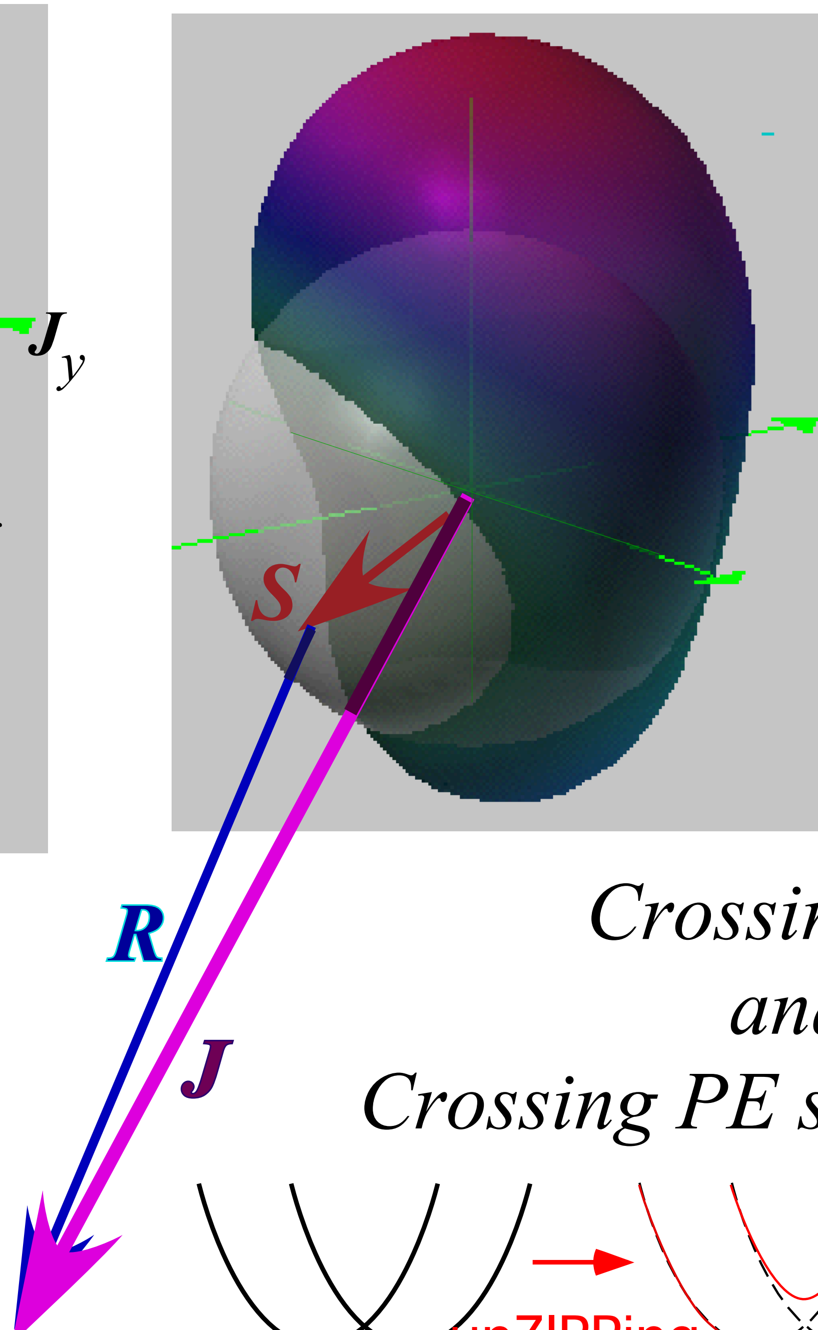
Introducing "Sherman the Shark" ZIPPed*

*ZIPP (Zero-Interaction-Potential-`Proximation

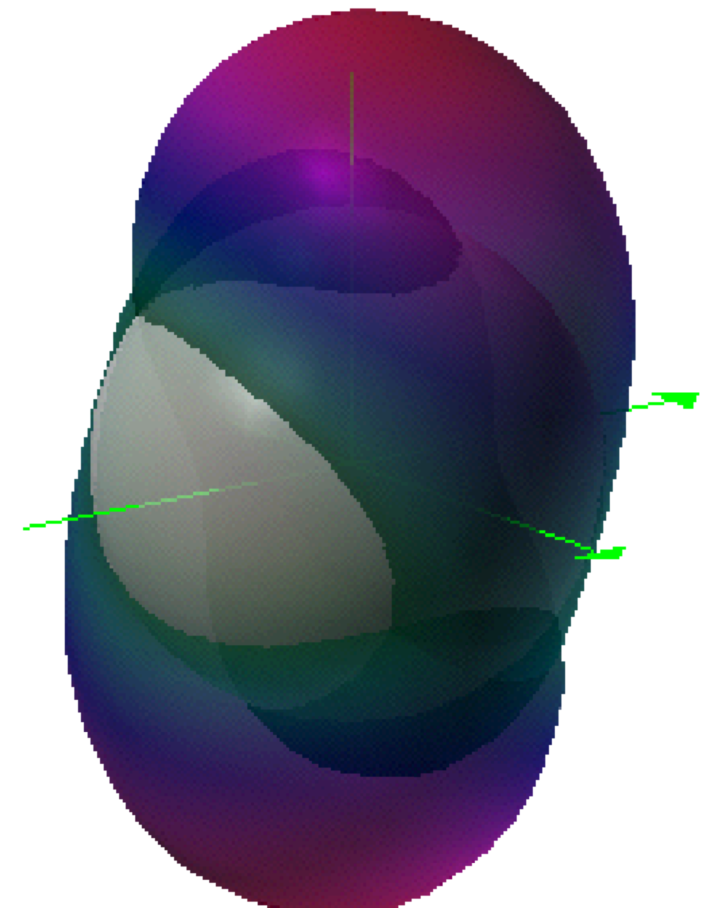


"Sherman" (The shark)

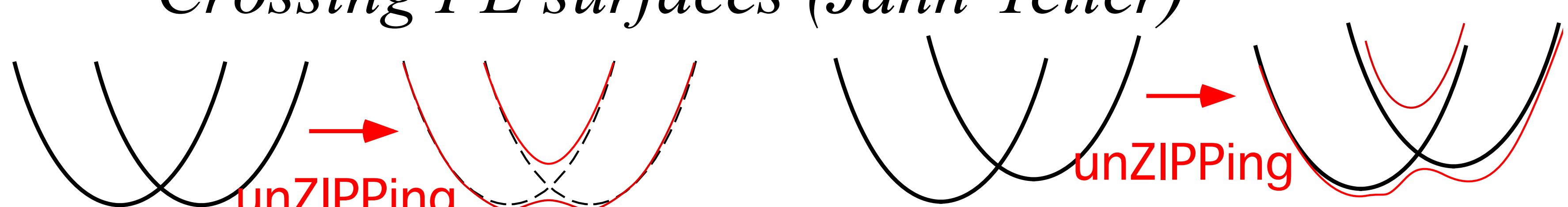
Time reversed gyro $-S=(-1,-1,-1)$



The two together (ZIPPed*)



Crossing RE surfaces analogous to Crossing PE surfaces (Jahn-Teller)



Rotational energy eigenvalue surfaces (REES)

Two or more RE's beg to be unZIPPed. $\langle\mathbf{H}\rangle = \begin{pmatrix} \text{Spin-up } RE(\beta,\gamma) & \text{Coupling}(\beta,\gamma) \\ \text{Coupling}(\beta,\gamma)^* & \text{Spin-down } RE(\beta,\gamma) \end{pmatrix}$

Base RE surfaces are eigenvalues of matrix.

Classical RE

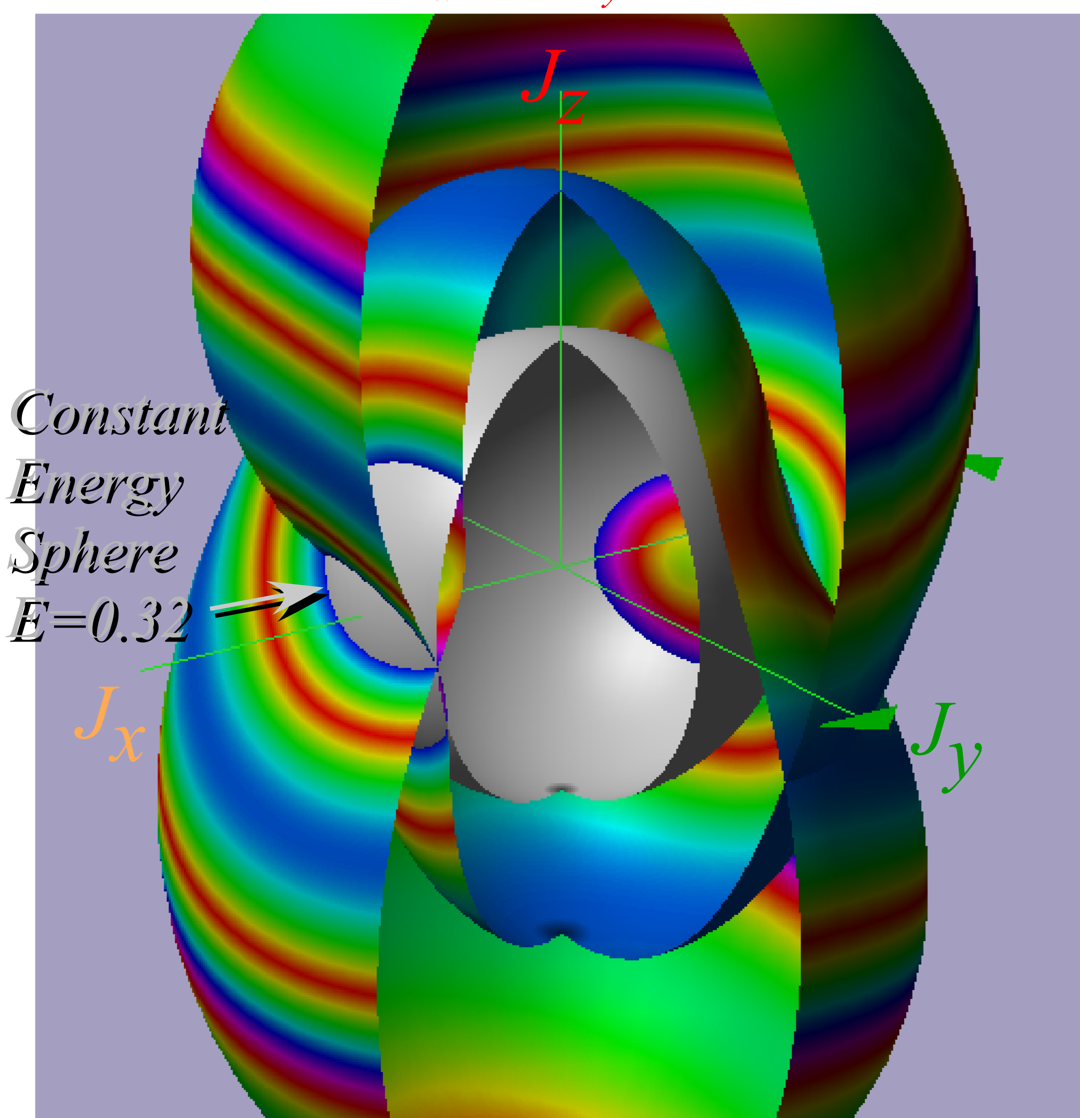
$$H = AJ_x{}^2 + BJ_y{}^2 + CJ_z{}^2 + \ldots - 2AJ_xS_x - 2BJ_yS_y - 2CJ_zS_z + \ldots + \textit{(more constant terms)}$$

Semi-Classical Spin-1/2 RE $\quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ *makes matrix*

$$\mathbf{H} = (AJ_x{}^2 + BJ_y{}^2 + CJ_z{}^2)\mathbf{1} \ldots - AJ_xs_x\sigma_x \; - BJ_ys_y\sigma_y \; - CJ_zs_z\sigma_z + \ldots + \mathbf{1}\textit{(more constant terms)}$$

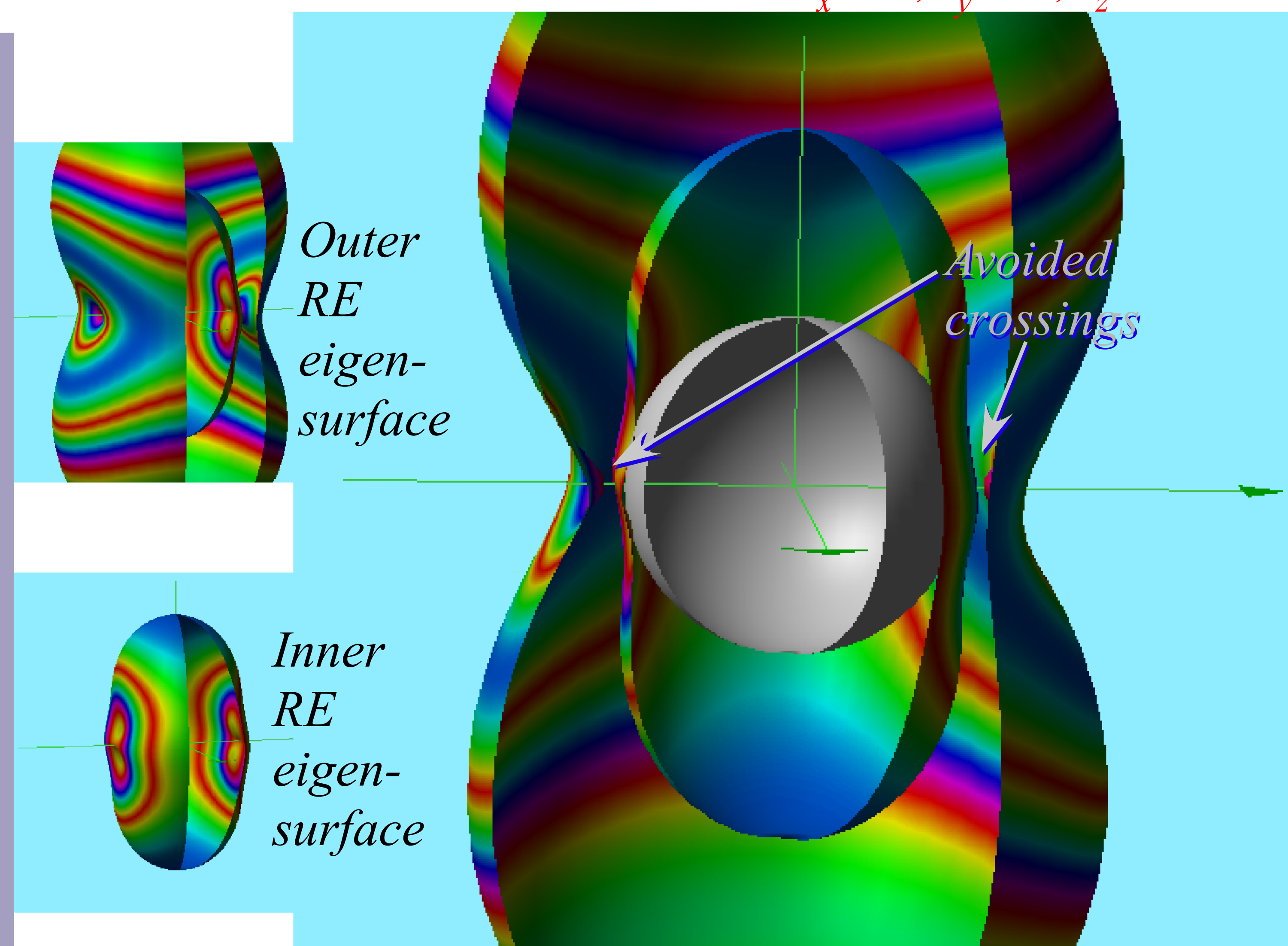
Classical ZIPP $A=0.2$, $B=0.8$, $C=1.4$

$S_x=0.0$, $S_y=0.1$, $S_z=0.2$



Semi-Classical spin-1/2 unZIPP $A=0.2$, $B=0.8$, $C=1.4$

$s_x=0.0$, $s_y=0.1$, $s_z=0.2$



Rotational energy eigenvalue surfaces (REES)

$$H_{R,S(quantized)} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 - A\mathbf{J}_x\boldsymbol{\sigma}_x - B\mathbf{J}_y\boldsymbol{\sigma}_y - C\mathbf{J}_z\boldsymbol{\sigma}_z + const.$$

$$= \begin{pmatrix} \mathrm{RE}_{\mathrm{rotor}} - JC\cos\beta & -AJ\cos\gamma\sin\beta - iBJ\sin\gamma\sin\beta \\ -AJ\cos\gamma\sin\beta + iBJ\sin\gamma\sin\beta & \mathrm{RE}_{\mathrm{rotor}} + JC\cos\beta \end{pmatrix}$$

$$\text{where: } \mathrm{RE}_{\mathrm{rotor}} = J^2(A\cos^2\gamma\sin^2\beta + B\sin^2\gamma\sin^2\beta + C\cos^2\beta)$$

(ZIPPed)*

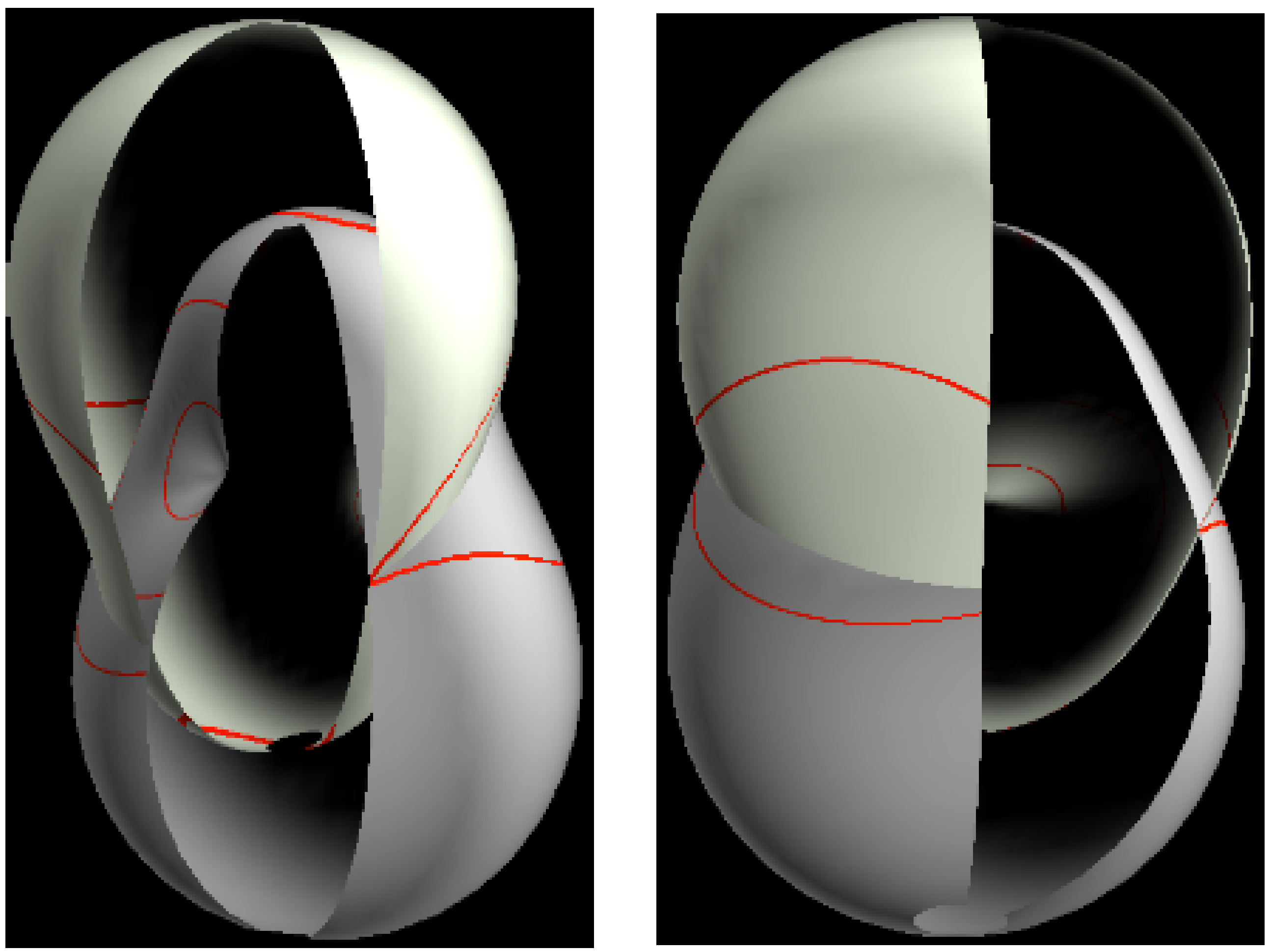


Fig. 25.5.5 (a) Views of classical gyro-rotor c-RES in Fig. 25.5.4 (a) based on (25.5.2).

(unZIPPed)*

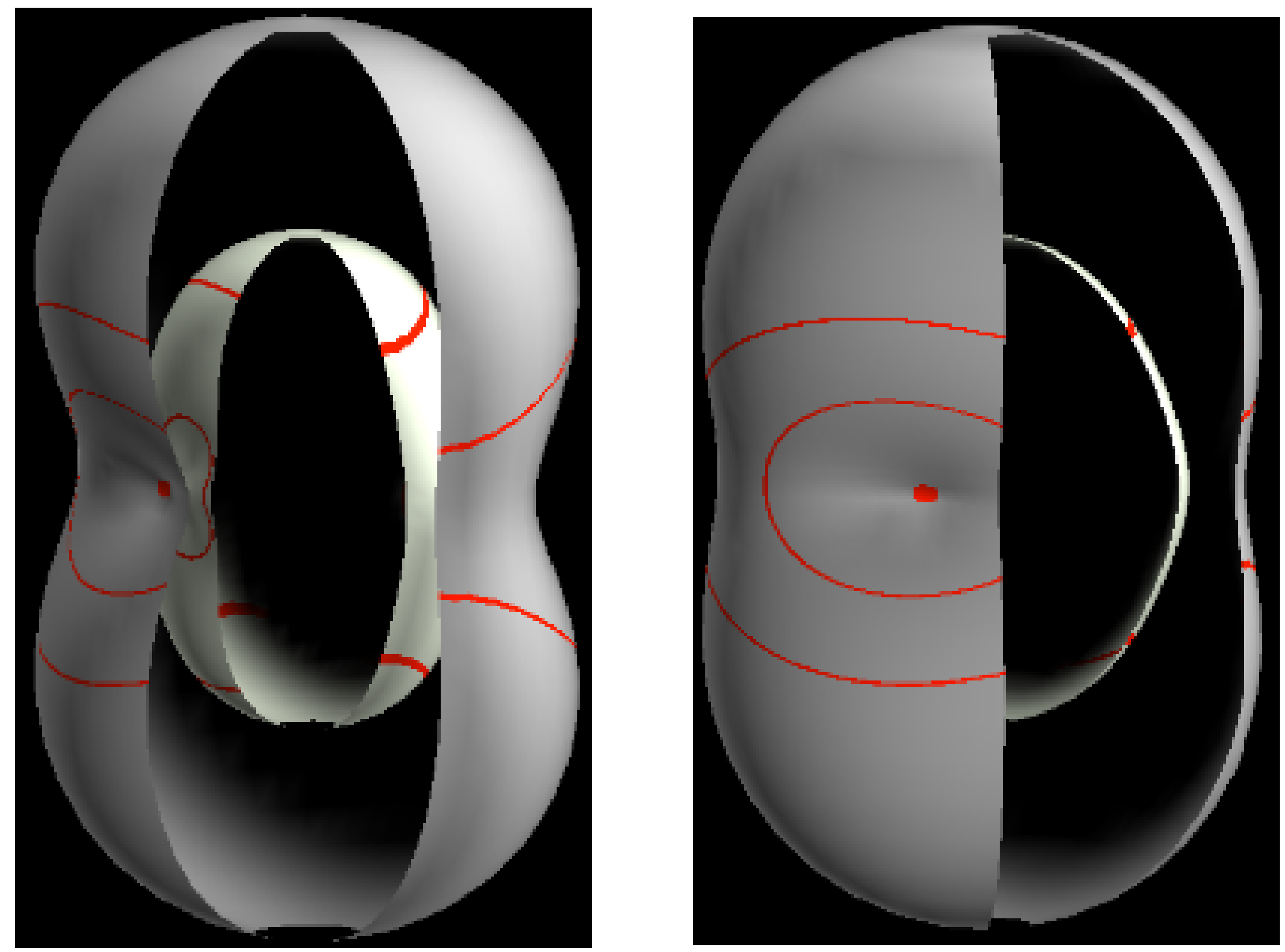


Fig. 25.5.5(b) Views of semi-classical gyro-rotor sc-RES plot of eigenvalues of (25.5.12) with **S**=σ/2.

**ZIPP (Zero-Interaction-Potential-`Proximation*

AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6

REES for high-J Coriolis spectra in υ_3 CF_4

REES for high-J and high-υ rovibration polyads

**ZIPP (Zero-Interaction-Potential-`Proximation*

REES for high-J Coriolis spectra in SF_6

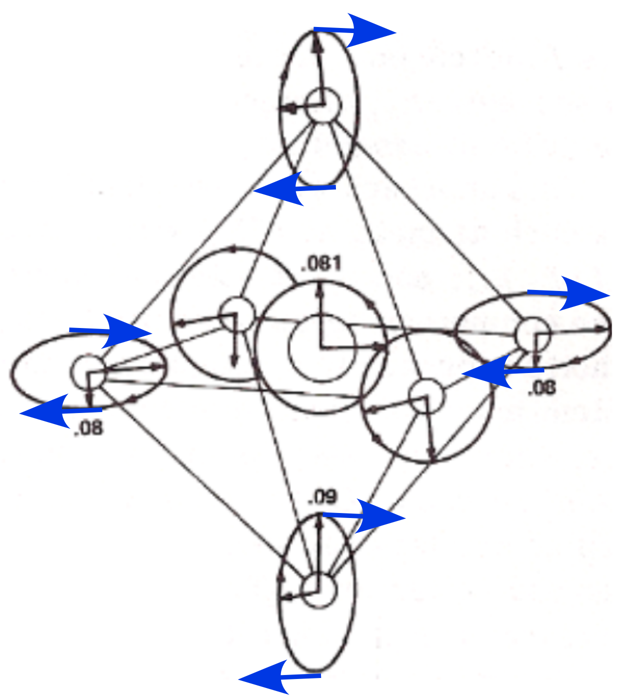
$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$

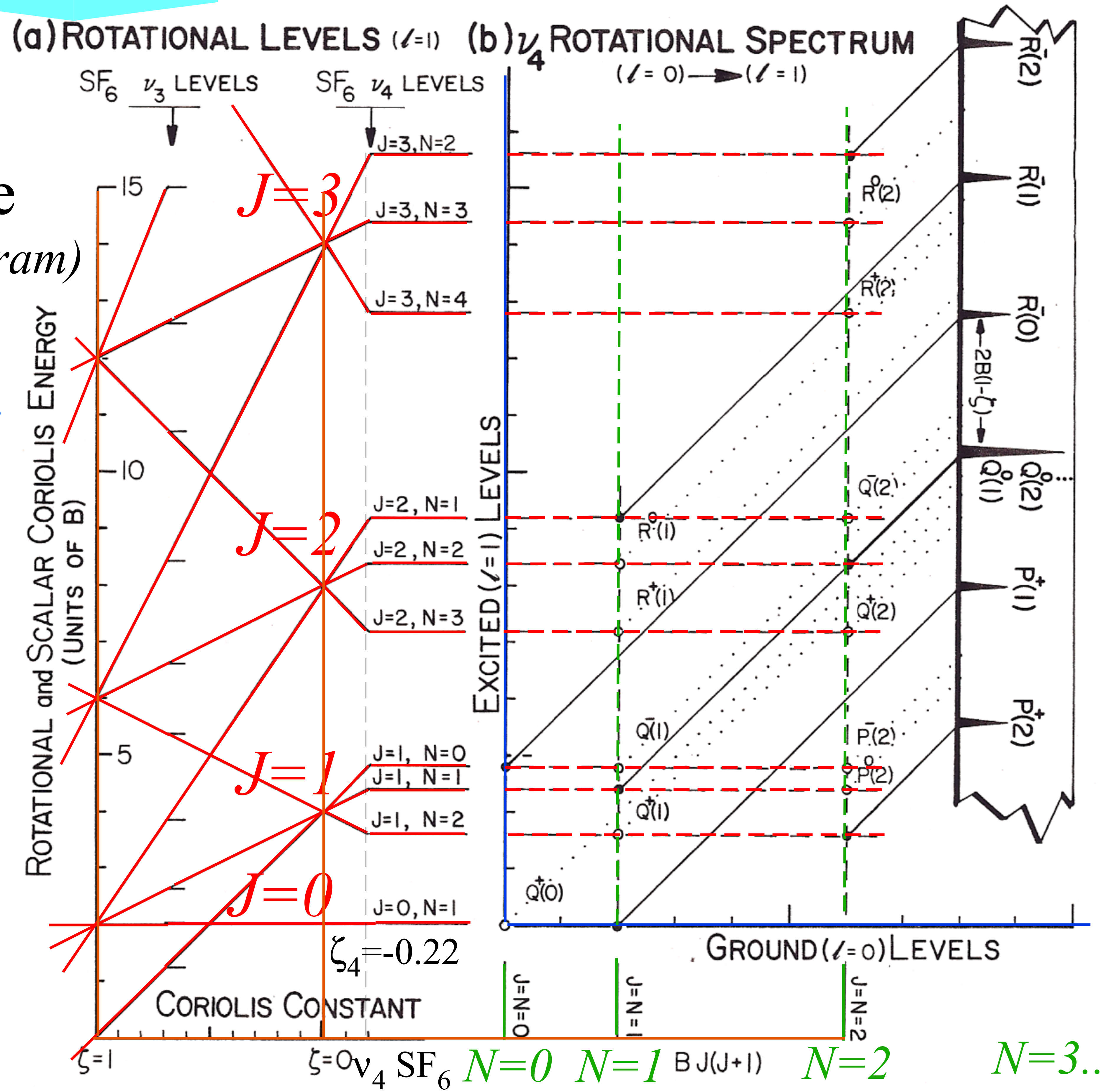
Summary of low-J (PQR) ro-vibe structure

(Using rovib. nomogram)

Review:

SF_6 Coriolis PQR structure

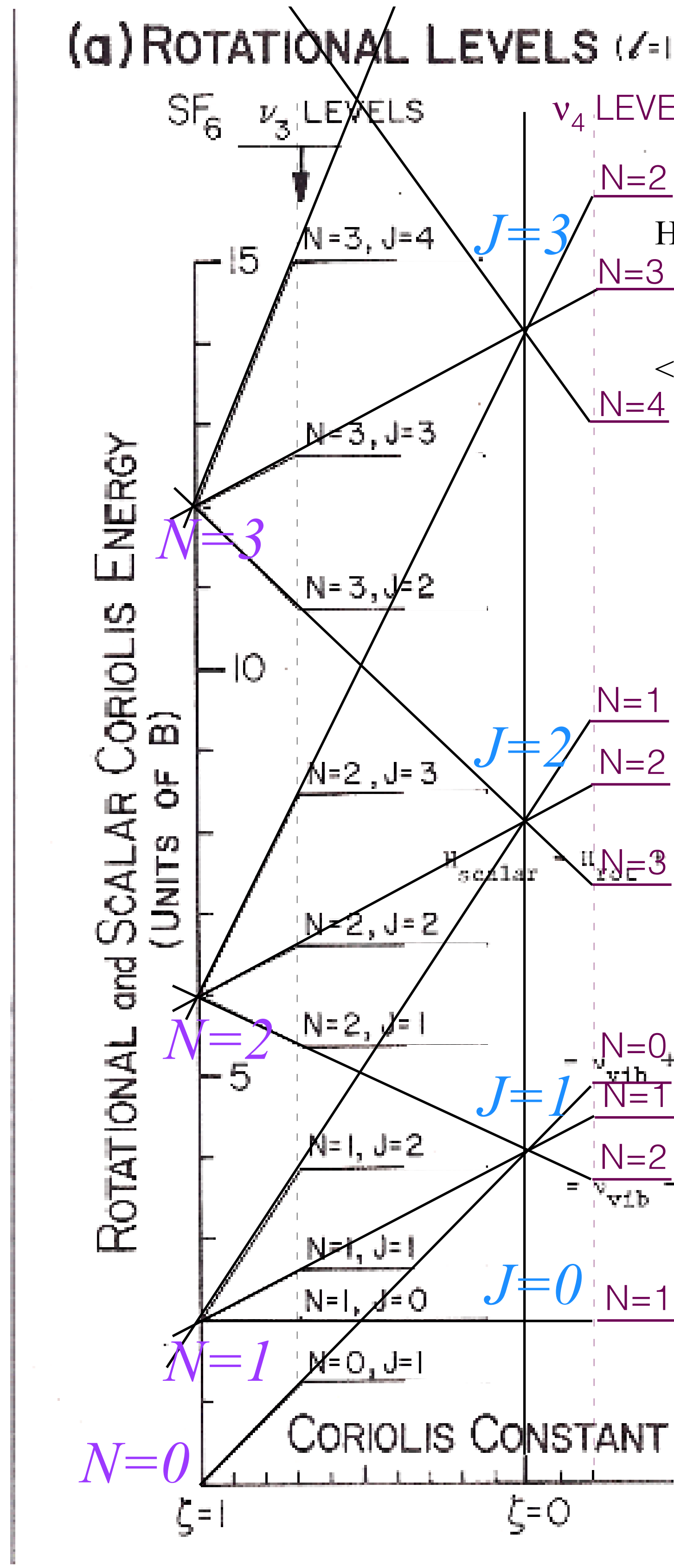




REES for high-J Coriolis spectra in SF_6

Review:

SF_6 Coriolis PQR structure



$$H^{Scalar\ Coriolis} = -B\zeta\, 2\mathbf{J}^{Total}\bullet\ell^{vibe}$$
$$= -B\zeta[\,\mathbf{J}^2-(\mathbf{J}^2-\ell)^2+\ell^2]$$
$$= -B\zeta[\,\mathbf{J}^2-\ \mathbf{N}^2\ +\ell^2]$$
$$\langle H^{Scalar\ Coriolis}\rangle = -B\zeta[\,J(J+1)-N(N+1)+\ell(\ell+1)]$$

$$J^{Total} = N^{Rotation} + \ell^{Vibration}$$

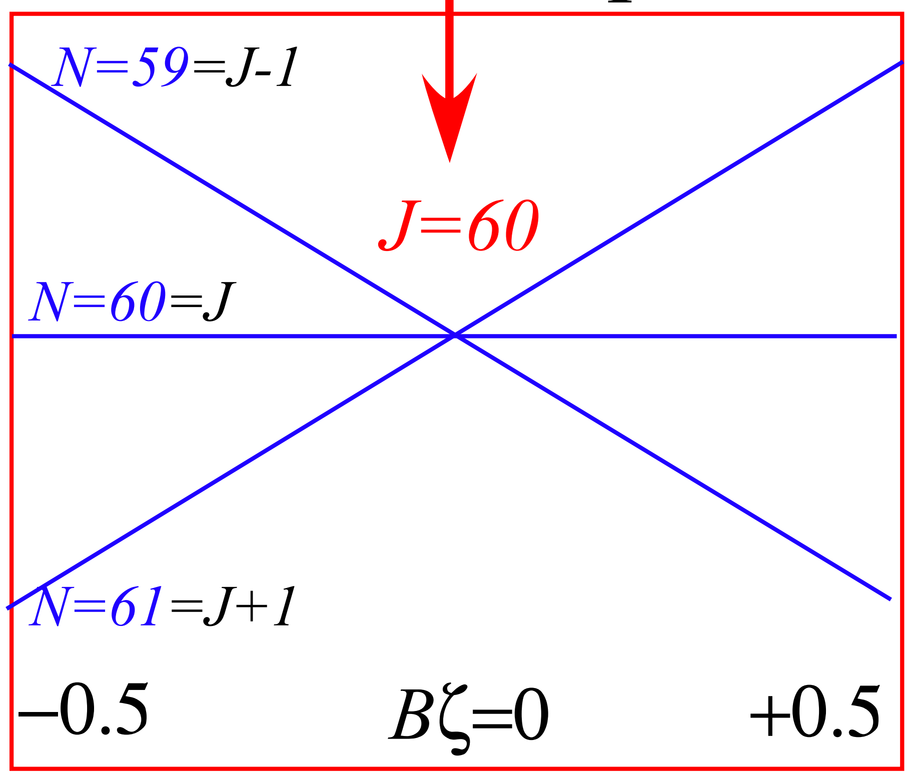
$$H_{scalar} = H_{rot} + \nu_{vib} - 2B\zeta\ \ J\cdot\ell$$

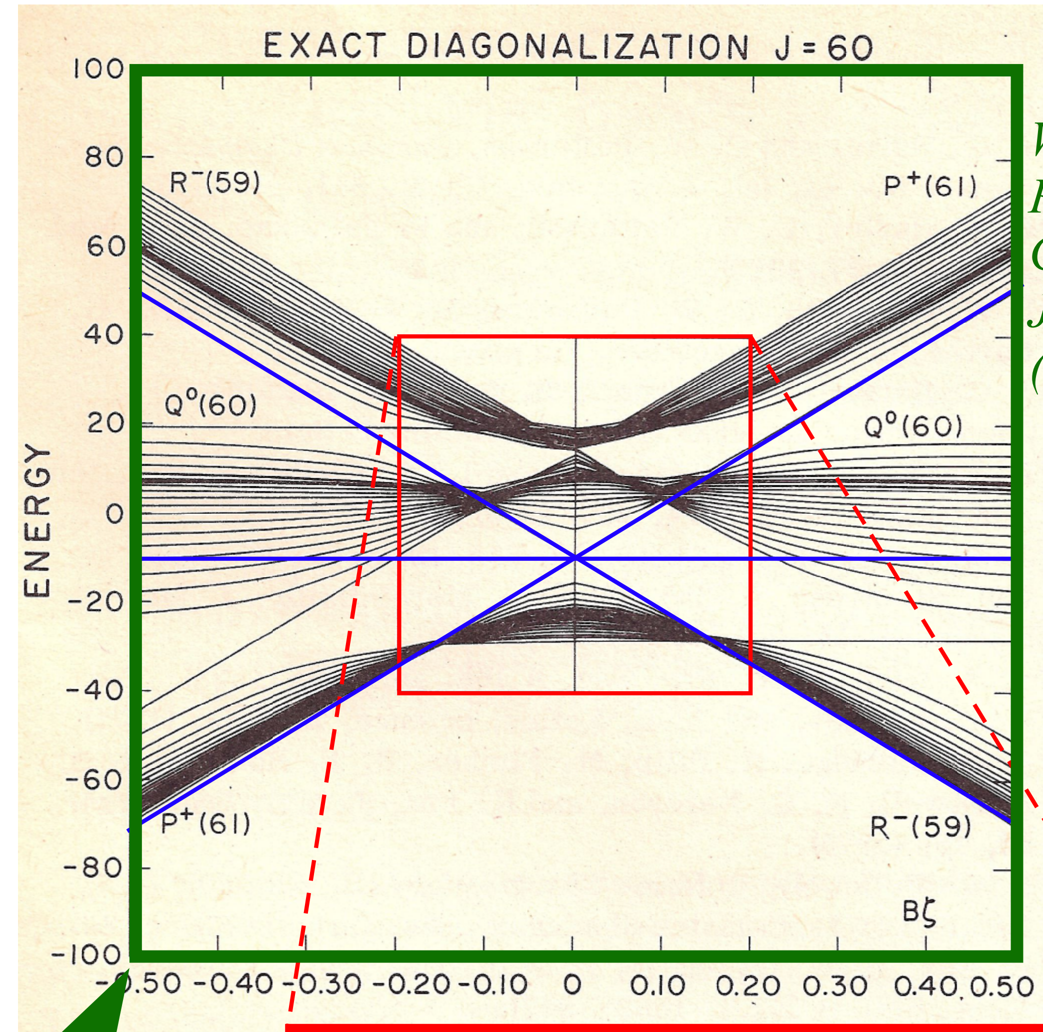
$$2J\cdot\ell = J^2-(J-\ell)^2+\ell^2 = J^2-N^2+\ell^2$$

$$= \nu_{vib} + BJ(J+1) - B\zeta[J(J+1) - N(N+1)+\ell(\ell+1)]$$

$$= \nu_{vib} - 2B\zeta + BN(N+1) + \begin{cases} 2B(1-\zeta)(N+1) & \text{for: } J=N+1 \\ 0 & \text{for: } J=N \\ -2B(1-\zeta)N & \text{for: } J=N-1 \end{cases}$$

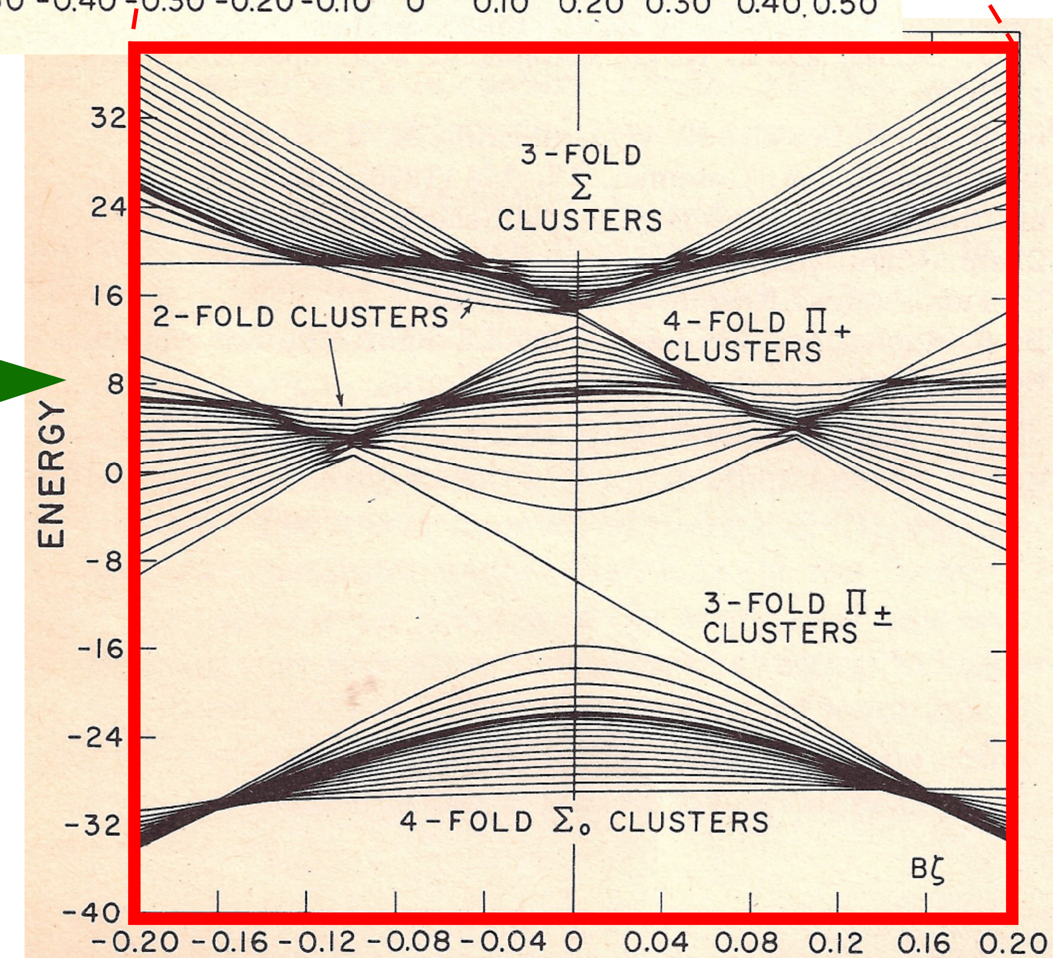
Recall scalar Coriolis
PQR plots vs. $B\zeta$
Here is a *J=60* piece of it:





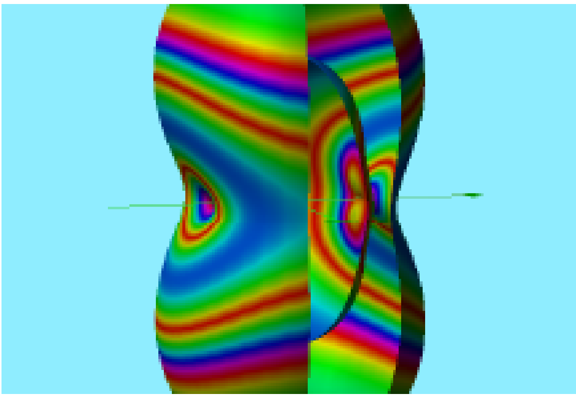
WGH, Patterson, Galbraith JCP 69, 4906 (1978)

Now consider this plot with *tensor* Coriolis, too
(Just 4^{th}-rank $[2x2]^4$ tensor here.)



How to display such monstrous avoided cluster crossings:
REES: *Rotational Energy Eigenvalue Surfaces*

Vibration (or vibronic) momentum ℓ retains its quantum representaion(s).



For $\ell=1$ that is the usual *3-by-3* matrices.

Rotational momentum J is treated semi-classically. $|J|=\sqrt{J(J+1)}$

Usually **J** is written in Euler coordinates: $J_x=|J|\cos\gamma\sin\beta$, etc.

Plot resulting H-matrix eigenvalues *vs.* classical variables.

($\ell=1$) *3-by-3* H-matrix e-values are polar plotted *vs.* azimuth γ and polar β.

REES for high-J Coriolis spectra in SF_6

Body-ΣΠ±-Basis

$$
\langle H\rangle=(\nu_3+B|J|^2)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+2B\zeta|J|\begin{array}{c}
\begin{array}{ccc}|\Pi+\rangle & |\Sigma+\rangle & |\Pi-\rangle\end{array}\\
\begin{pmatrix}\cos\beta & \frac{1}{\sqrt{2}}e^{-i\gamma}\sin\beta & 0\\ \frac{1}{\sqrt{2}}e^{i\gamma}\sin\beta & 0 & \frac{1}{\sqrt{2}}e^{-i\gamma}\sin\beta\\ 0 & \frac{1}{\sqrt{2}}e^{i\gamma}\sin\beta & -\cos\beta\end{pmatrix}
\end{array}
$$

$$
+2t_{224}|J|^2\begin{pmatrix}3\cos^2\beta-1 & -\sqrt{8}e^{-i\gamma}\sin\beta\cos\beta & \sin^2\beta\,(6\cos2\gamma+i4\sin2\gamma)\\ -\sqrt{8}e^{i\gamma}\sin\beta\cos\beta\;\;0 & -6\cos^2\beta+2 & \sqrt{8}e^{-i\gamma}\sin\beta\cos\beta\\ \sin^2\beta\,(6\cos2\gamma-i4\sin2\gamma) & \sqrt{8}e^{i\gamma}\sin\beta\cos\beta & 3\cos^2\beta-1\end{pmatrix}
$$

Lab-PQR-Basis

(Either basis should give same REES)

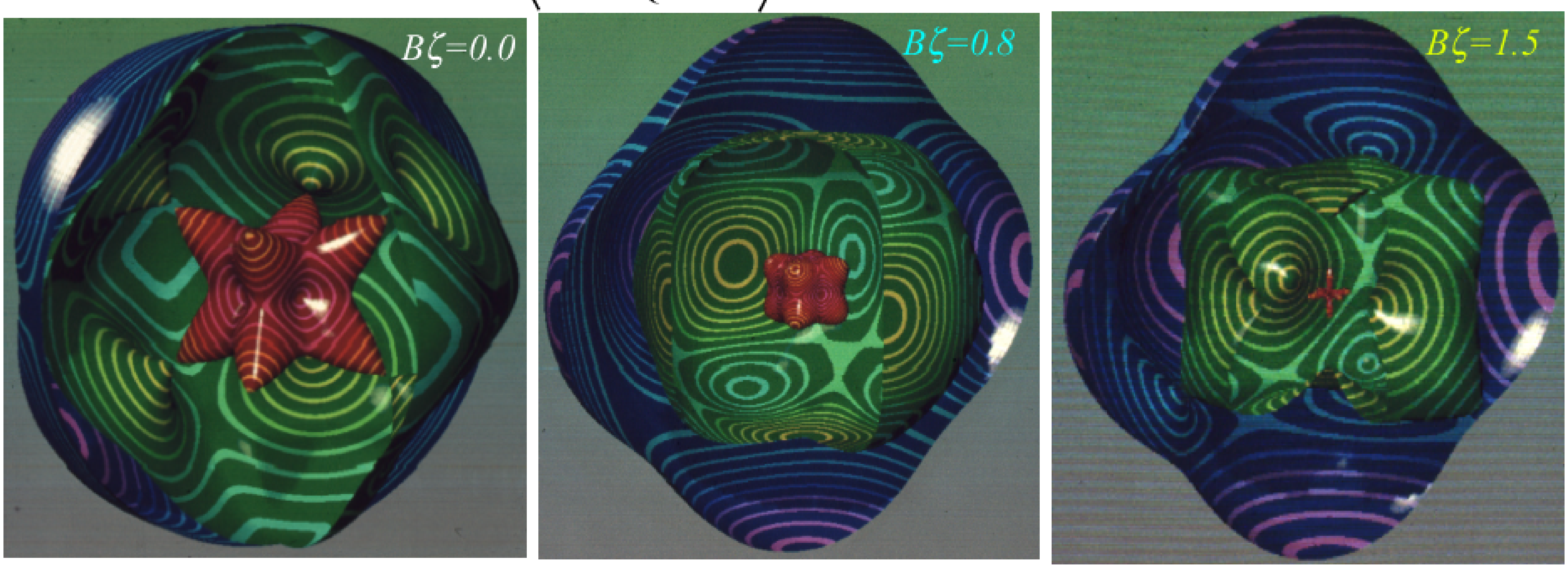
$$
\langle H\rangle=(\nu_3+B|J|^2)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+2B\zeta|J|\begin{array}{c}
\begin{array}{ccc}|P\rangle & |Q\rangle & |R\rangle\end{array}\\
\begin{pmatrix}+1&0&0\\0&0&0\\0&0&-1\end{pmatrix}
\end{array}
$$

$$
+2t_{224}|J|^2\begin{pmatrix}H_{PP} & H_{PQ} & H_{PR}\\ H^*_{PQ} & H_{QQ} & H_{QR}\\ H^*_{RP} & H^*_{QR} & H_{RR}\end{pmatrix}
$$

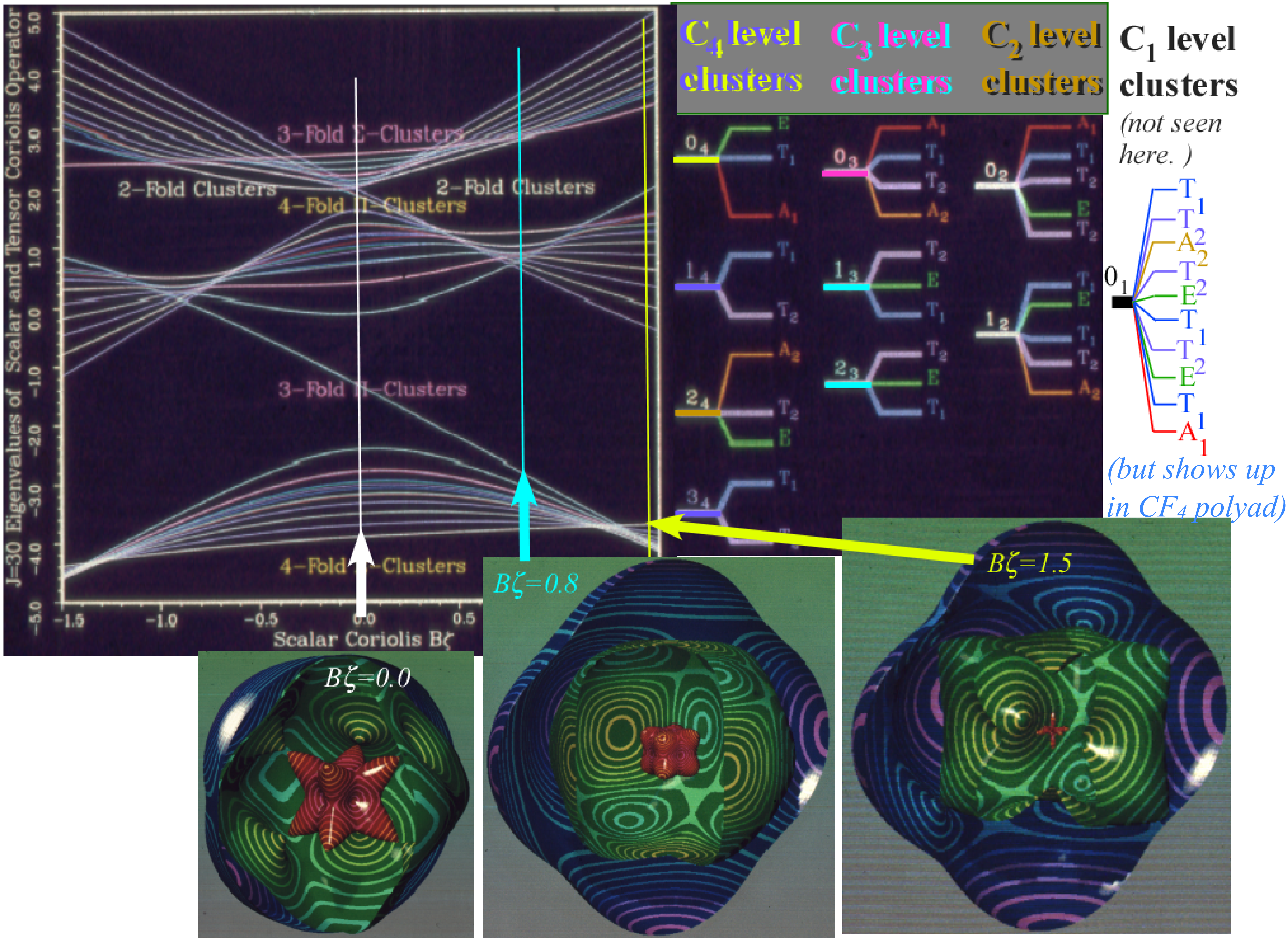
$$H_{PP}=(35\cos^4\beta-30\cos^2\beta+5\sin^2\beta\sin4\gamma+5)/4=H_{RR}$$

$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

$$H_{PQ}=5(-7\cos^4\beta+8\cos^2\beta+(1-\cos^4\beta)\cos4\gamma+2i\cos\beta\sin^2\beta\sin4\gamma-1)/4$$



REES for high-J Coriolis spectra in SF_6



AMOP reference links on pages 2-4

5.02.18 class 28: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Symmetry spin species for C_2, CH_4, SF_6, and molecular energy surfaces: Born-Oppenheimer-Adiabadicity: How BOA works until it doesn't

Conservation of rovibronic spin species-Two views: Herzberg vs. 2005

Where SF_6 spin species go to die: $O\supset C_4$ and $O\supset C_3$ symmetry breaking

Diatomic or linear molecule symmetry $O(3)\supset D_{\infty h}$

State labels by symmetry $O(3)\supset D_{\infty h}$

Coriolis and λ-doubling levels

Nomograms for dipole-allowed transitions

XY_n molecules: S_3-S_6 tableau-characters

Tableau dimension formulae for X_4 and XY_4 molecules

CH_4 and DH_4 (J=7) transitions. SiF_4 (J=30) spectra

Possible SiF_4 High J superhyperfine levels

Calculating SF_6 characters and correlations of symmetry O_h to S_6 SF_6 levels&spectra

Born-Oppenheimer Approximation (BOA) for RES

Born-Oppenheimer Approximation (BOA)-constricted body wave vs. lab-wave

Weak-coupling "hook-up" vs. stronger "BOA-constricted" wavefunctions

Semiclassical Rotor-"Gyro"-Spin coupling

Semiclassical Rotor-"Gyro"-Spin Rotational Energy Surfaces (ZIPPed)*

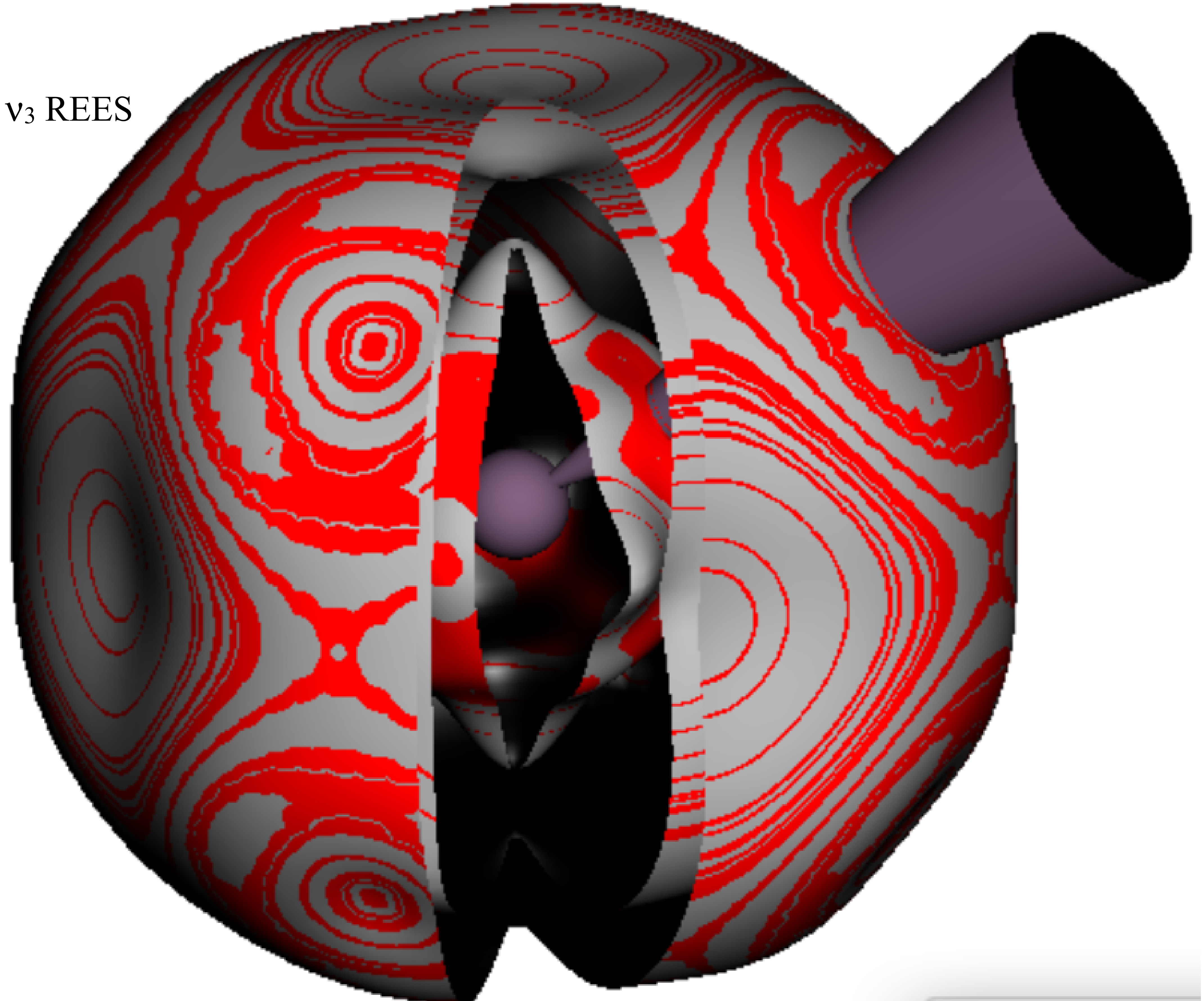
Rotational energy eigenvalue surfaces (REES) (UnZIPPed)

REES for high-J Coriolis spectra in SF_6 *ZIPP (Zero-Interaction-Potential-`Proximation

REES for high-J Coriolis spectra in υ_3 CF_4

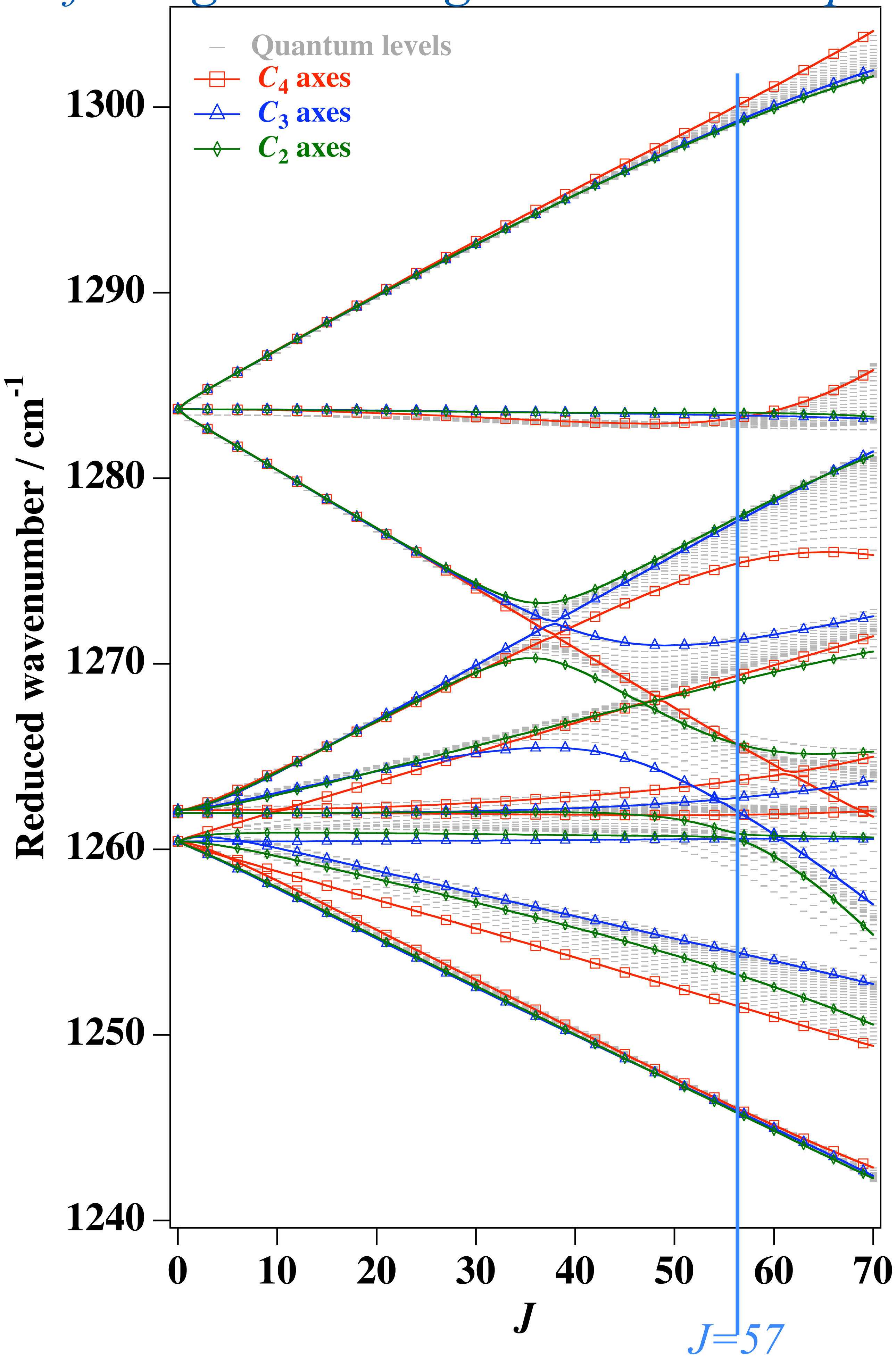
. REES for high-J and high-υ rovibration polyads

REES for high-J Coriolis spectra in υ_3 CF_4



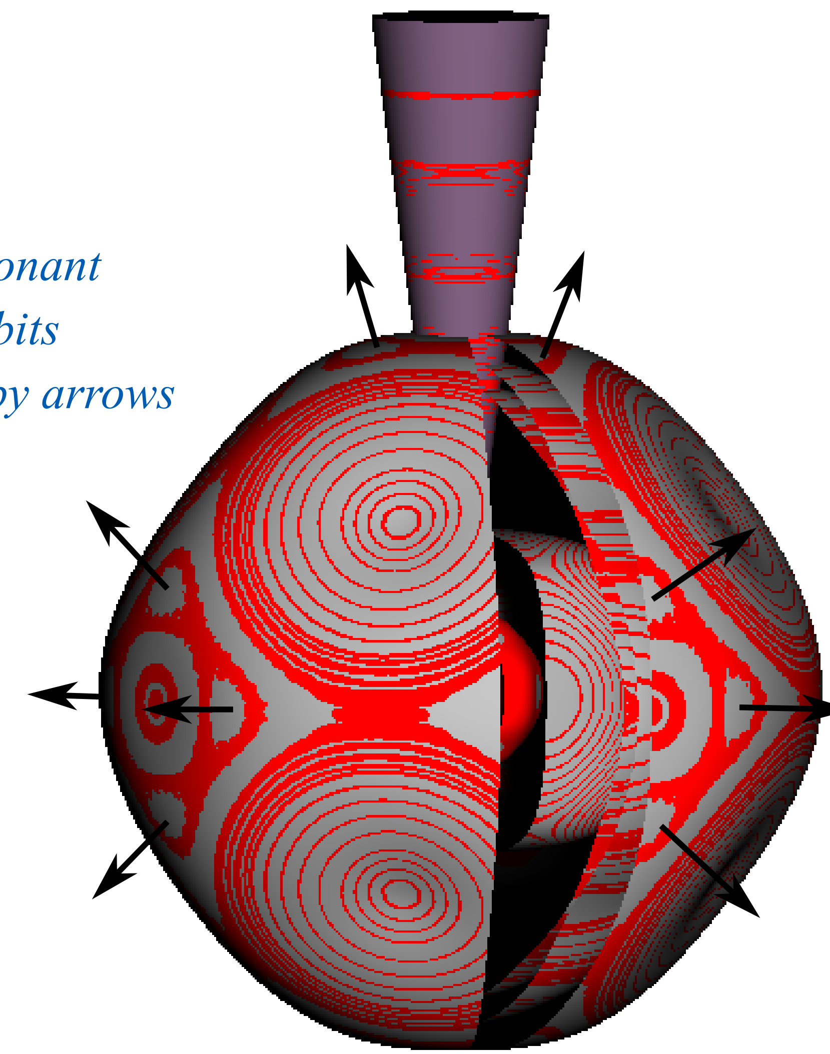
REES issues discussed in:
Int. J. Mol. Sci. 14,714(2013)p.84

REES for high-J and high-υ rovibration polyads

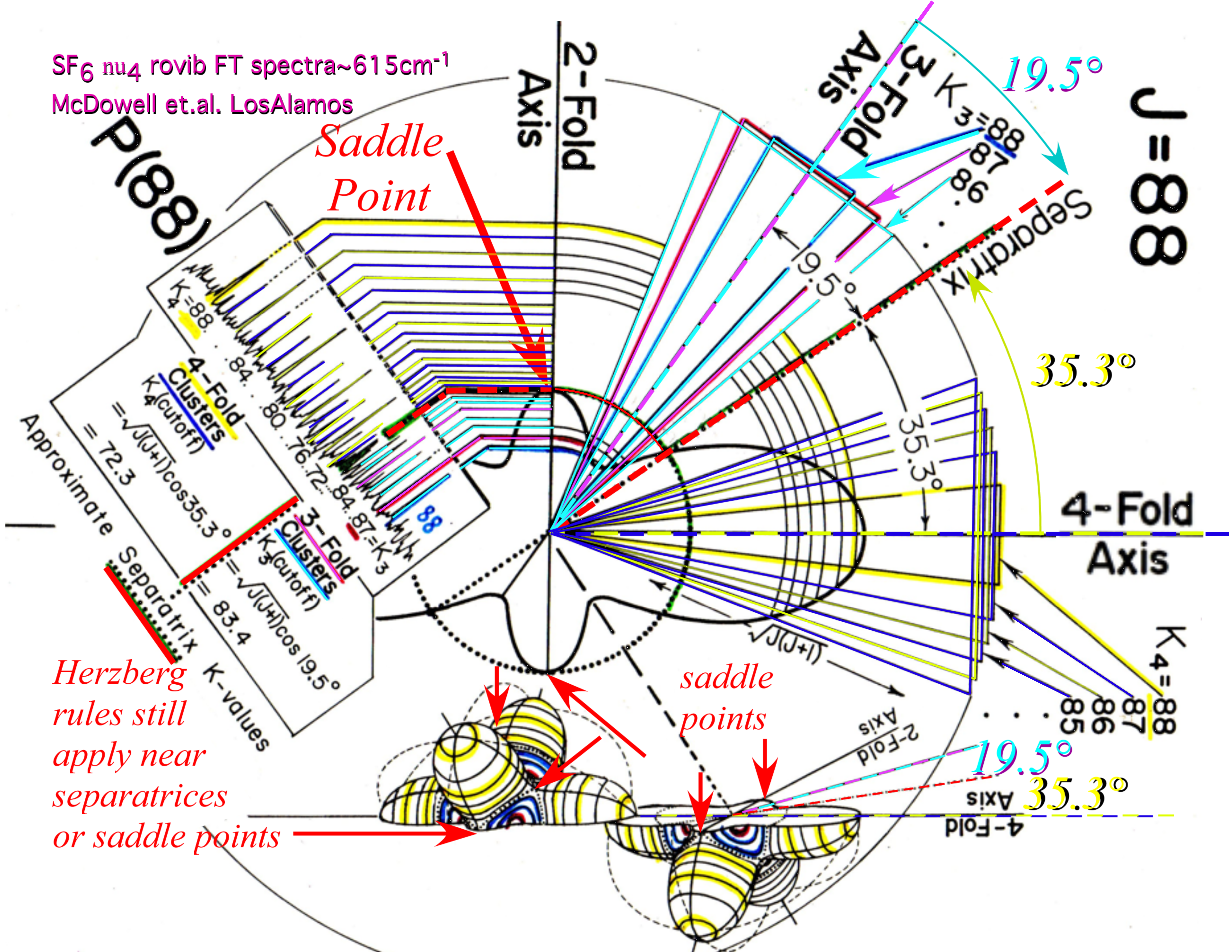


REES of CF_4 -$\upsilon_4/2\upsilon_3$ dyad
showing rare (J=57)-$1_2(C_2)\uparrow O$
24-level cluster on 5th REES

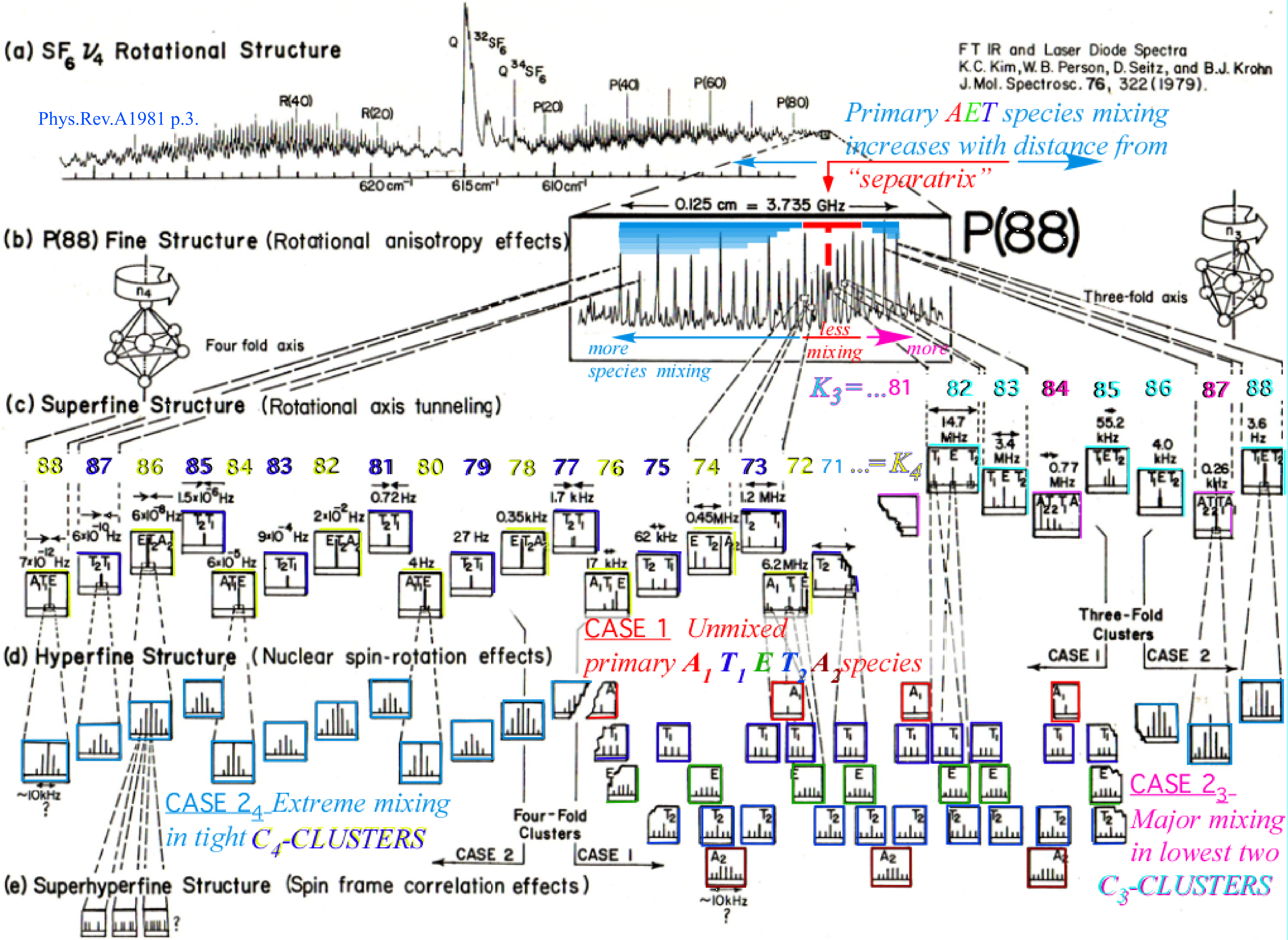
24-resonant
J-orbits
indicated by arrows



REES issues discussed in:
Int. J. Mol. Sci. 14,[714(2013)p.83]



SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
Saddle Point
2-Fold Axis
3-Fold Axis
19.5°
J=88
Separatrix
35.3°
4-Fold Axis
4-Fold Clusters
K4(cutoff) = √J(J+1)cos35.3° = 72.3
3-Fold Clusters
K3(cutoff) = √J(J+1)cos 19.5° = 83.4
Approximate Separatrix K-values
Herzberg rules still apply near separatrices or saddle points
saddle points
√J(J+1)
K4=88 87 86 85
K3=88 87 86


(a) SF6 ν4 Rotational Structure
Phys.Rev.A1981 p.3.
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).
Q 32SF6
Q 34SF6
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
Primary AET species mixing
increases with distance from
"separatrix"
0.125 cm = 3.735 GHz
P(88)
(b) P(88) Fine Structure (Rotational anisotropy effects)
Four fold axis
Three-fold axis
more
species mixing
less
mixing
more
K3 = ...81 82 83 84 85 86 87 88
(c) Superfine Structure (Rotational axis tunneling)
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ... = K4
CASE 1 Unmixed
primary A1 T1 E T2 A2 species
(d) Hyperfine Structure (Nuclear spin-rotation effects)
Three-Fold
Clusters
CASE 1
CASE 2
CASE 24 Extreme mixing
in tight C4-CLUSTERS
Four-Fold
Clusters
CASE 2
CASE 1
CASE 23-
Major mixing
in lowest two
C3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)
~10kHz
?