AMOP
reference links
on following page

2.14.18 class 10.0: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* D_2 of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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Algebra of geometric series. *Geometry of algebraic series*

Molecular $(2\ell+1)$-multiplet D_2-level splitting *Examples: $\ell=1, 2, 3,\ldots$*

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(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*

Completing diagonalization from new D_2 basis:

J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group$\supset$Sub-group correlation

AMOP reference links *(Updated list given on 2nd page 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

Frame Transformation Relations And Multipole Transitions In Symmetric Polyatomic Molecules - RMP-1978 (Alt Scanned version)
Rotational energy surfaces and high- J eigenvalue structure of polyatomic molecules - Harter - Patterson - 1984
Galloping waves and their relativistic properties - ajp-1985-Harter
Asymptotic eigensolutions of fourth and sixth rank octahedral tensor operators - Harter-Patterson-JMP-1979
Nuclear spin weights and gas phase spectral structure of 12C60 and 13C60 buckminsterfullerene -Harter-Reimer-Cpl-1992 - (Alt1, Alt2 Erratum)

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 scalar coupling zeta coefficients and spectroscopic band shapes of buckminsterfullerene - Weeks-Harter-CPL-1991 (Alt scan)
Fullerene symmetry reduction and rotational level fine structure/ the Buckyball isotopomer 12C 13C59 - jcp-Reimer-Harter-1997 (HiRez)
Molecular Eigensolution Symmetry Analysis and Fine Structure - IJMS-harter-mitchell-2013

Rotation–vibration spectra of icosahedral molecules.

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

QTCA Unit 10 Ch 30 - 2013
AMOP Ch 32 Molecular Symmetry and Dynamics - 2019
AMOP Ch 0 Space-Time Symmetry - 2019

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)

Rovibrational Spectral Fine Structure Of Icosahedral Molecules - Cpl 1986 (Alt Scan)
Gas Phase Level Structure of C60 Buckyball and Derivatives Exhibiting Broken Icosahedral Symmetry - reimer-diss-1996
Resonance and Revivals in Quantum Rotors - Comparing Half-integer Spin and Integer Spin - Alva-ISMS-Ohio2013-R777 (Talk)
Quantum Revivals of Morse Oscillators and Farey-Ford Geometry - Li-Harter-cpl-2013
Wave Node Dynamics and Revival Symmetry in Quantum Rotors - harter - jms - 2001

**In development - a Web based AMOP Reference page, with more options/control over display*

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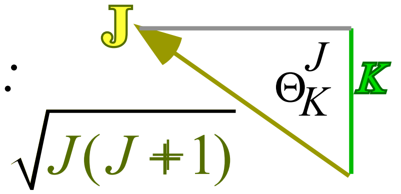
Review of angular momentum cone geometry

$$\mathbf{J}^2 \left| \begin{matrix} J \\ K \end{matrix} \right\rangle = J(J+1) \left| \begin{matrix} J \\ K \end{matrix} \right\rangle$$

$$\mathbf{J}_z \left| \begin{matrix} J \\ K \end{matrix} \right\rangle = K \left| \begin{matrix} J \\ K \end{matrix} \right\rangle$$

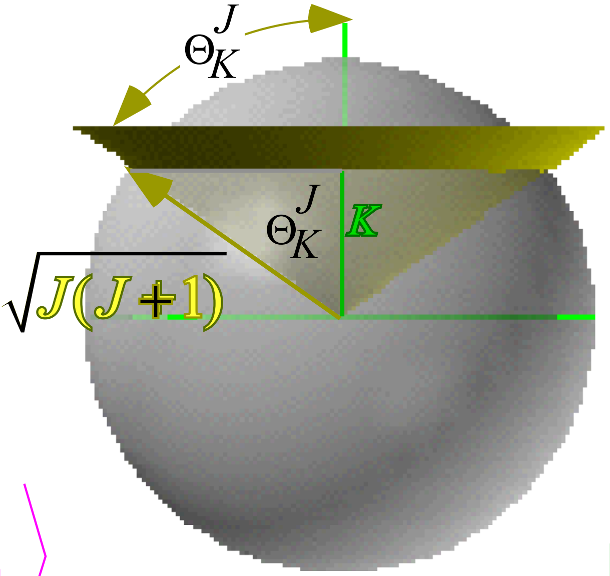
Interpreted "Literally" is:



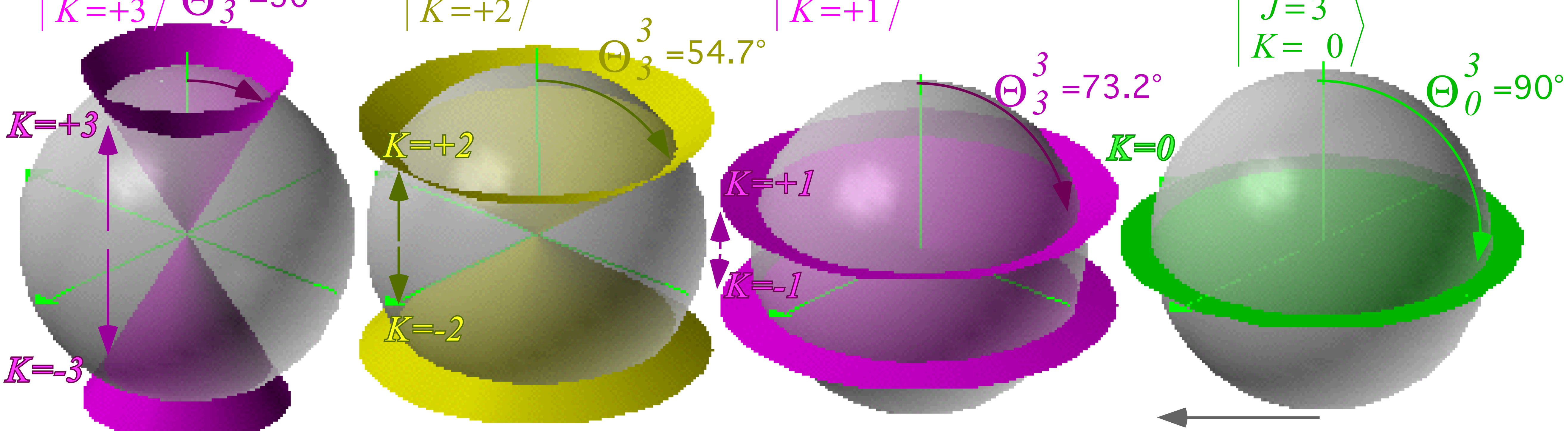
~J+1/2

Quantum Angular Cone Uncertainty Angles

$$\cos\Theta^J_K = \frac{K}{\sqrt{J(J+1)}}$$



$\left| \begin{matrix} J=3 \\ K=+3 \end{matrix} \right\rangle$ $\left| \begin{matrix} J=3 \\ K=+2 \end{matrix} \right\rangle$ $\left| \begin{matrix} J=3 \\ K=+1 \end{matrix} \right\rangle$ $\left| \begin{matrix} J=3 \\ K=\ \ 0 \end{matrix} \right\rangle$



$\left| \begin{matrix} J=3 \\ K=-3 \end{matrix} \right\rangle$ $\left| \begin{matrix} J=3 \\ K=-2 \end{matrix} \right\rangle$ $\left| \begin{matrix} J=3 \\ K=-1 \end{matrix} \right\rangle$

$\sqrt{J(J+1)}$ *=√(3)(4)=3.461*
for J=3

Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions

Plot Hamiltonian $\mathbf{H}=B\mathbf{J}^2+(C-B)\mathbf{J}_z{}^2$ radially as $H(\Theta)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta$

$$H(\Theta^J_K)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta^J_K$$

$$=BJ(J+1)+(C-B)K^2$$

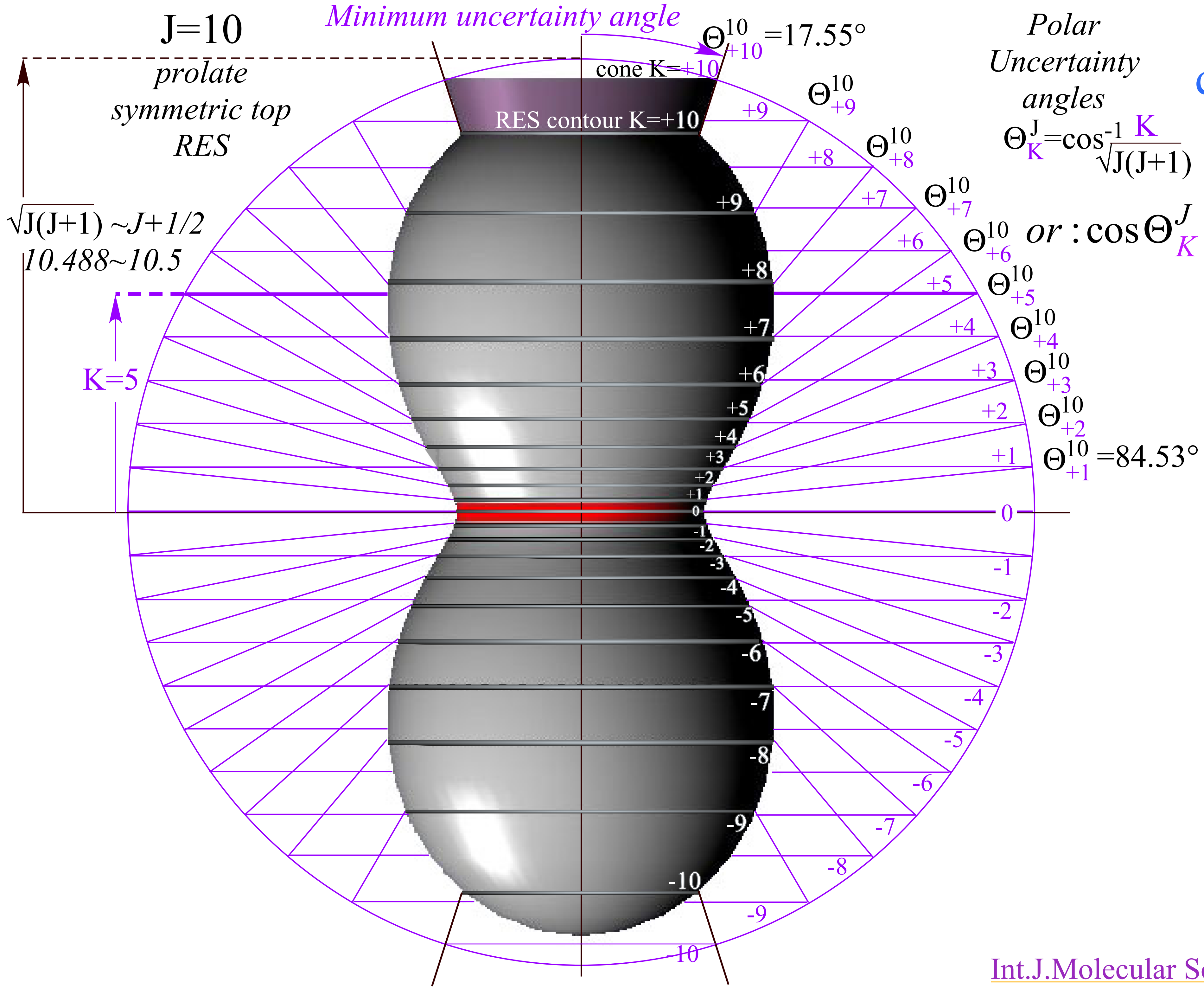
$$\boxed{\begin{aligned}\text{where}: \mathbf{J}_z &= |\mathbf{J}|\cos\Theta\\ &=\sqrt{J(J+1)}\cos\Theta\end{aligned}}$$

$\left|{j \atop m,n}\right\rangle$

LAB $m=M$ *BOD* $n=K$

Conventional notation:

$$n=K=\mathbf{J}_z=\sqrt{J(J+1)}\cos\Theta$$

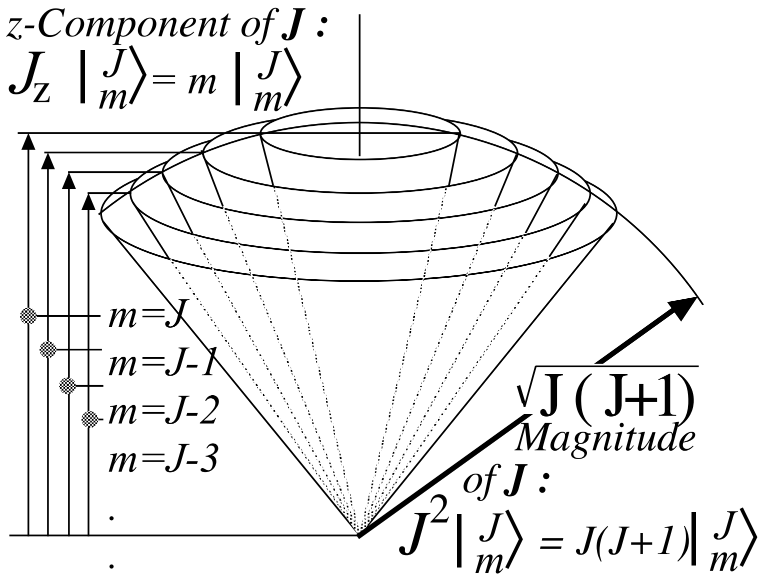


Polar Uncertainty angles

$$\Theta^J_K=\cos^{-1}\frac{K}{\sqrt{J(J+1)}}$$

$$or: \cos\Theta^J_K=\frac{K}{\sqrt{J(J+1)}}$$

(Here* *J*-cone *uncertainty* gives *exact* quantum eigenvalues!)



**not exact for lower symmetry*

Int.J.Molecular Science 14.(2013) Fig.1 p. 730

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RES and Multipole $\mathbf{T}_q^k$ *tensor expansions*

Momentum 101 $p = m\,v$ (*linear*) $J = L = I\,\omega$ (*rotation*) BANG!

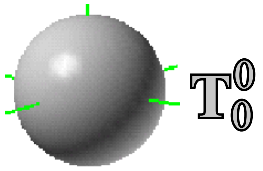
Energy 101 $E = \frac{1}{2} m\,v^2 = p^2/2m$ $E = \frac{1}{2} I\,\omega^2 = J^2/2I$ $BUCK$

Simple Rigid Rotor Hamiltonian... (Hamiltonian H=E is $BUCK$ energy in terms of BANG! momentum)

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + \cdots$$

...and its multi-pole expansion...

$$\left(\frac{A+B+C}{3}\right)\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right)$$



Spherical Top

(A=B=C)

$\mathbf{H} = B\,\mathbf{J}^2$

$$\mathbf{T}_0^{(0)} = \mathbf{J}^2$$

(Derivation in preceding Class 9)

RES and Multipole $\mathbf{T}_q^k$ tensor expansions

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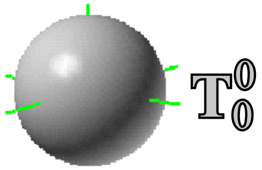
...and its multi-pole expansion...

$$\left(\frac{A+B+C}{3}\right)\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + \left(\frac{2C-A-B}{6}\right)\left(2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2\right)$$



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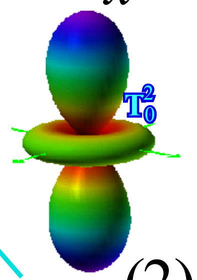

$$2\mathbf{T}_0^{(2)}$$

Symmetric Top

(A=B≠C)

$\mathbf{H} = B\,\mathbf{J}^2 + (C - B)(2/3)\mathbf{T}_0^{(2)}$

(Derivation in preceding Class 9)

RES and Multipole $\mathbf{T}_q^k$ *tensor expansions*

Momentum 101 $p = m\,v$ (*linear*) $J = L = I\,\omega$ (*rotation*) BANG!

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Simple Rigid Rotor Hamiltonian... (Hamiltonian H=E is energy in terms of momentum)

$BUCK$ BANG!

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + \cdots$$

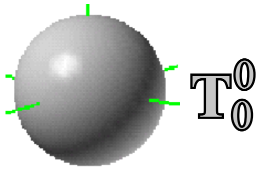
...and its multi-pole expansion...

$$\frac{(A+B+C)}{3}\left(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2\right) + \frac{(2C-A-B)}{6}\left(2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2\right) + \frac{(A-B)}{2}\left(\mathbf{J}_x^2-\mathbf{J}_y^2\right)$$

Spherical Top

(A=B=C)

$\mathbf{H} = B\,\mathbf{J}^2$



$$\mathbf{T}_0^{(0)} = \mathbf{J}^2$$

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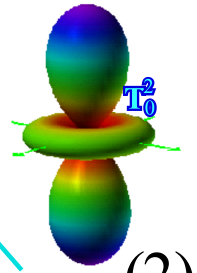
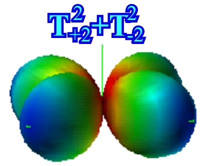


$$2\mathbf{T}_0^{(2)}$$



$$\sqrt{\frac{2}{3}}\left(\mathbf{T}_2^{(2)} + \mathbf{T}_{-2}^{(2)}\right)$$

Asymmetric Top

(A≠B≠C)

$$\mathbf{H} = B\,\mathbf{J}^2 + (2C - A - B)/3\ \mathbf{T}_0^{(2)} + (A - B)/\sqrt{6}\left(\mathbf{T}_2^{(2)} + \mathbf{T}_{-2}^{(2)}\right)$$

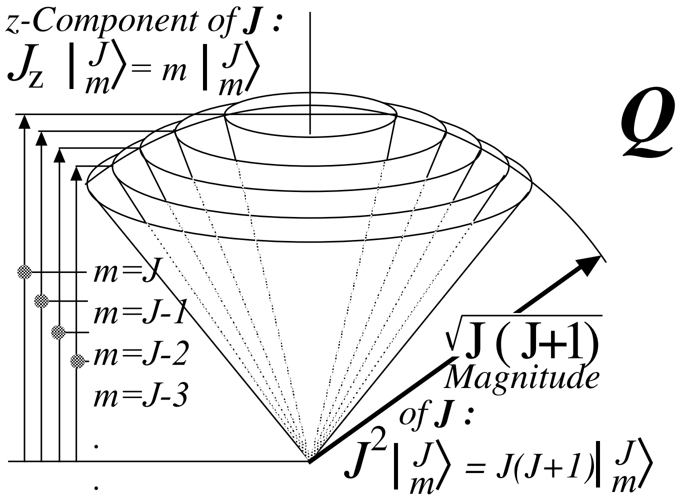
(Derivation in preceding Class 9)

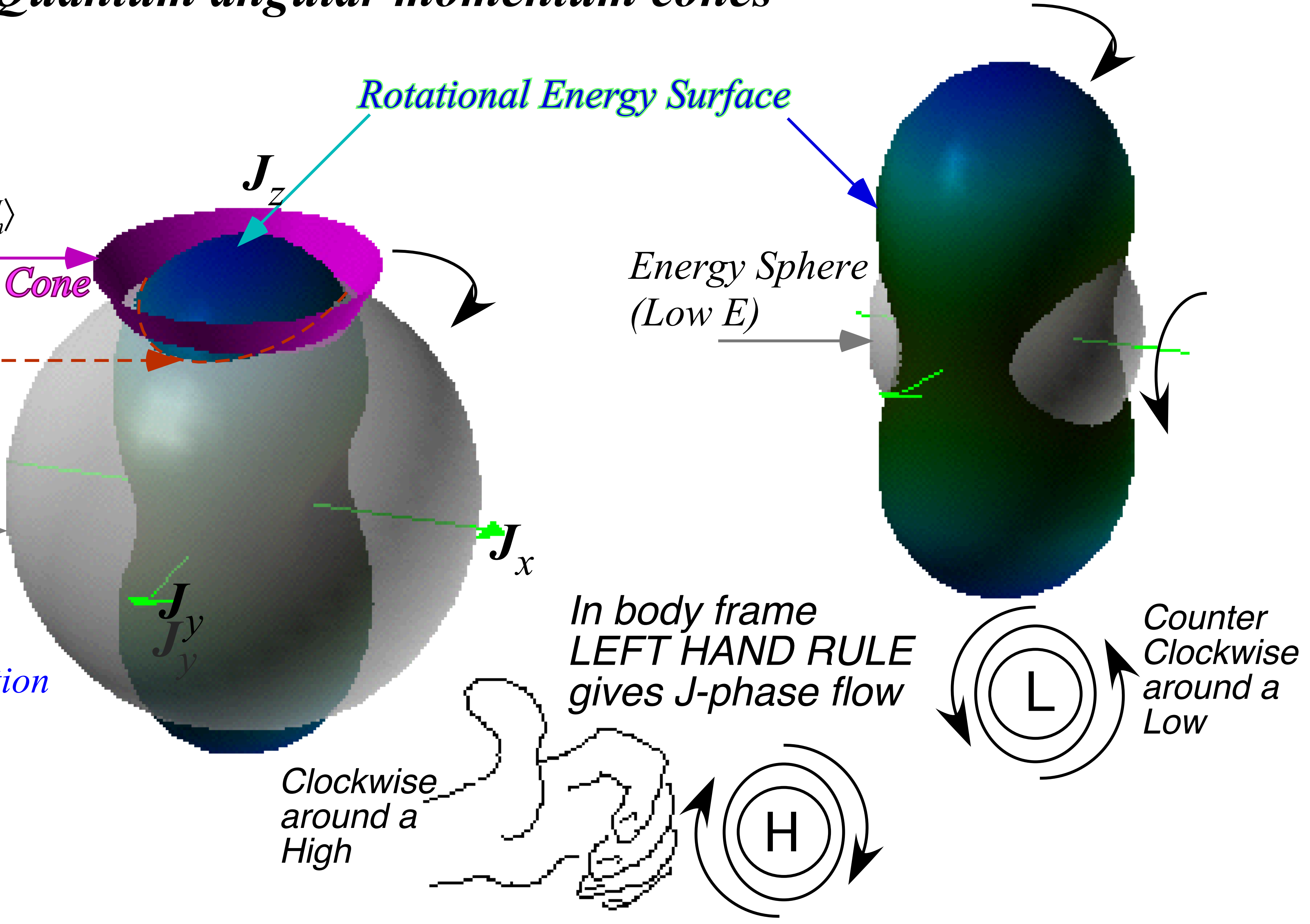
RES and Multipole $\mathbf{T}_q^k$ *tensor expansions*

J-Phase Paths *(Intersection(s) of RE Surface and Energy Sphere)*

and

Quantum angular momentum cones





Angular Momentum Cone

J-Phase Path

(High E)

Energy Sphere
(High E)

RE Surface
Energy plotted radially
vs.
BOD frame **J***-vector direction*
*for fixed magnitude |***J***|*

In body frame
LEFT HAND RULE
gives J-phase flow

Counter
Clockwise
around a
Low

Clockwise
around a
High

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$$\mathbf{H}_{symmetric\ top} = B\mathbf{J}_{\bar{X}}^2 + B\mathbf{J}_{\bar{Y}}^2 + B\mathbf{J}_{\bar{Z}}^2 + (A-B)\mathbf{J}_{\bar{Z}}^2 = B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2$$

Kinetic energy inertial coefficients:

$$B = \frac{1}{2I_{\bar{X}}} = C = \frac{1}{2I_{\bar{Y}}}, A = \frac{1}{2I_{\bar{Z}}}$$

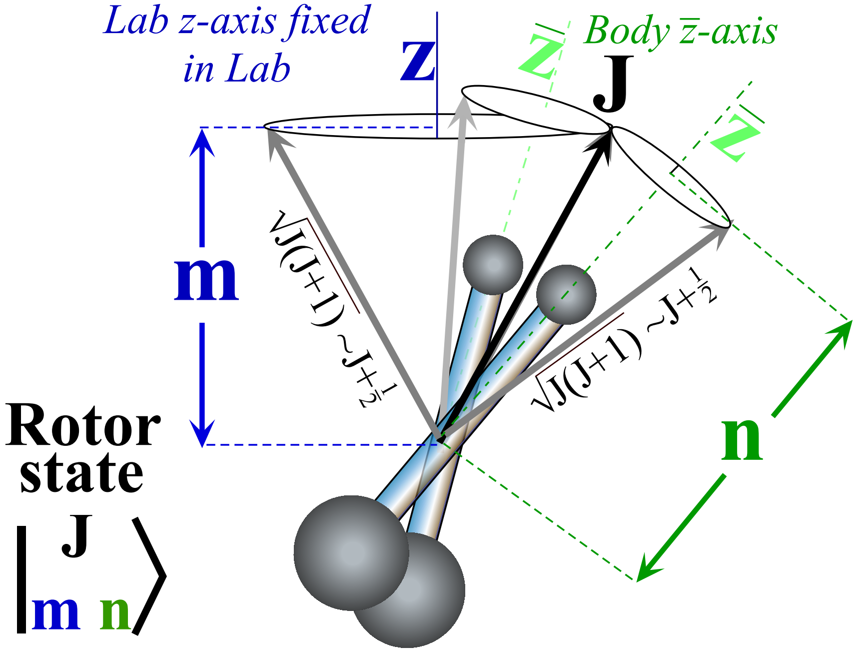
Eigensolution equations:

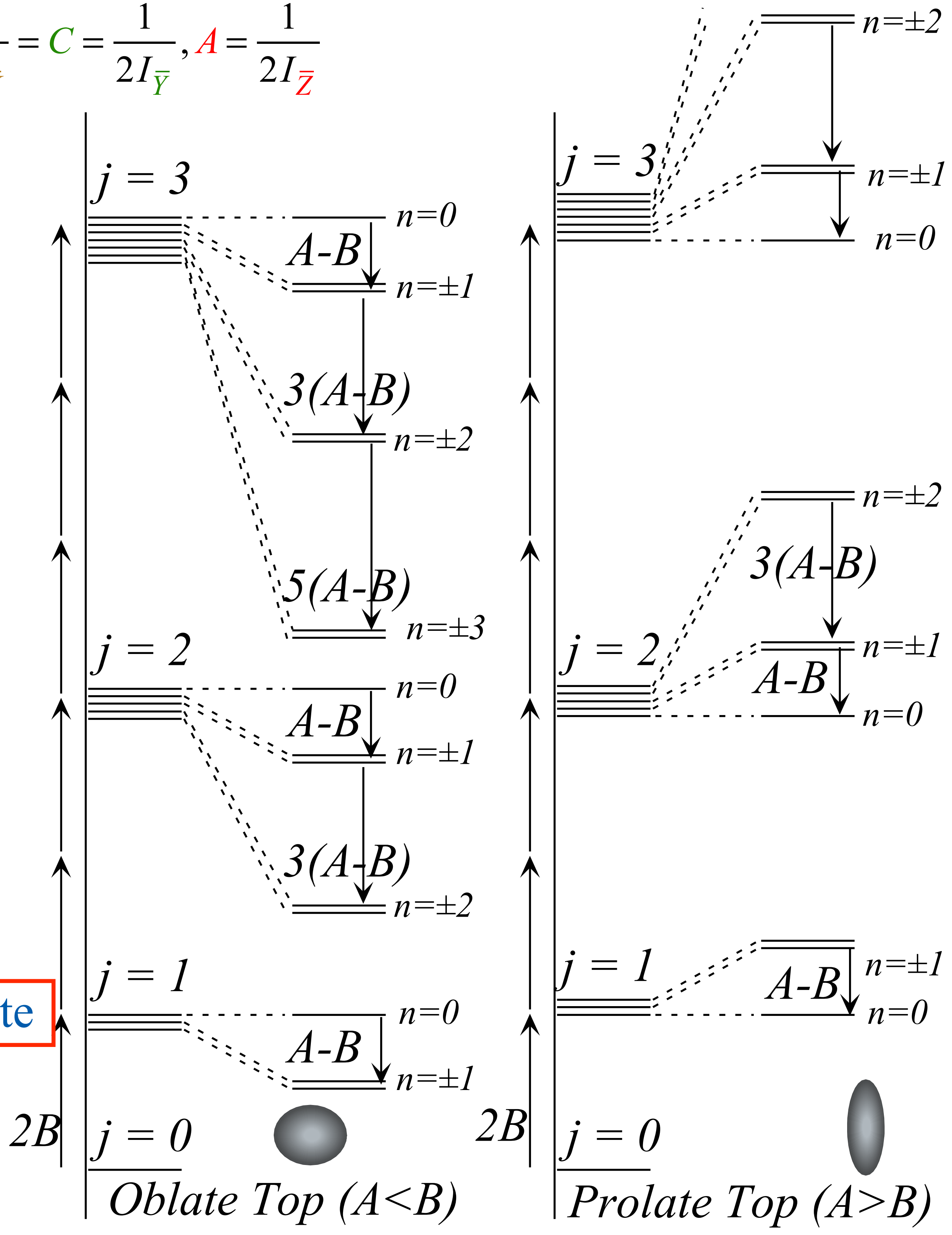
$$\mathbf{H}_{symmetric\ top}\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

$$= B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

$$= \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

Mock-Mach-Multiplicity
is *(2j+1)*^{2} for each *j*





Even *n*=*0* levels are *2j+1*-fold degenerate

If *n* is non-zero the degeneracy is *4j+2*.

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

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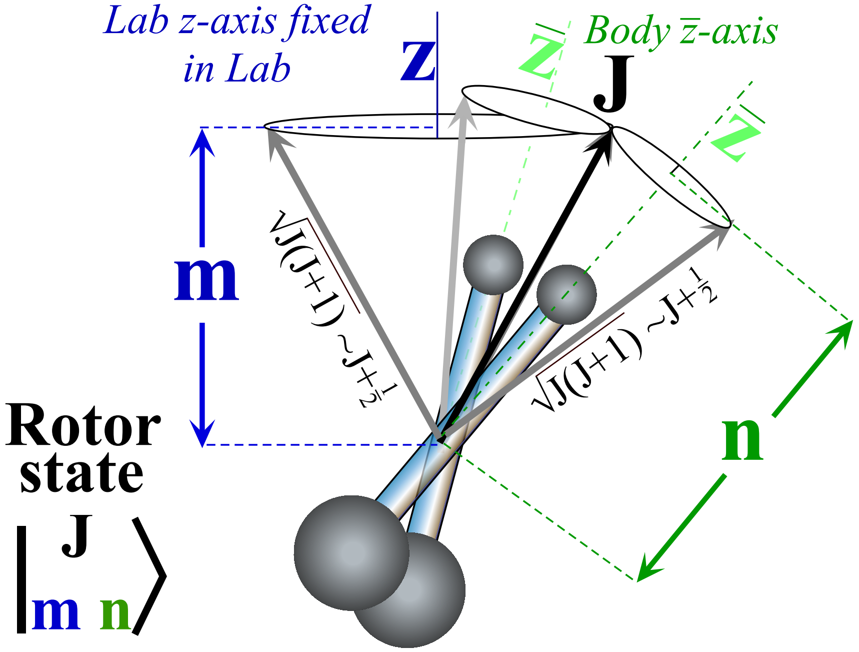

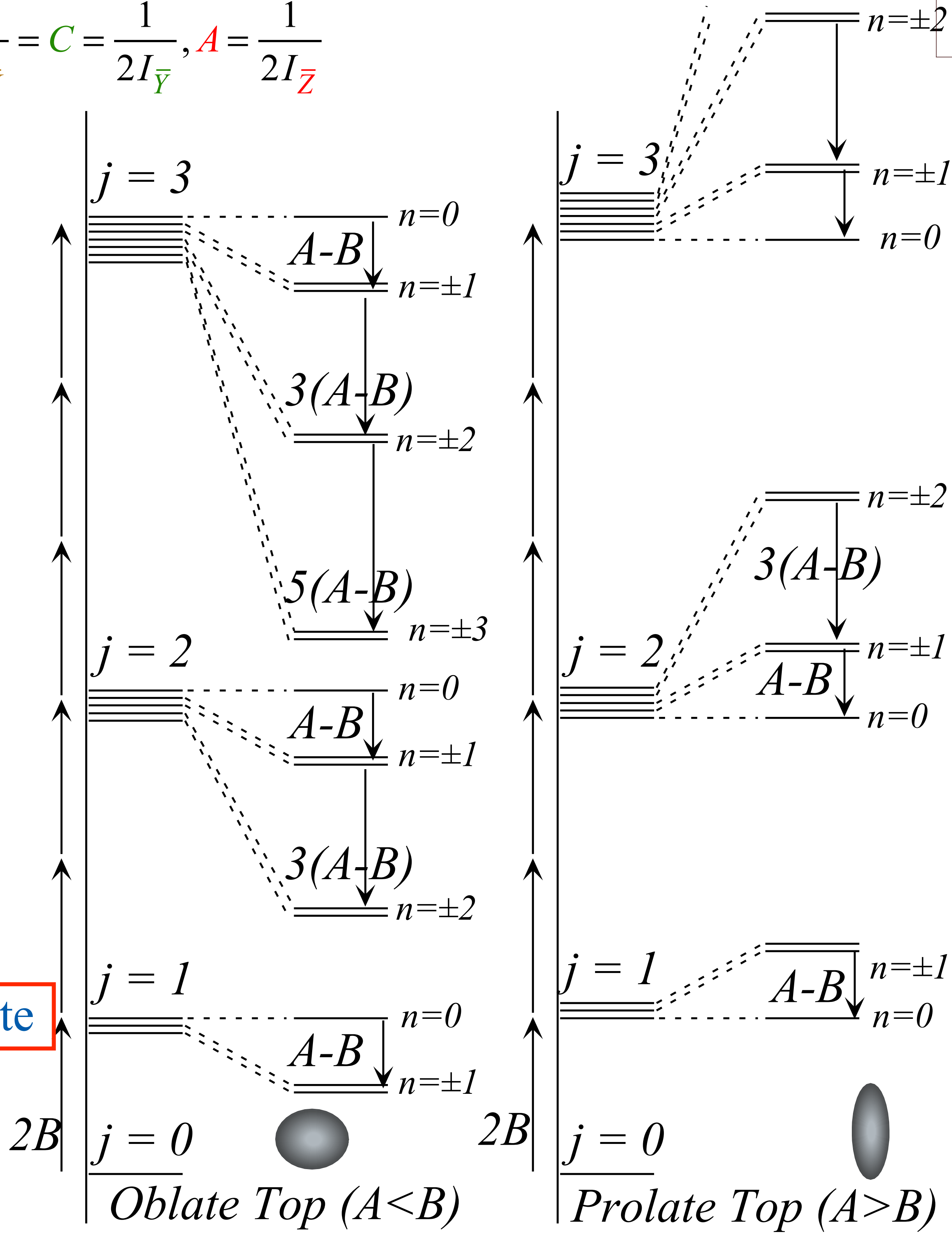

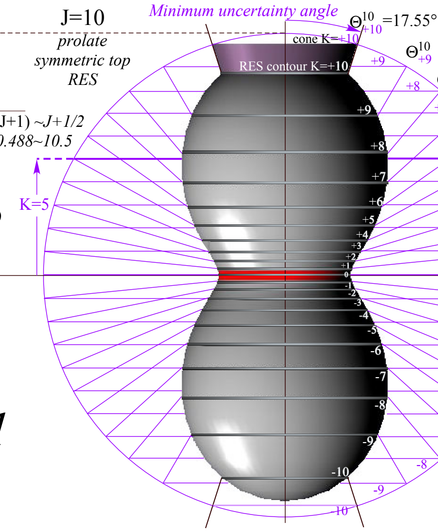

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Kinetic energy inertial coefficients:

$$B = \frac{1}{2I_{\bar{X}}} = C = \frac{1}{2I_{\bar{Y}}},\ A = \frac{1}{2I_{\bar{Z}}} \rightarrow \infty$$

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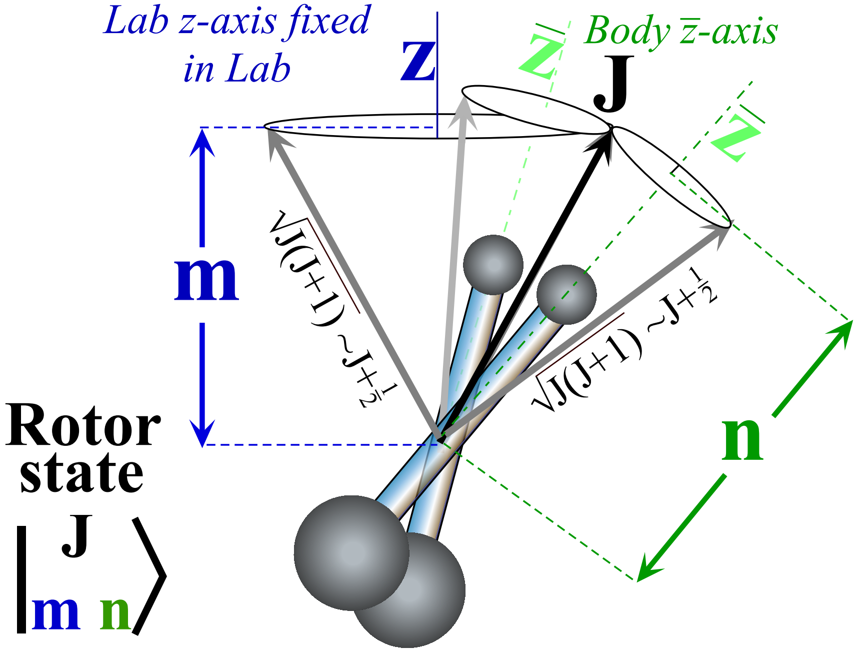

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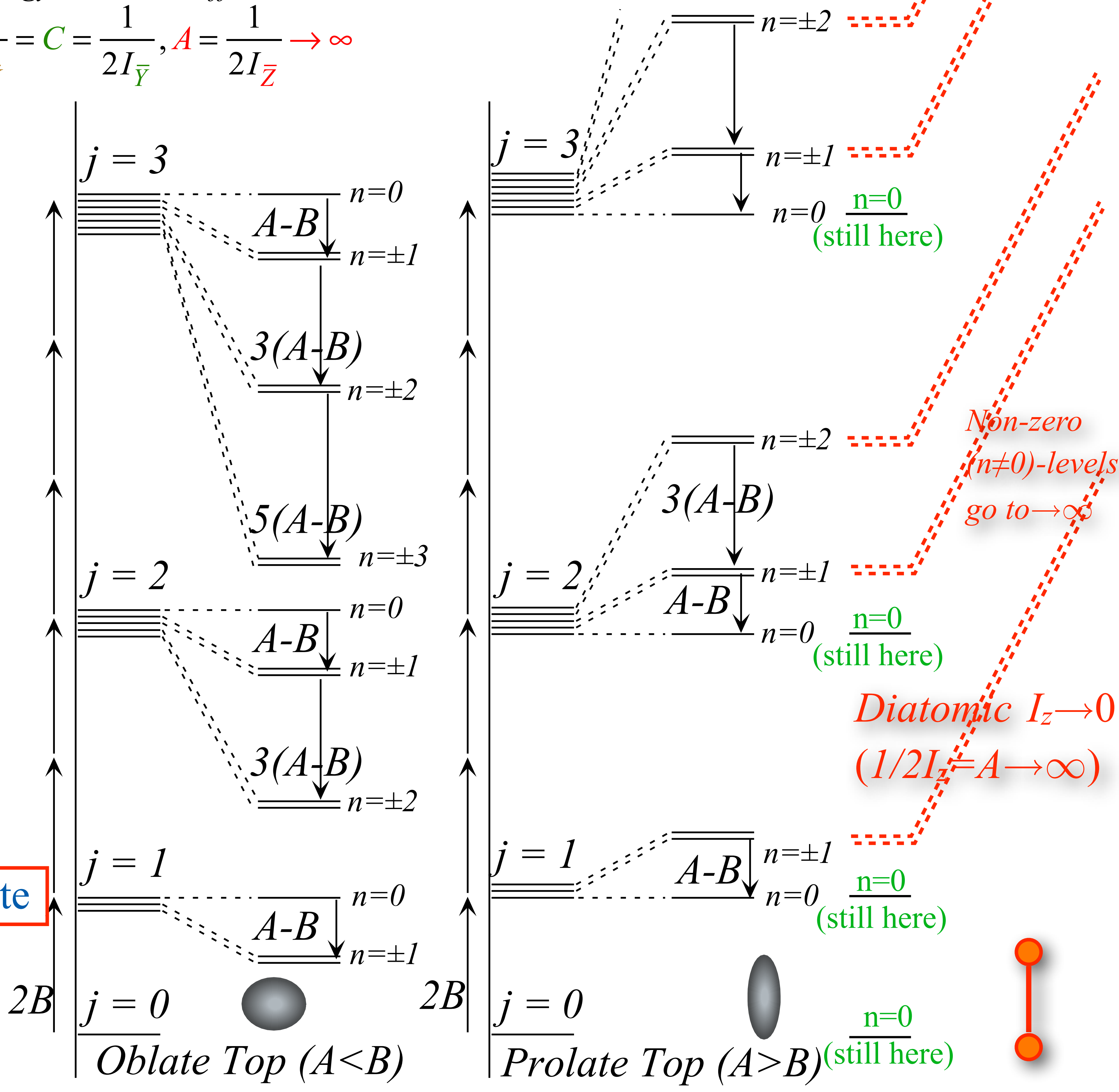

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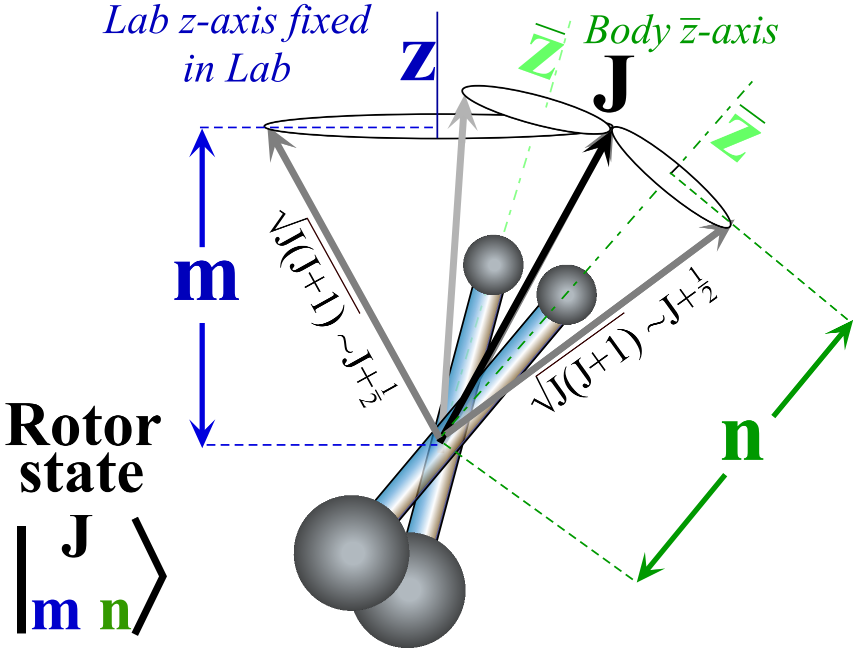
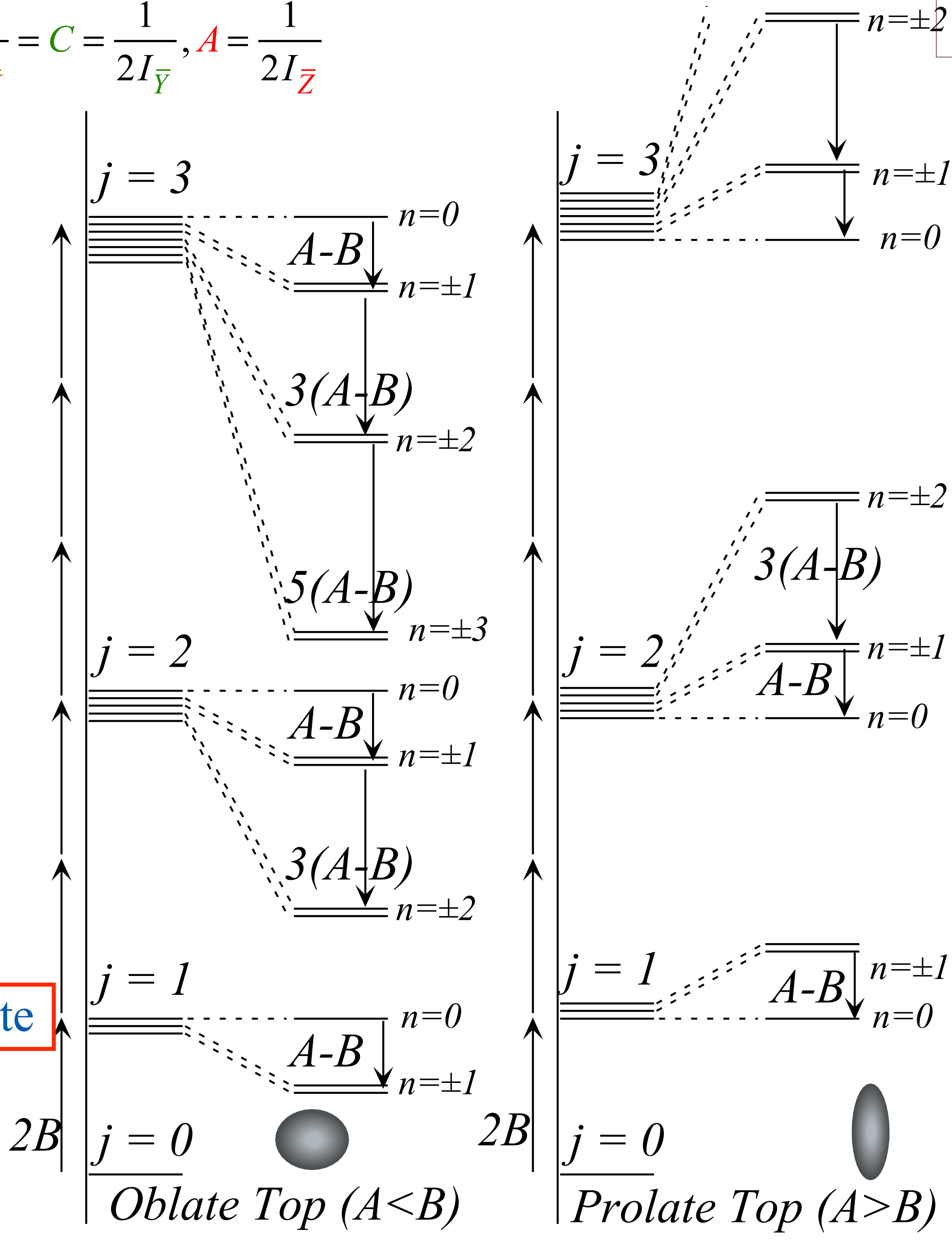
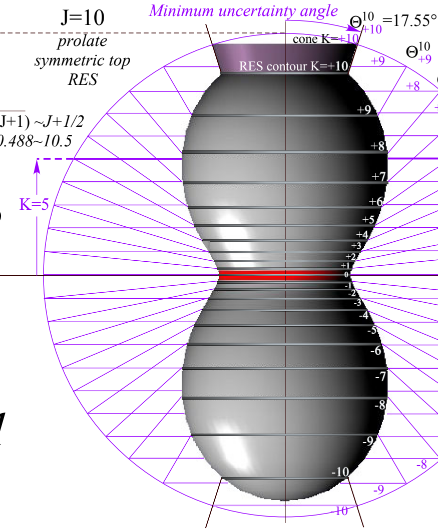
Mock-Mach-Multiplicity
is $(2j+1)^2$ for each *j*



Even n=0 levels are 2*j*+1-fold degenerate

If n is non-zero the degeneracy is 4*j*+2.





QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

Energy levels and RES of symmetric rotors: prolate vs. oblate cases

$$\mathbf{H}_{symmetric\ top} = B\mathbf{J}_{\bar{X}}^2 + B\mathbf{J}_{\bar{Y}}^2 + B\mathbf{J}_{\bar{Z}}^2 + (A-B)\mathbf{J}_{\bar{Z}}^2 = B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2$$

Kinetic energy inertial coefficients:

$$B = \frac{1}{2I_{\bar{X}}} = C = \frac{1}{2I_{\bar{Y}}},\ A = \frac{1}{2I_{\bar{Z}}}$$

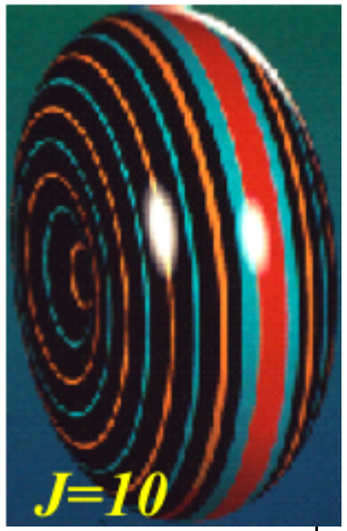
Eigensolution equations:

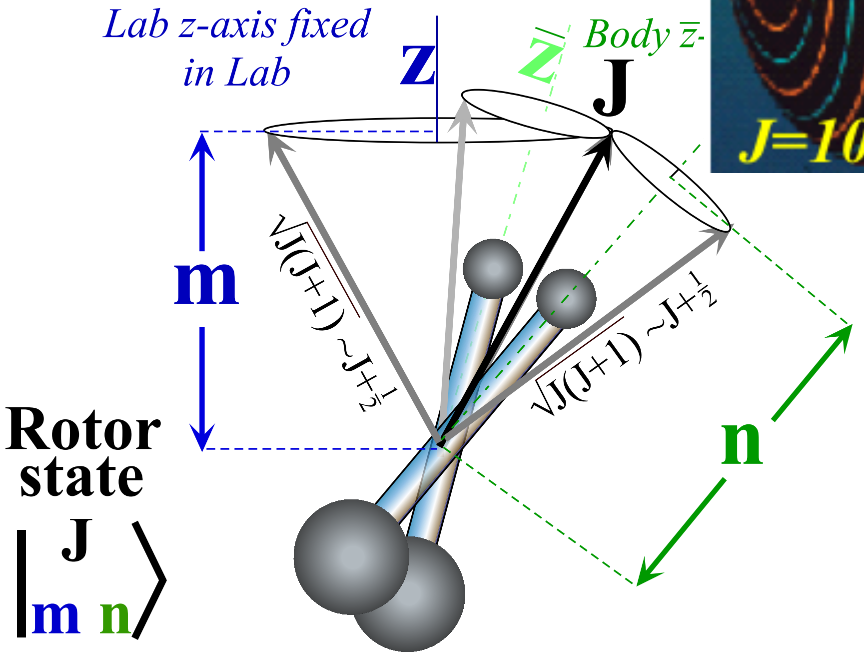
$$\mathbf{H}_{symmetric\ top}\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

$$= B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

$$= \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

Mock-Mach-Multiplicity
is $(2j+1)^2$ for each j





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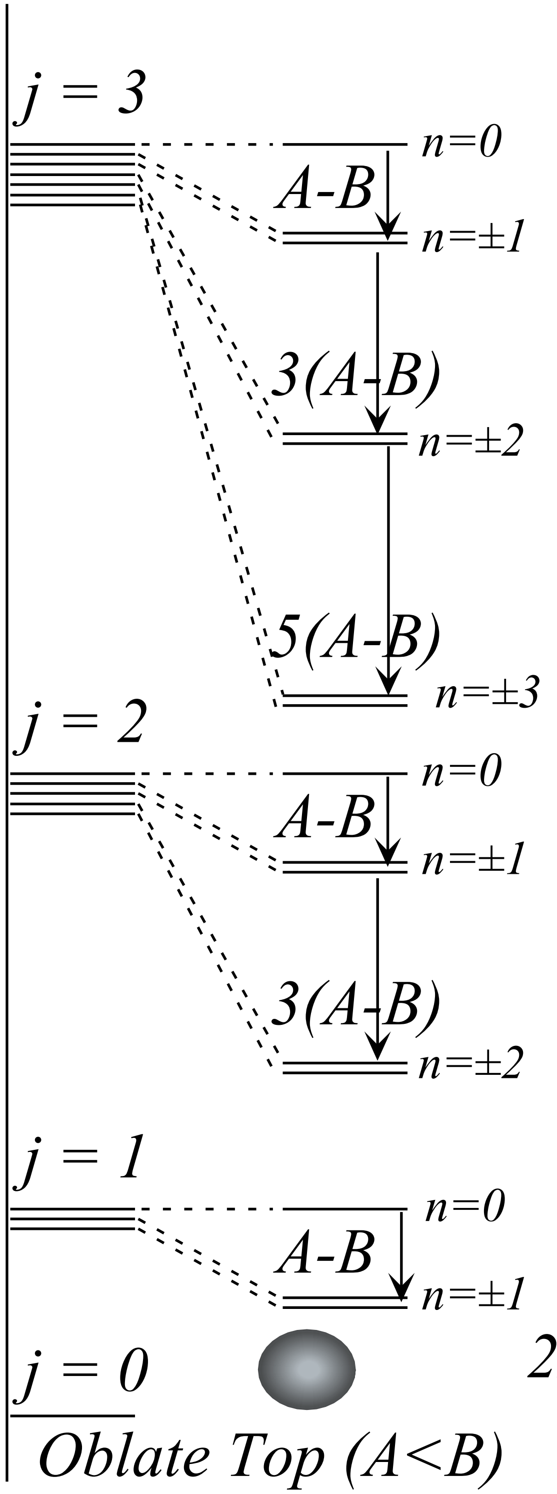

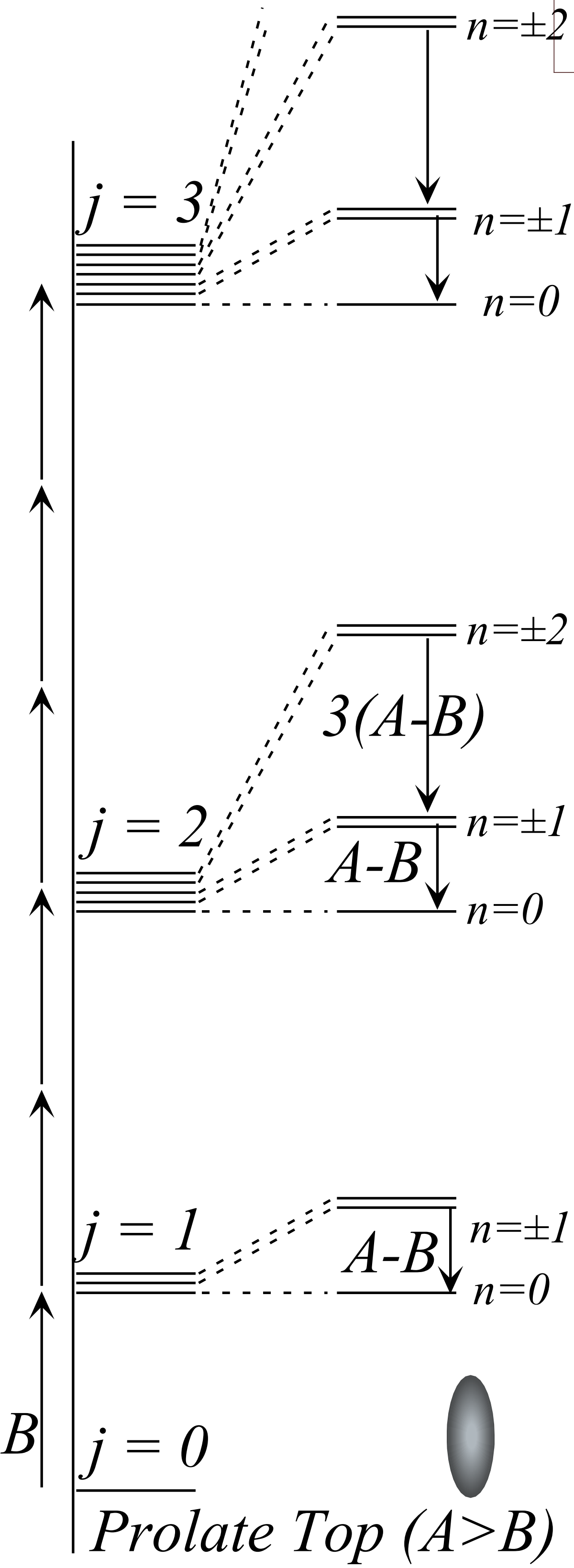

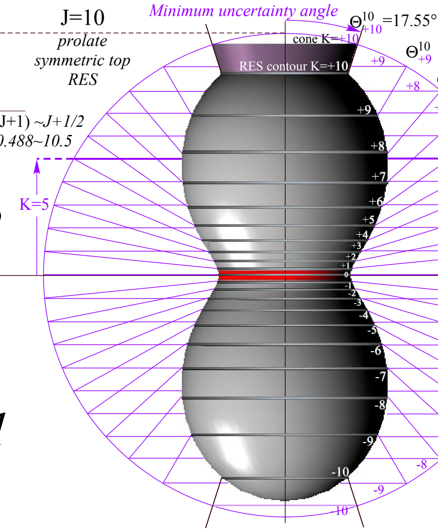

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* D_2 of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Review 1. *Review of angular momentum cone geometry*

Review 2. *Review of Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions*

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RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 symmetry labels)

Asymmetric rotor is not Unsymmetric rotor

Polygonal algebra & geometry of $U(2)\supset C_N$ character spectral function

Algebra of geometric series. *Geometry of algebraic series*

Molecular (2ℓ+1)-multiplet D_2-level splitting *Examples: ℓ=1, 2, 3,…*

j,m,n formulas for momentum operator matrix elements:Hamiltonian matrix for asymmetric rotor

(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*

Completing diagonalization from new D_2 basis:

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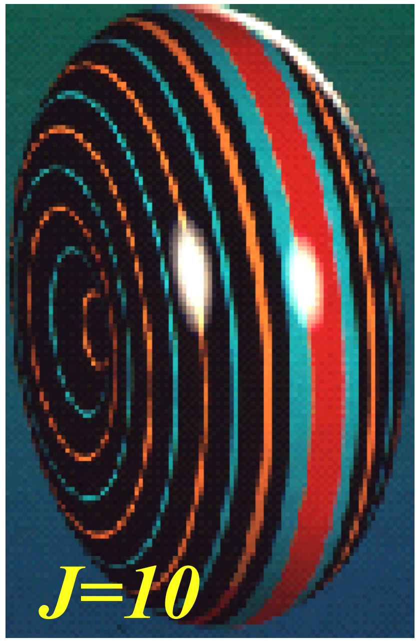
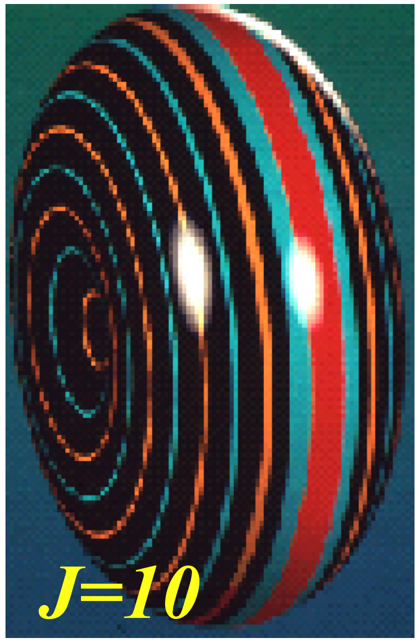
Examples of Group⊃Sub-group correlation

RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 symmetry labels)

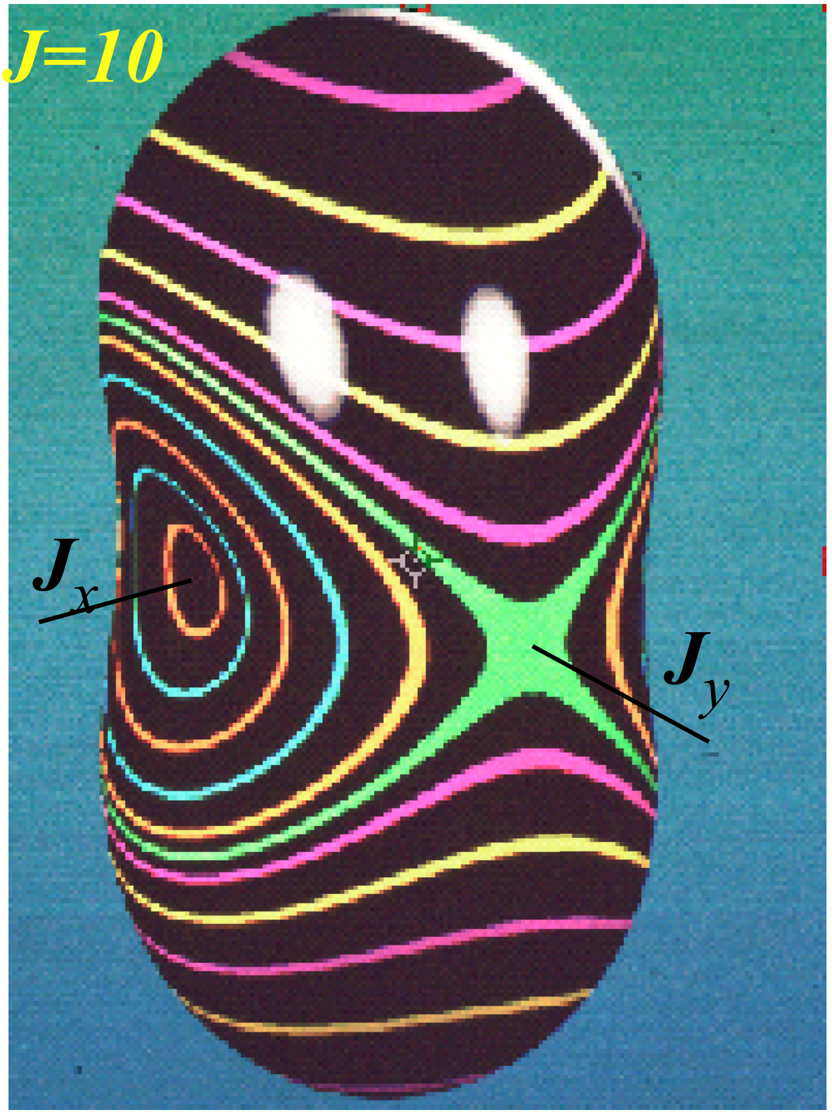


after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 symmetry labels)



Asymmetric Top Eigensolutions
Related to RE Surface
and semi-classical J-phase paths



after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

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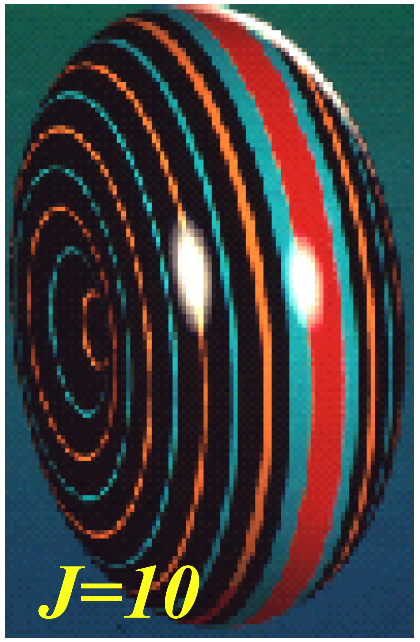

Asymmetric Top Eigensolutions
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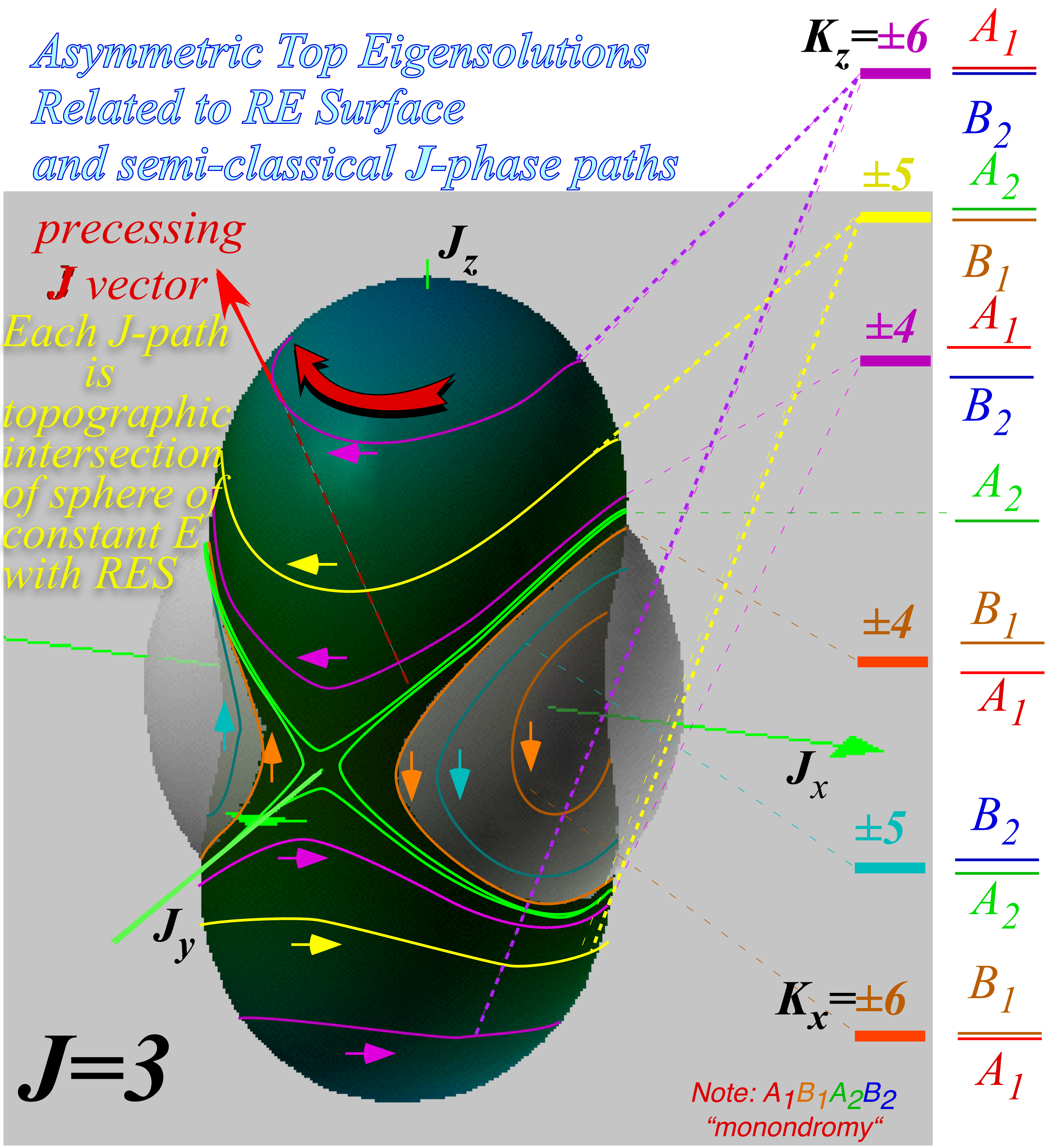

Each J-path is topographic intersection of sphere of constant E with RES

Note: $A_1B_1A_2B_2$ "monondromy"

after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* *D*₂ of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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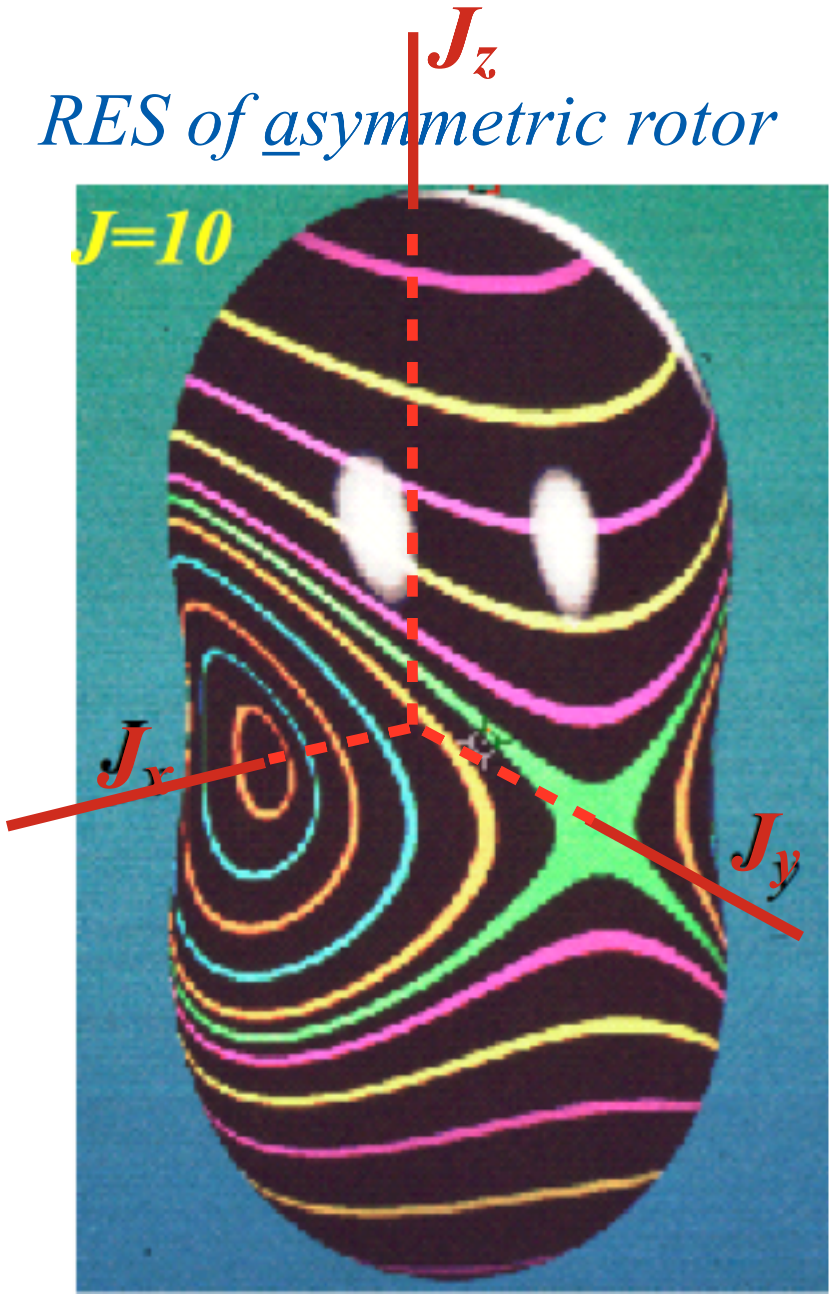
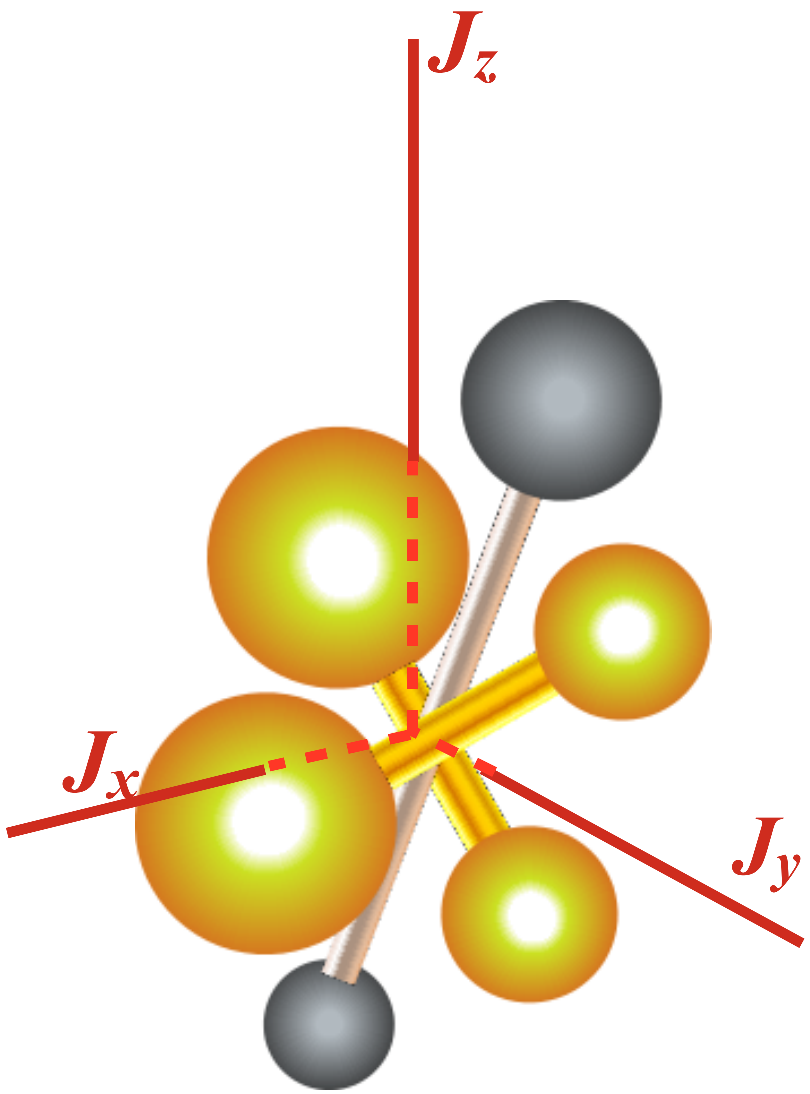
Asymmetric rotor is not Unsymmetric rotor

Even an ugly rigid body has inertial tensor ▌ with *at least* D_2 symmetry…

…*in* ▌ Principal Axis BODY frame *(eigenvectors of* ▌*)*

RES of asymmetric rotor



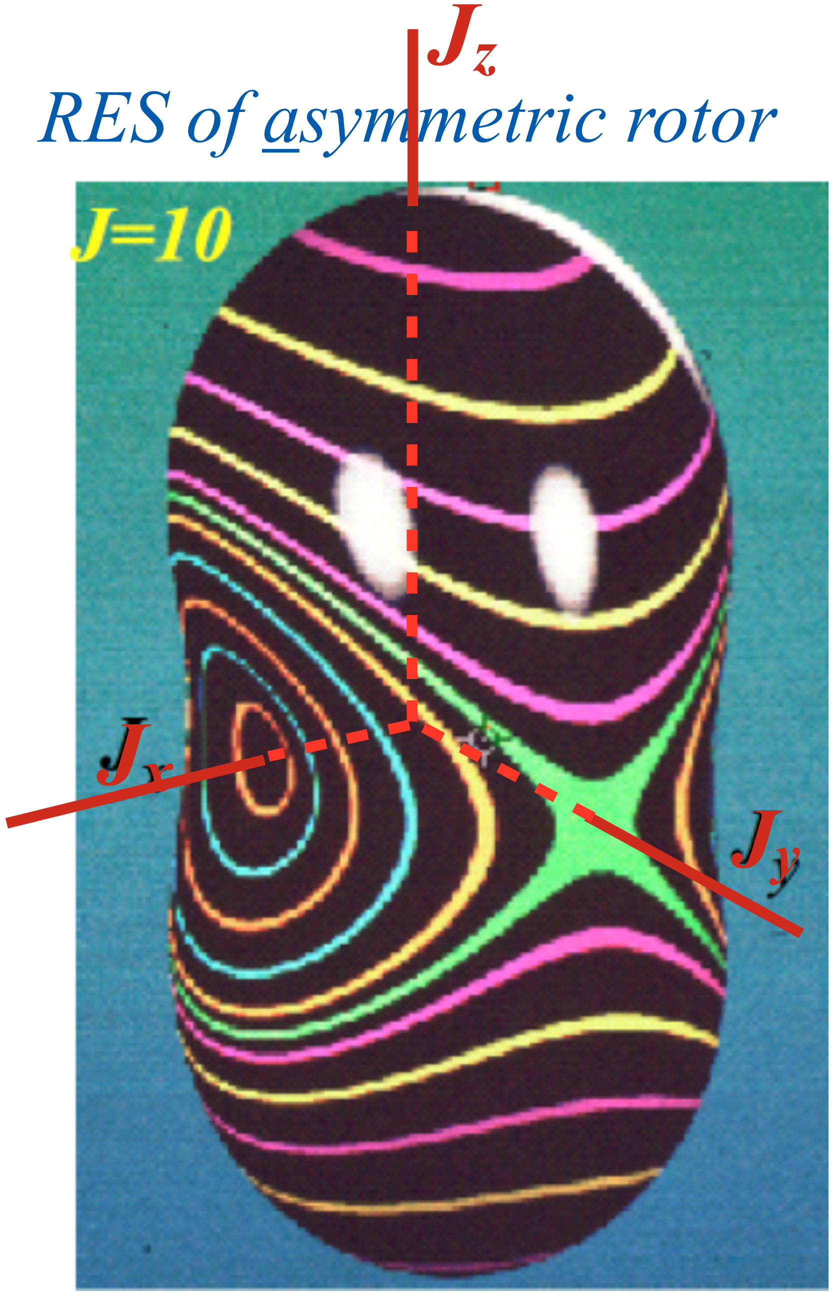


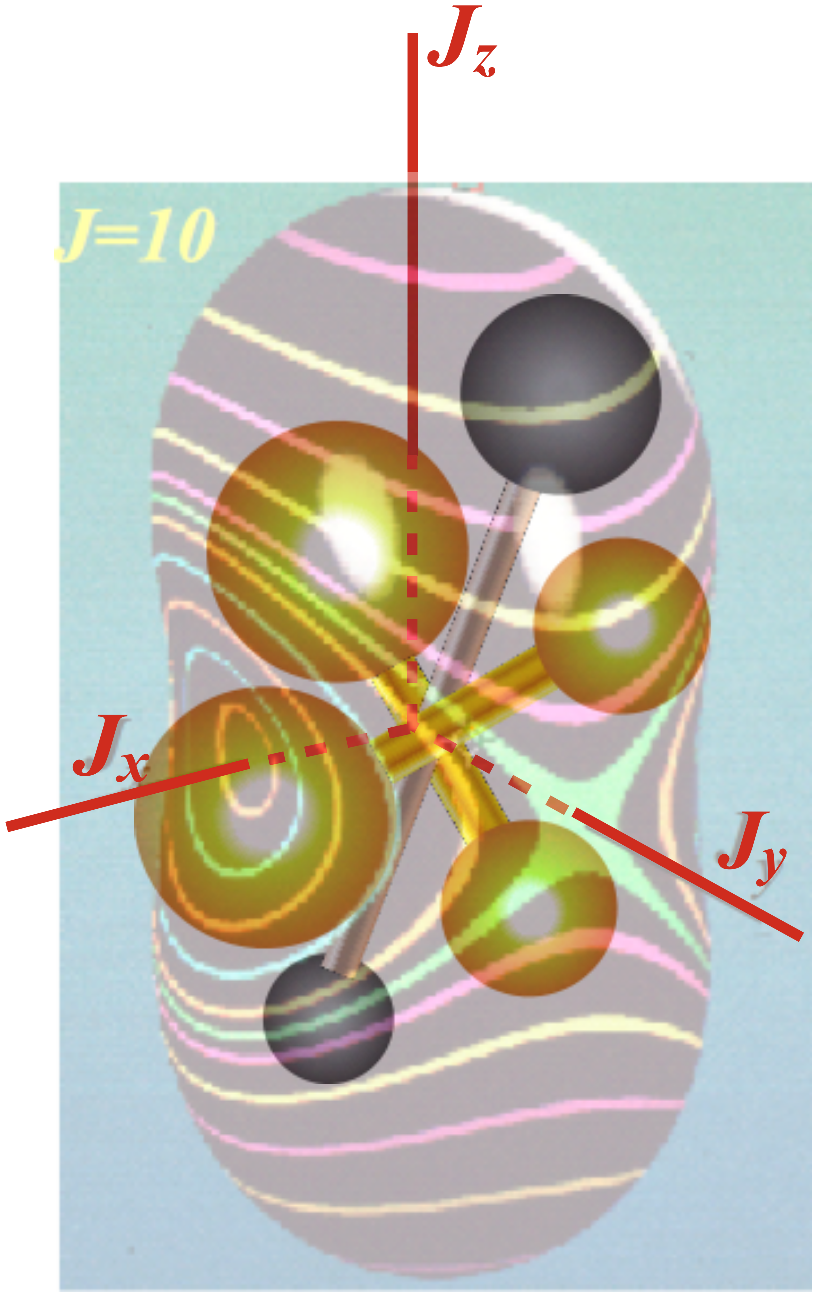
Asymmetric rotor is not Unsymmetric rotor

Even an ugly rigid body has inertial tensor $\mathbf{I}$ with *at least* D_2 symmetry…

…in $\mathbf{I}$ Principal Axis BODY frame *(eigenvectors of* $\mathbf{I}$*)*

RES of asymmetric rotor





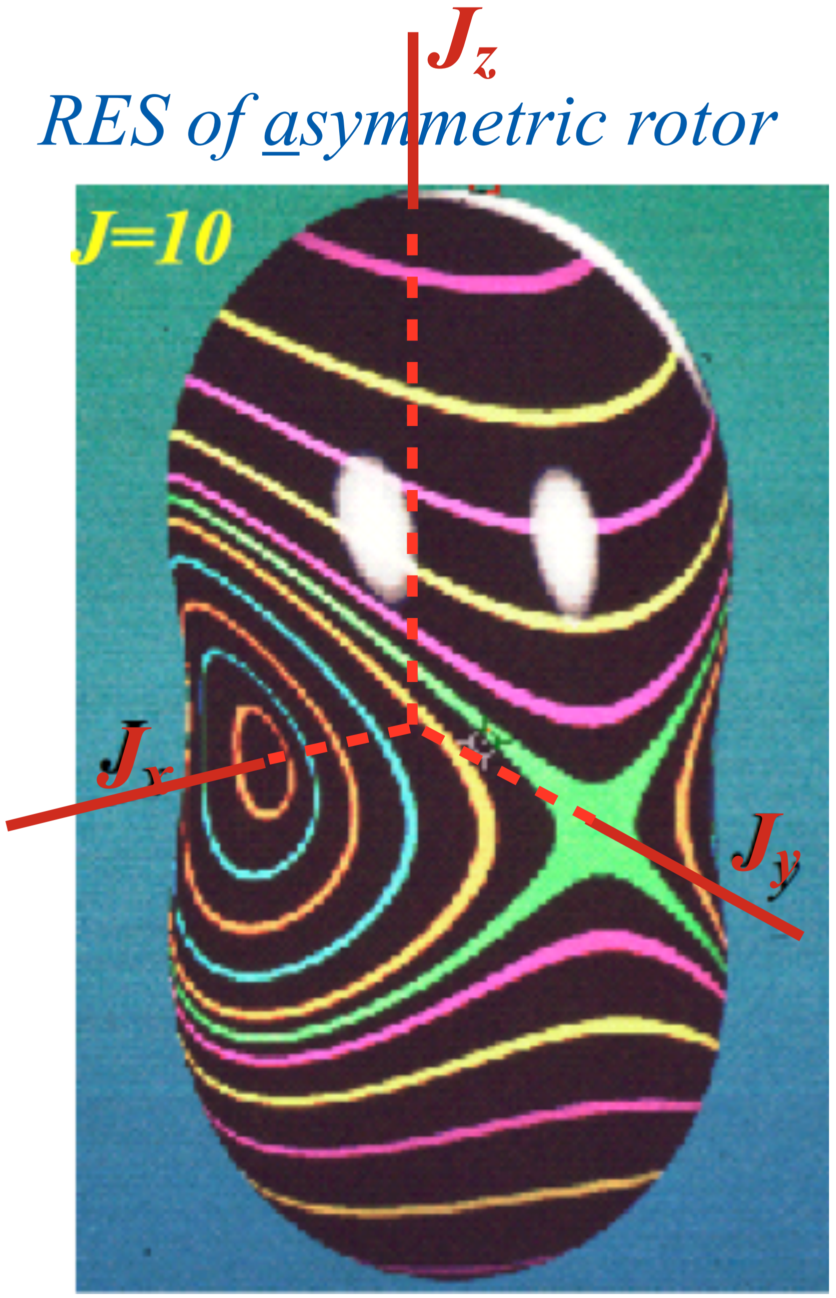
Always $\mathbf{I}$ tensor is *symmetric* ($\mathbf{I}_{ij}= \mathbf{I}_{ji}$) so *eigenvectors* must be *orthogonal*.

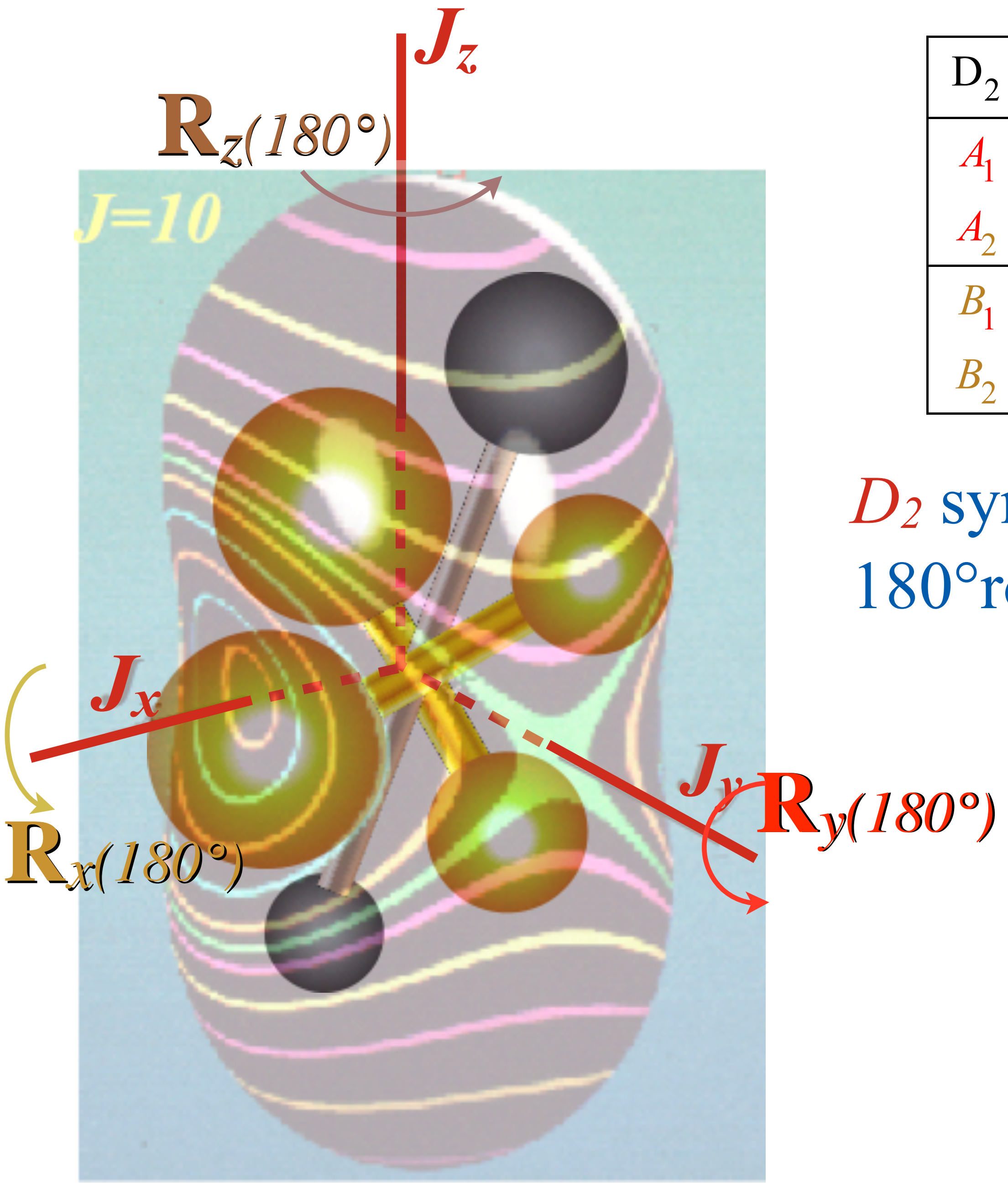
Asymmetric rotor is not Unsymmetric rotor: D_2 character table

Even an ugly rigid body has inertial tensor **I** with *at least D_2* symmetry…

…*in* **I** Principal Axis BODY frame *(eigenvectors of* **I***)*

RES of asymmetric rotor





D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

D_2 symmetry has three 180°rotations $\mathbf{R}_x$ $\mathbf{R}_y$ $\mathbf{R}_z$

Always **I** tensor is *symmetric* ($\mathbf{I}_{ij}$= $\mathbf{I}_{ji}$) so *eigenvectors* must be *orthogonal.*

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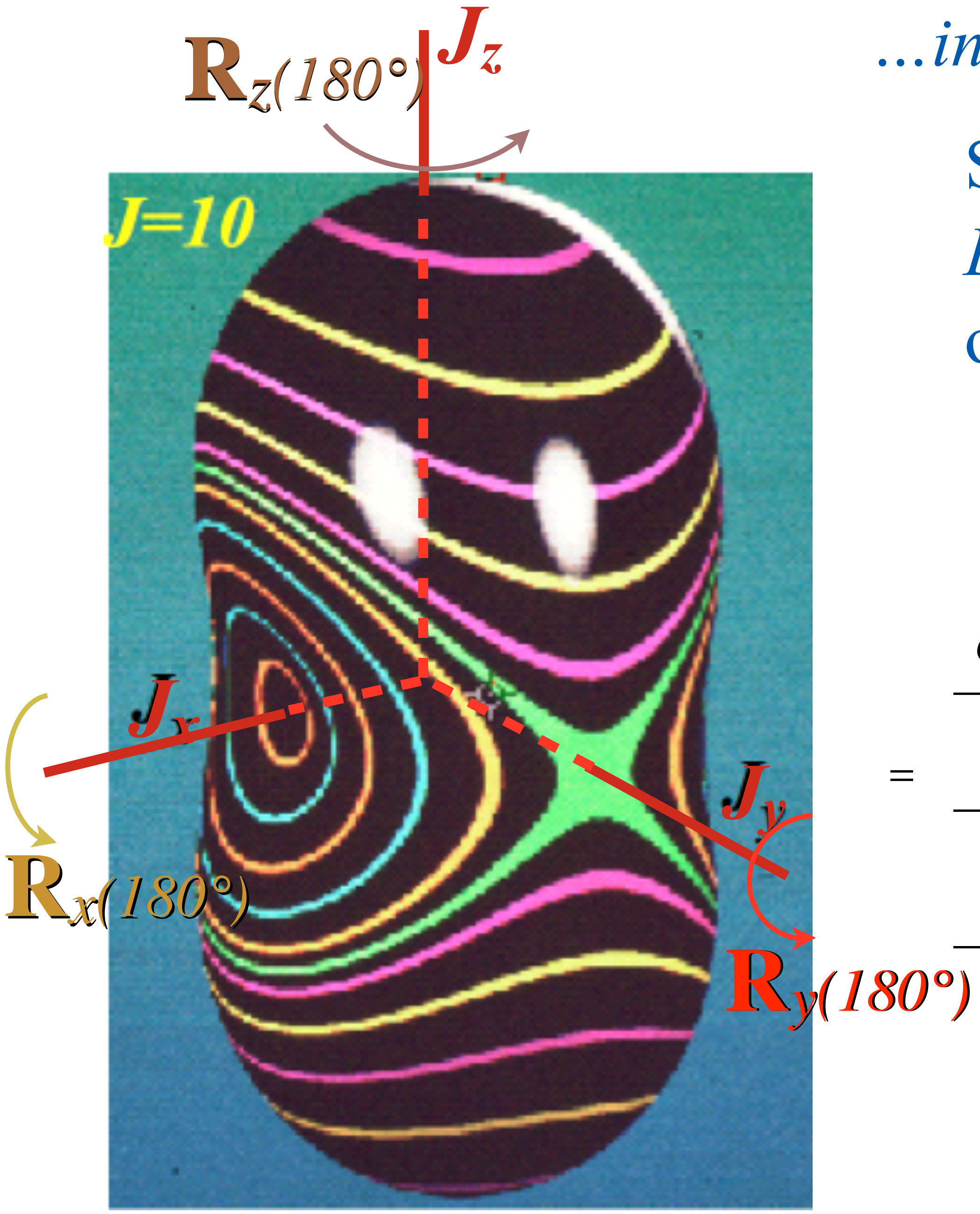
Even an ugly rigid body has inertial tensor **I** with *at least D_2* symmetry…



…in **I** Principal Axis BODY frame *(eigenvectors of* **I***)*

Since $\mathbf{R}_z = \mathbf{R}_x \cdot \mathbf{R}_y$

D_2 characters are xy outer product:

C_2^x	**1**	$\mathbf{R}_x$
+	1	1
−	1	−1

×

C_2^y	**1**	$\mathbf{R}_y$
+	1	1
−	1	−1

=

$C_2^x \times C_2^y$	$\mathbf{1}\cdot\mathbf{1}$	$\mathbf{R}_x\cdot\mathbf{1}$	$\mathbf{1}\cdot\mathbf{R}_y$	$\mathbf{R}_x\cdot\mathbf{R}_y$
$+\cdot+$	$1\cdot1$	$1\cdot1$	$1\cdot1$	$1\cdot1$
$-\cdot+$	$1\cdot1$	$-1\cdot1$	$1\cdot1$	$-1\cdot1$
$+\cdot-$	$1\cdot1$	$1\cdot1$	$1\cdot(-1)$	$1\cdot(-1)$
$-\cdot-$	$1\cdot1$	$-1\cdot1$	$1\cdot(-1)$	$-1\cdot(-1)$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

D_2 symmetry has three 180°rotations

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Even an ugly rigid body has inertial tensor **I** with *at least D_2* symmetry…

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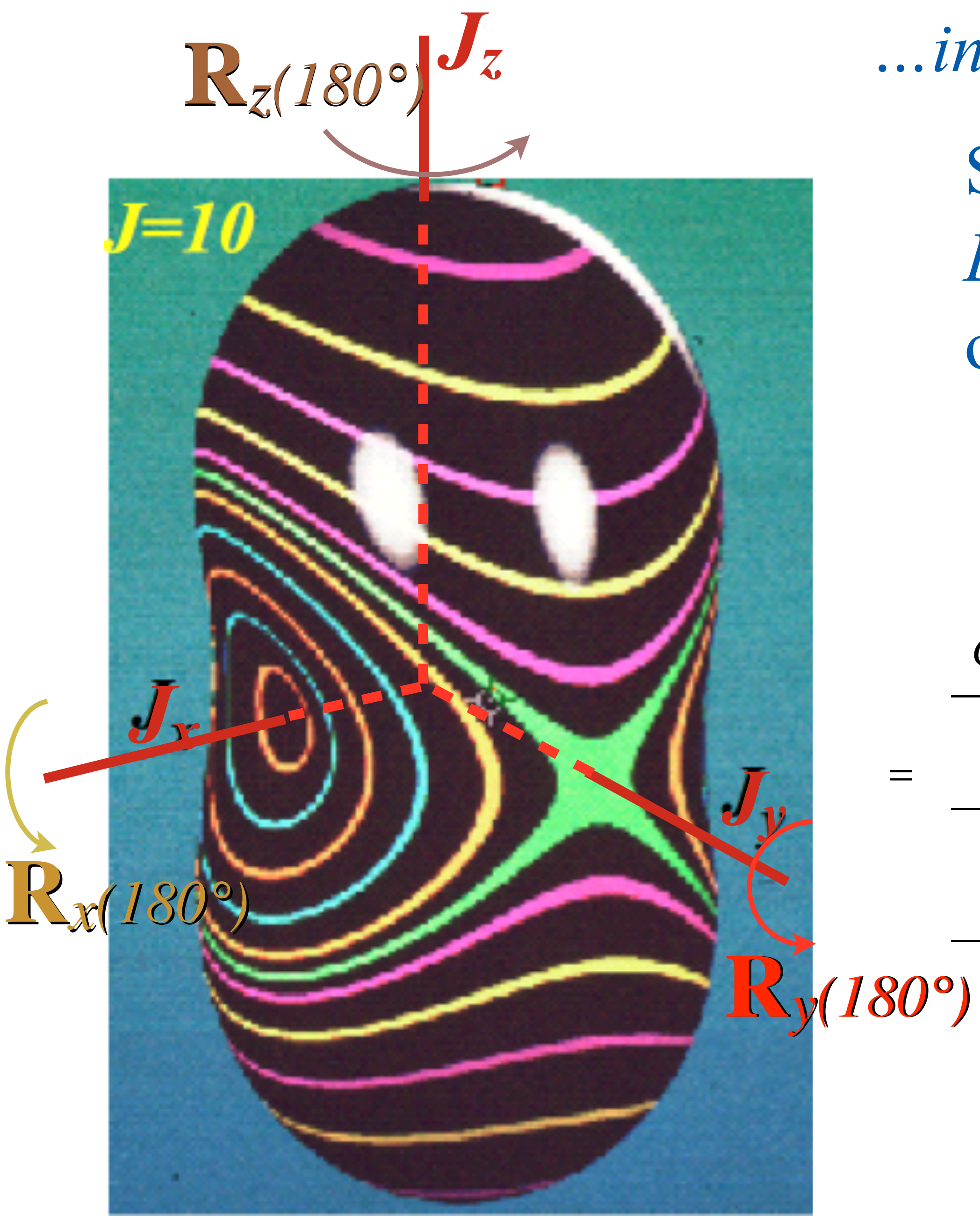

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C_2^x	**1**	$\mathbf{R}_x$
+	1	1
−	1	−1

×

C_2^y	**1**	$\mathbf{R}_y$
+	1	1
−	1	−1

=

$C_2^x \times C_2^y$	$\mathbf{1}\cdot\mathbf{1}$	$\mathbf{R}_x\cdot\mathbf{1}$	$\mathbf{1}\cdot\mathbf{R}_y$	$\mathbf{R}_x\cdot\mathbf{R}_y$
+·+	1·1	1·1	1·1	1·1
−·+	1·1	−1·1	1·1	−1·1
+·−	1·1	1·1	1·(−1)	1·(−1)
−·−	1·1	−1·1	1·(−1)	−1·(−1)

…that gives:

=

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
$+\cdot+ = A_1$	1	1	1	1
$-\cdot+ = A_2$	1	-1	1	−1
$+\cdot- = B_1$	1	1	-1	−1
$-\cdot- = B_2$	1	-1	-1	1

$_1$ subscript is R_x-symmetry

$_2$ subscript is R_x-anti-symmetry

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

D_2 symmetry has three 180°rotations

Deciphering notation:

A is R_y-symmetry “Always-the-same”

B is R_y-anti-symmetry “Back-n-forth”

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Examples of Group⊃Sub-group correlation

Polygonal geometry of U(2)⊃C_N character spectral function

Trace-character $\chi^j(\Theta)$ of U(2) rotation by C_n angle $\Theta=2\pi/n$

is an ($\ell^j=2j+1$)-term sum of $e^{-im\Theta}$ over allowed *m*-quanta $m=\{-j, -j+1, \ldots, j-1, j\}$.

$$\chi^{1/2}(\Theta)=traceD^{1/2}(\Theta)=trace\begin{pmatrix} e^{-i\theta/2} & \cdot \\ \cdot & e^{+i\theta/2} \end{pmatrix}$$

(spinor-j=1/2)

$$\chi^{1}(\Theta)=traceD^{1}(\Theta)=trace\begin{pmatrix} e^{-i\theta} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{+i\theta} \end{pmatrix}$$

(vector-j=1)

Polygonal algebra&geometry of U(2)⊃D₂ character spectral function

Trace-character $\chi^j(\Theta)$ of U(2) rotation by C_n angle $\Theta=2\pi/n$

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(vector-j=1)

$\chi^j(\Theta)$ involves a sum of $2\cos(m\,\Theta/2)$ for $m\geq 0$ up to $m=j$.

$$\chi^{1/2}(\Theta)=e^{-i\frac{\Theta}{2}}+e^{i\frac{\Theta}{2}} \qquad =2\cos\frac{\Theta}{2}$$

(spinor-j=1/2)

$$\chi^{3/2}(\Theta)=e^{-i\frac{3\Theta}{2}}+\ldots \qquad +e^{i\frac{3\Theta}{2}}=2\cos\frac{\Theta}{2}+2\cos\frac{3\Theta}{2}$$

$$\chi^{5/2}(\Theta)=e^{-i\frac{5\Theta}{2}}+\ldots \qquad +e^{i\frac{5\Theta}{2}}=2\cos\frac{\Theta}{2}+2\cos\frac{3\Theta}{2}+2\cos\frac{5\Theta}{2}$$

$$\chi^{0}(\Theta)=e^{-i\Theta\cdot 0} \qquad =1$$

(scalar-j=0)

$$\chi^{1}(\Theta)=e^{-i\Theta}+1+e^{i\Theta} \quad =1+2\cos\Theta$$

(vector-j=1)

$$\chi^{2}(\Theta)=e^{-i2\Theta}+\ldots e^{i2\Theta}=1+2\cos\Theta+2\cos 2\Theta$$

(tensor-j=2)

Algebra of $U(2)\supset D_2$ *character spectral geometric series*

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(spinor-j=1/2)

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$$\chi^{2}(\Theta)=e^{-i2\Theta}+\ldots e^{i2\Theta}=1+2\cos\Theta+2\cos 2\Theta$$

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$\chi^j(\Theta)$ is a geometric series with ratio $e^{i\Theta}$ between each successive term.

$$\chi^{j}(\Theta)=TraceD^{(j)}(\Theta)=e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\ldots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}+e^{+i\Theta j}$$

Algebra of U(2)⊃D₂ character spectral geometric series

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$$\chi^{1/2}(\Theta)=traceD^{1/2}(\Theta)=trace\begin{pmatrix} e^{-i\theta/2} & \cdot \\ \cdot & e^{+i\theta/2}\end{pmatrix}$$

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$$\chi^{j}(\Theta)e^{-i\Theta}=e^{-i\Theta(j+1)}+e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\ldots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}$$

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(spinor-j=1/2)

$$\chi^{0}(\Theta)=e^{-i\Theta\cdot 0} \qquad =1$$

(scalar-j=0)

$$\chi^{3/2}(\Theta)=e^{-i\frac{3\Theta}{2}}+\ldots \qquad +e^{i\frac{3\Theta}{2}}=2\cos\frac{\Theta}{2}+2\cos\frac{3\Theta}{2}$$

$$\chi^{1}(\Theta)=e^{-i\Theta}+1+e^{i\Theta} \quad =1+2\cos\Theta$$

(vector-j=1)

$$\chi^{5/2}(\Theta)=e^{-i\frac{5\Theta}{2}}+\ldots \qquad +e^{i\frac{5\Theta}{2}}=2\cos\frac{\Theta}{2}+2\cos\frac{3\Theta}{2}+2\cos\frac{5\Theta}{2}$$

$$\chi^{2}(\Theta)=e^{-i2\Theta}+\ldots e^{i2\Theta}=1+2\cos\Theta+2\cos 2\Theta$$

(tensor-j=2)

$\chi^j(\Theta)$ is a geometric series with ratio $e^{i\Theta}$ between each successive term.

$$\chi^{j}(\Theta)=TraceD^{(j)}(\Theta)=e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\ldots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}+e^{+i\Theta j}$$

$$\chi^{j}(\Theta)e^{-i\Theta}=e^{-i\Theta(j+1)}+e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\ldots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}$$

Subtracting gives:

$$\chi^{j}(\Theta)(1-e^{-i\Theta})=-e^{-i\Theta(j+1)} \qquad + \qquad e^{+i\Theta j}$$

Algebra of $U(2)\supset D_2$ character spectral geometric series

Trace-character $\chi^j(\Theta)$ of U(2) rotation by C_n angle $\Theta=2\pi/n$

is an ($\ell^j=2j+1$)-term sum of $e^{-im\Theta}$ over allowed m-quanta $m=\{-j, -j+1, \ldots, j-1, j\}$.

$$\chi^{1/2}(\Theta)=traceD^{1/2}(\Theta)=trace\begin{pmatrix} e^{-i\theta/2} & \cdot \\ \cdot & e^{+i\theta/2} \end{pmatrix}$$

(spinor-j=1/2)

$$\chi^{1}(\Theta)=traceD^{1}(\Theta)=trace\begin{pmatrix} e^{-i\theta} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{+i\theta} \end{pmatrix}$$

(vector-j=1)

$\chi^j(\Theta)$ involves a sum of $2\cos(m\,\Theta/2)$ for $m\geq 0$ up to $m=j$.

$$\chi^{1/2}(\Theta)=e^{-i\frac{\Theta}{2}}+e^{i\frac{\Theta}{2}} \qquad =2\cos\frac{\Theta}{2}$$

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$$\chi^{3/2}(\Theta)=e^{-i\frac{3\Theta}{2}}+\ldots \qquad +e^{i\frac{3\Theta}{2}}=2\cos\frac{\Theta}{2}+2\cos\frac{3\Theta}{2}$$

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(vector-j=1)

$$\chi^{5/2}(\Theta)=e^{-i\frac{5\Theta}{2}}+\ldots \qquad +e^{i\frac{5\Theta}{2}}=2\cos\frac{\Theta}{2}+2\cos\frac{3\Theta}{2}+2\cos\frac{5\Theta}{2}$$

$$\chi^{2}(\Theta)=e^{-i2\Theta}+\ldots e^{i2\Theta}=1+2\cos\Theta+2\cos 2\Theta$$

(tensor-j=2)

$\chi^j(\Theta)$ is a geometric series with ratio $e^{i\Theta}$ between each successive term.

$$\chi^{j}(\Theta)=TraceD^{(j)}(\Theta)=\cancel{e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\ldots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}}+e^{+i\Theta j}$$

$$\chi^{j}(\Theta)e^{-i\Theta}=e^{-i\Theta(j+1)}\cancel{+e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\ldots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}}$$

Subtracting/dividing gives $\chi^j(\Theta)$ formula.

$$\chi^{j}(\Theta)=\frac{e^{+i\Theta j}-e^{-i\Theta(j+1)}}{1-e^{-i\Theta}}=\frac{e^{+i\Theta(j+\frac{1}{2})}-e^{-i\Theta(j+\frac{1}{2})}}{e^{+i\frac{\Theta}{2}}-e^{-i\frac{\Theta}{2}}}=\frac{\sin\Theta(j+\frac{1}{2})}{\sin\frac{\Theta}{2}}$$

Algebra of $U(2)\supset D_2$ character spectral geometric series

Trace-character $\chi^j(\Theta)$ of U(2) rotation by C_n angle $\Theta=2\pi/n$

is an ($\ell^j=2j+1$)-term sum of $e^{-im\Theta}$ over allowed *m*-quanta $m=\{-j, -j+1, \dots, j-1, j\}$.

$$\chi^{1/2}(\Theta)=traceD^{1/2}(\Theta)=trace\begin{pmatrix} e^{-i\theta/2} & \cdot \\ \cdot & e^{+i\theta/2}\end{pmatrix}$$

(spinor-j=1/2)

$$\chi^{1}(\Theta)=traceD^{1}(\Theta)=trace\begin{pmatrix} e^{-i\theta} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{+i\theta}\end{pmatrix}$$

(vector-j=1)

$\chi^j(\Theta)$ involves a sum of $2\cos(m\,\Theta/2)$ for $m\geq 0$ up to $m=j$.

$$\chi^{1/2}(\Theta)=e^{-i\frac{\Theta}{2}}+e^{i\frac{\Theta}{2}}\quad =2\cos\frac{\Theta}{2}$$

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(vector-j=1)

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$$\chi^{2}(\Theta)=e^{-i2\Theta}+\dots e^{i2\Theta}=1+2\cos\Theta+2\cos2\Theta$$

(tensor-j=2)

$\chi^j(\Theta)$ is a geometric series with ratio $e^{i\Theta}$ between each successive term.

$$\chi^{j}(\Theta)=TraceD^{(j)}(\Theta)=e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\dots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}+e^{+i\Theta j}$$

$$\chi^{j}(\Theta)e^{-i\Theta}=e^{-i\Theta(j+1)}+e^{-i\Theta j}+e^{-i\Theta(j-1)}+e^{-i\Theta(j-2)}+\dots+e^{+i\Theta(j-2)}+e^{+i\Theta(j-1)}$$

Subtracting/dividing gives $\chi^j(\Theta)$ formula.

$$\chi^{j}(\Theta)=\frac{e^{+i\Theta j}-e^{-i\Theta(j+1)}}{1-e^{-i\Theta}}=\frac{e^{+i\Theta(j+\frac{1}{2})}-e^{-i\Theta(j+\frac{1}{2})}}{e^{+i\frac{\Theta}{2}}-e^{-i\frac{\Theta}{2}}}=\frac{\sin\Theta(j+\frac{1}{2})}{\sin\frac{\Theta}{2}}$$

For C_n angle $\Theta=2\pi/n$ this χ^j has a lot of geometric significance.

$$\boxed{\chi^{j}\left(\frac{2\pi}{n}\right)=\frac{\sin\frac{\pi}{n}(2j+1)}{\sin\frac{\pi}{n}}=\frac{\sin\frac{\pi\ell^{j}}{n}}{\sin\frac{\pi}{n}}}$$

Character Spectral Function
where: $\ell^j=2j+1$
is U(2) irrep dimension

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* *D₂* of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Review 1. *Review of angular momentum cone geometry*
Review 2. *Review of Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions*
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Energy levels and RES of symmetric rotors: prolate vs. oblate cases
RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 symmetry labels)
Asymmetric rotor is not Unsymmetric rotor

Polygonal algebra & geometry of $U(2)\supset C_N$ character spectral function
Algebra of geometric series. *Geometry of algebraic series*
Molecular $(2\ell+1)$-multiplet D_2-level splitting *Examples: $\ell=1, 2, 3,\ldots$*

j,m,n formulas for momentum operator matrix elements:Hamiltonian matrix for asymmetric rotor
(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*
Completing diagonalization from new D_2 basis:
J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group$\supset$Sub-group correlation

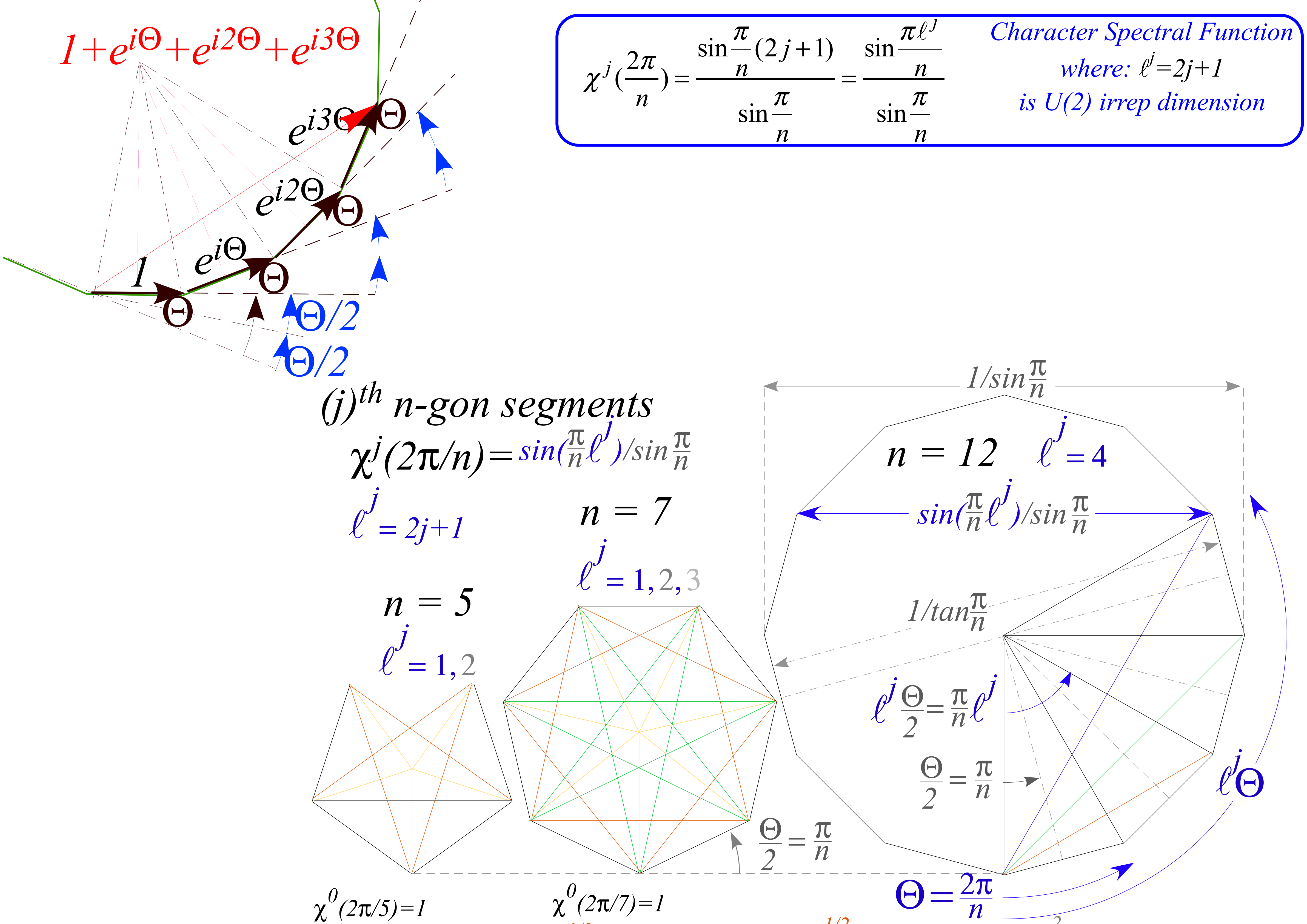
Polygonal geometry of $U(2)\supset C_N$ character spectral function

$$\chi^j\left(\frac{2\pi}{n}\right)=\frac{\sin\frac{\pi}{n}(2j+1)}{\sin\frac{\pi}{n}}=\frac{\sin\frac{\pi\ell^j}{n}}{\sin\frac{\pi}{n}}$$

Character Spectral Function

where: $\ell^j=2j+1$

is U(2) irrep dimension



(j)th n-gon segments

$\chi^j(2\pi/n)=\sin(\frac{\pi}{n}\ell^j)/\sin\frac{\pi}{n}$

$\ell^j=2j+1$

$\chi^0(2\pi/5)=1$

$\chi^{1/2}(2\pi/5)=1.618...$

$=(1+\sqrt{5})/2=$

$\chi^0(2\pi/7)=1$

$\chi^{1/2}(2\pi/7)=1.802...$

$\chi^1(2\pi/7)=2.247...$

$\chi^{3/2}(2\pi/7)=2.247...$

$\chi^{1/2}(2\pi/12)=1.932...$

$\chi^1(2\pi/12)=2.732...$

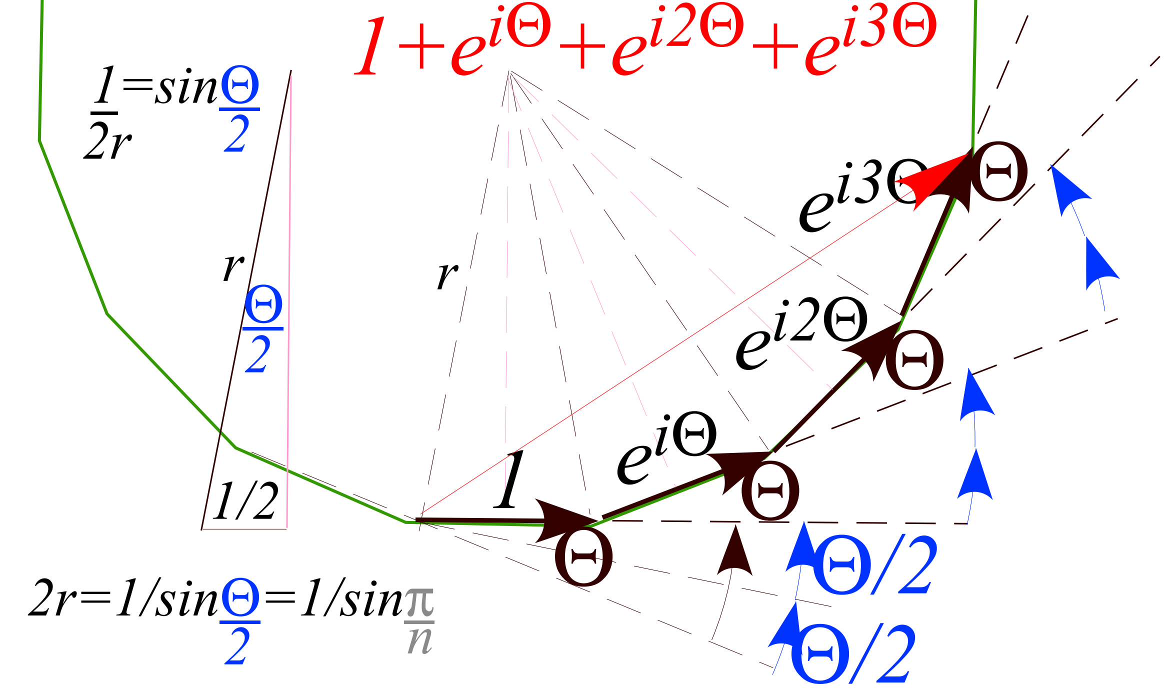
$\chi^{3/2}(2\pi/12)=3.346...$

$\chi^2(2\pi/12)=3.732...$

$\chi^{5/2}(2\pi/12)=3.864...$

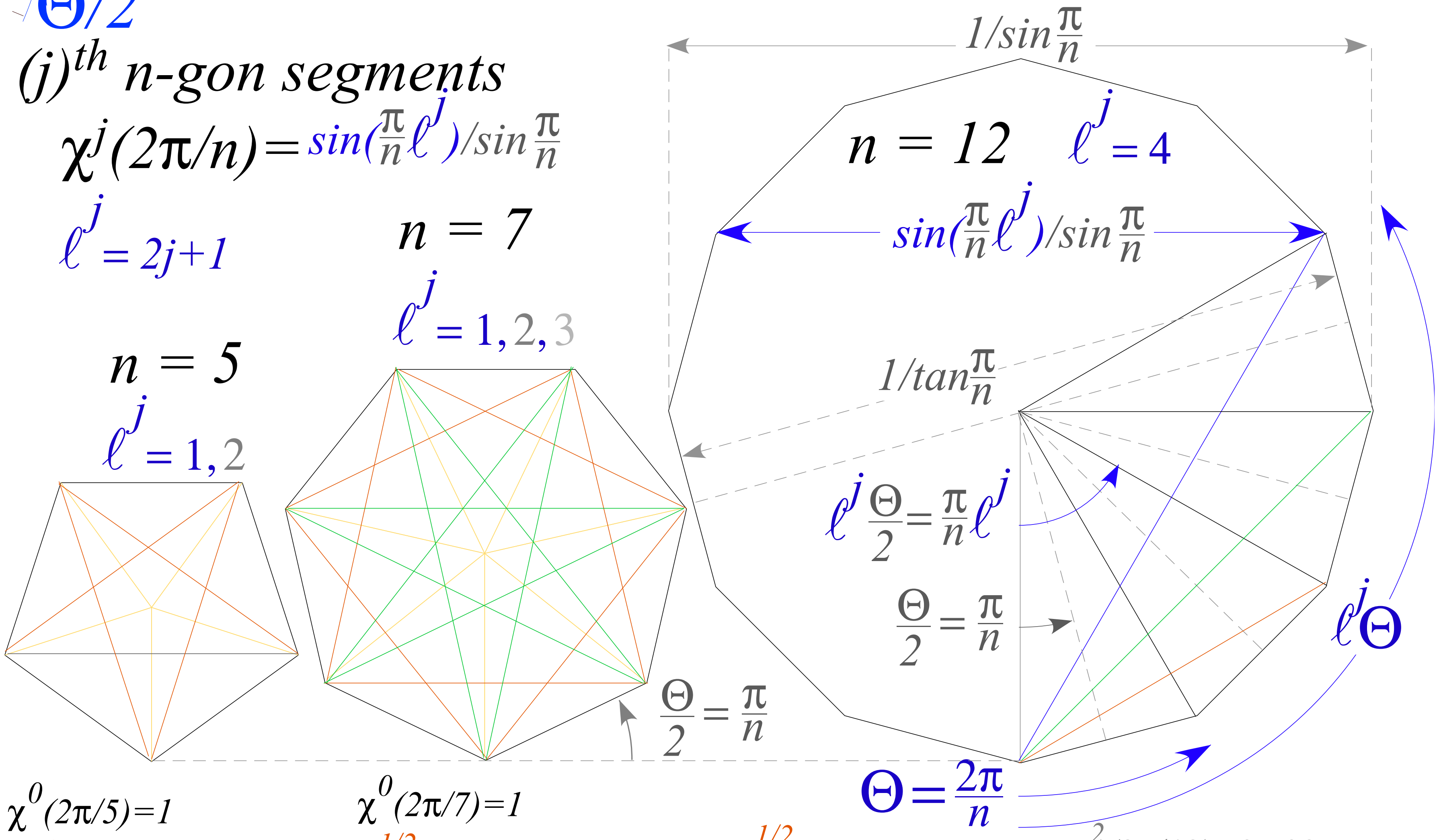
$\chi^3(2\pi/12)=3.732...$

Polygonal geometry of $U(2)\supset C_N$ character spectral function



$$\chi^j\left(\frac{2\pi}{n}\right)=\frac{\sin\frac{\pi}{n}(2j+1)}{\sin\frac{\pi}{n}}=\frac{\sin\frac{\pi\ell^j}{n}}{\sin\frac{\pi}{n}}$$

Character Spectral Function
where: $\ell^j=2j+1$
is U(2) irrep dimension



$(j)^{th}$ n-gon segments

$\chi^j(2\pi/n)=\sin(\frac{\pi}{n}\ell^j)/\sin\frac{\pi}{n}$

$\ell^j = 2j+1$

$\chi^0(2\pi/5)=1$
$\chi^{1/2}(2\pi/5)=1.618...$
$=(1+\sqrt{5})/2=$

$\chi^0(2\pi/7)=1$
$\chi^{1/2}(2\pi/7)=1.802...$
$\chi^1(2\pi/7)=2.247...$
$\chi^{3/2}(2\pi/7)=2.247...$

$\chi^{1/2}(2\pi/12)=1.932...$
$\chi^1(2\pi/12)=2.732...$
$\chi^{3/2}(2\pi/12)=3.346...$

$\chi^2(2\pi/12)=3.732...$
$\chi^{5/2}(2\pi/12)=3.864...$
$\chi^3(2\pi/12)=3.732...$

Polygonal geometry of $U(2)\supset C_N$ character spectral function

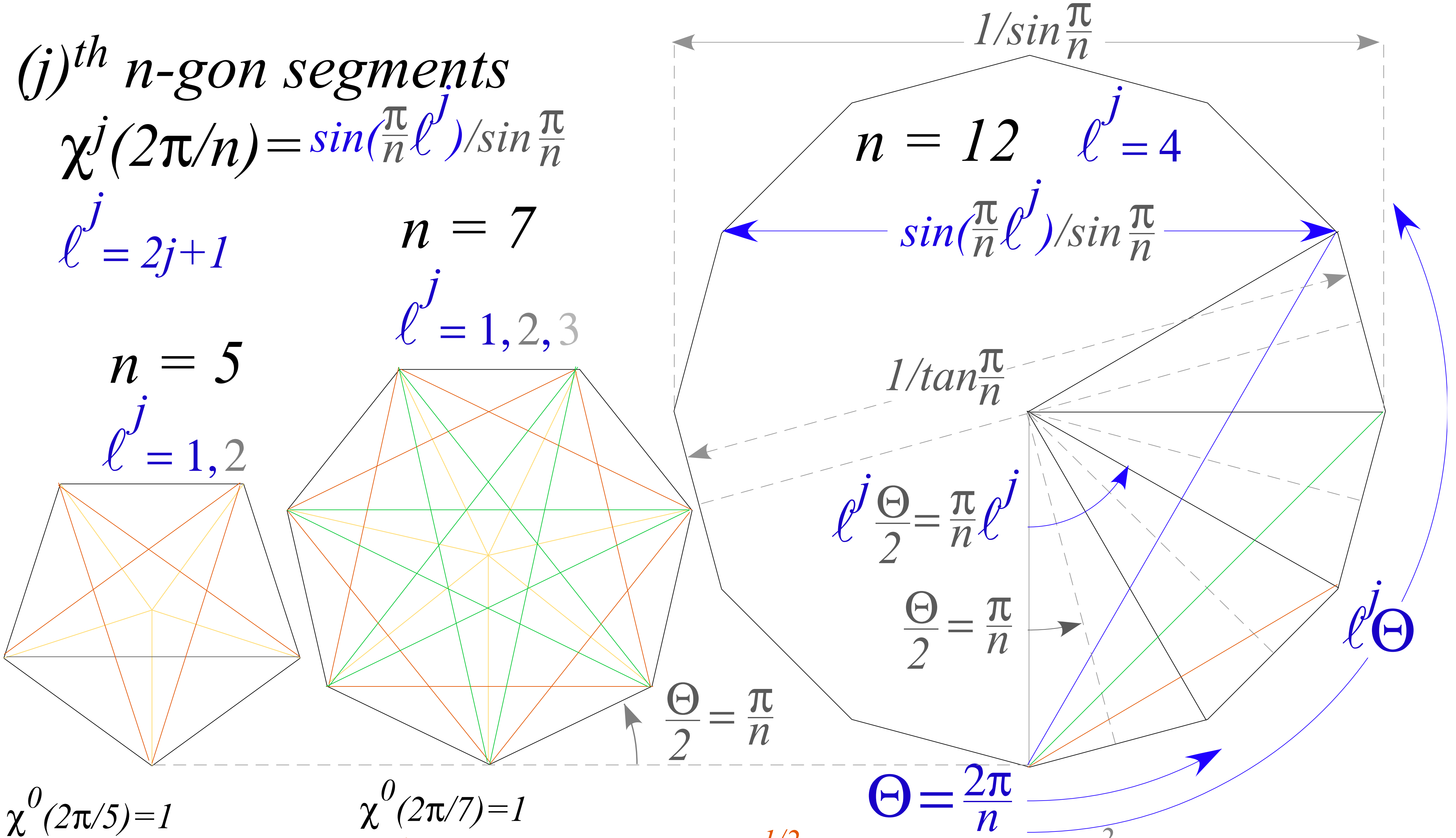
$$\chi^j\left(\frac{2\pi}{n}\right)=\frac{\sin\frac{\pi}{n}(2j+1)}{\sin\frac{\pi}{n}}=\frac{\sin\frac{\pi\ell^J}{n}}{\sin\frac{\pi}{n}}$$

Character Spectral Function
where: $\ell^j=2j+1$
is U(2) irrep dimension

$(j)^{th}$ *n-gon segments*

$$\chi^j(2\pi/n)=\sin(\tfrac{\pi}{n}\ell^j)/\sin\tfrac{\pi}{n}$$

$$\ell^j=2j+1$$



$\chi^0(2\pi/5)=1$

$\chi^{1/2}(2\pi/5)=1.618...$
$=(1+\sqrt{5})/2=$

$\chi^0(2\pi/7)=1$

$\chi^{1/2}(2\pi/7)=1.802...$

$\chi^1(2\pi/7)=2.247...$

$\chi^{3/2}(2\pi/7)=2.247...$

$\chi^{1/2}(2\pi/12)=1.932...$

$\chi^1(2\pi/12)=2.732...$

$\chi^{3/2}(2\pi/12)=3.346...$

$\chi^2(2\pi/12)=3.732...$

$\chi^{5/2}(2\pi/12)=3.864...$

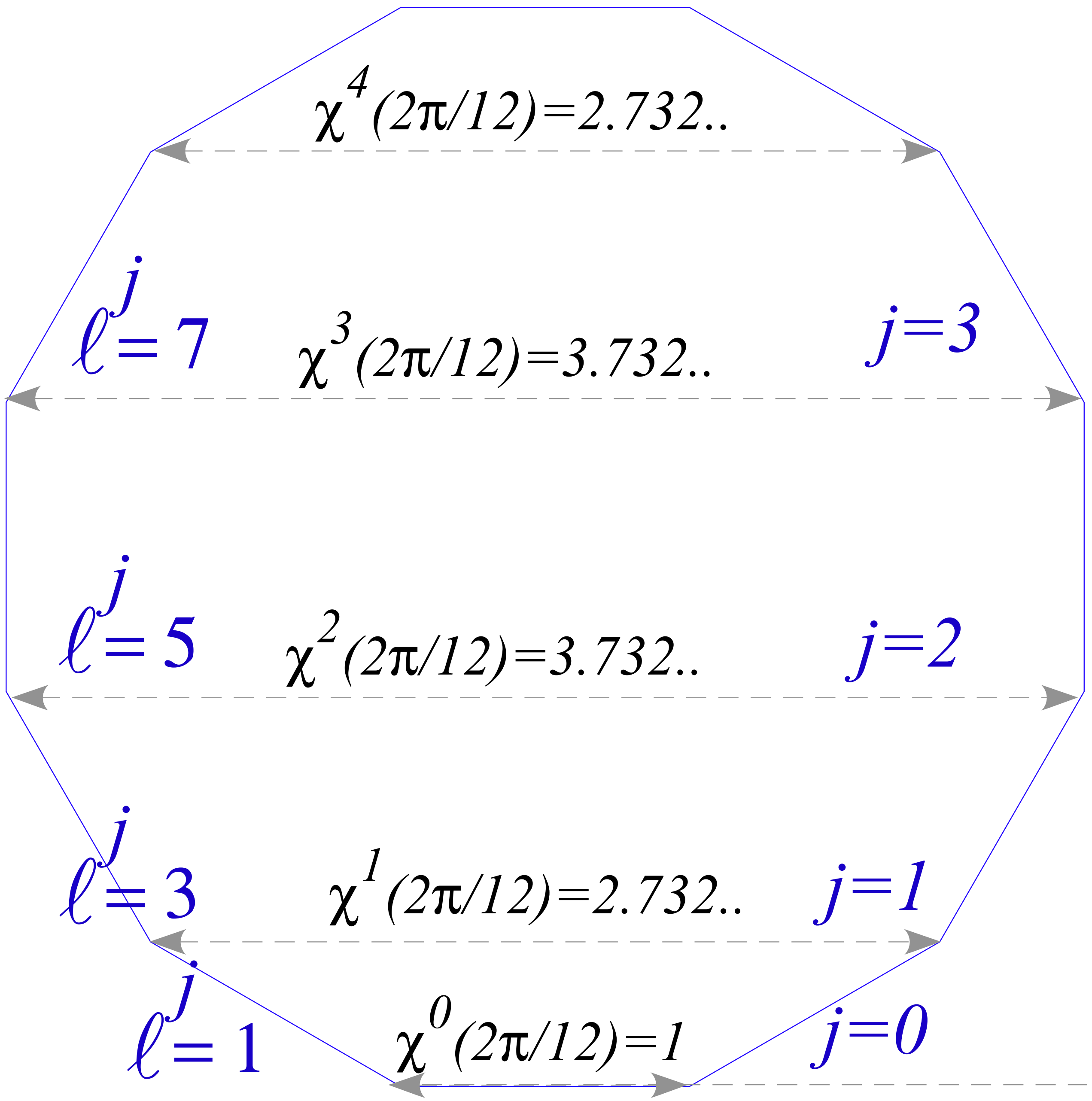
$\chi^3(2\pi/12)=3.732...$

Polygonal geometry of U(2)⊃C$_N$ character spectral function

$$\chi^j\left(\frac{2\pi}{n}\right) = \frac{\sin\frac{\pi}{n}(2j+1)}{\sin\frac{\pi}{n}} = \frac{\sin\frac{\pi\ell^j}{n}}{\sin\frac{\pi}{n}}$$

Character Spectral Function
where: $\ell^j=2j+1$
is U(2) irrep dimension

Integer j for n=12



$\chi^4(2\pi/12)=2.732..$

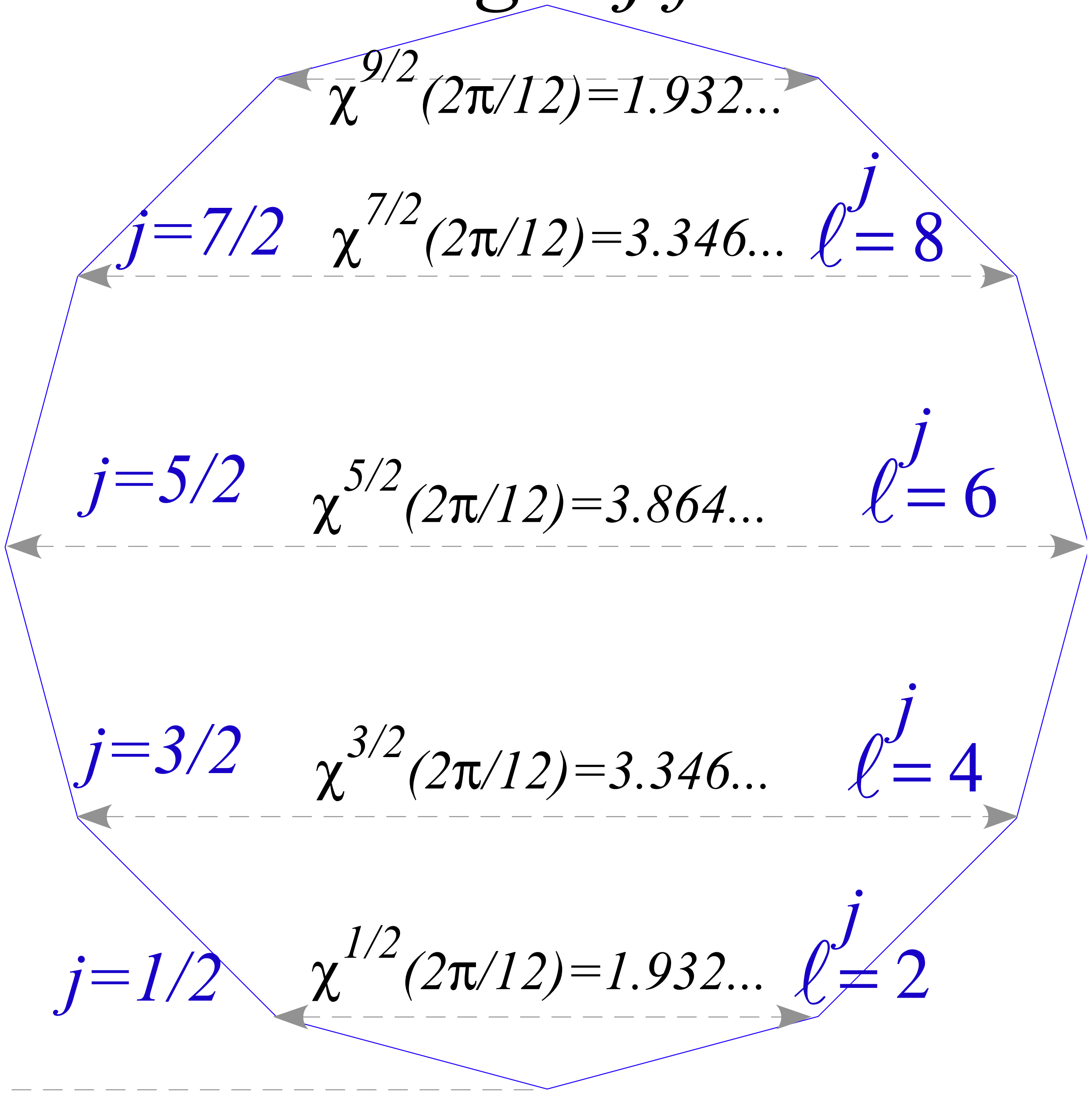
$\ell^j=7$ $\chi^3(2\pi/12)=3.732..$ $j=3$

$\ell^j=5$ $\chi^2(2\pi/12)=3.732..$ $j=2$

$\ell^j=3$ $\chi^1(2\pi/12)=2.732..$ $j=1$

$\ell^j=1$ $\chi^0(2\pi/12)=1$ $j=0$

1/2-Integer j for n=12



$\chi^{9/2}(2\pi/12)=1.932...$

$j=7/2$ $\chi^{7/2}(2\pi/12)=3.346...$ $\ell^j=8$

$j=5/2$ $\chi^{5/2}(2\pi/12)=3.864...$ $\ell^j=6$

$j=3/2$ $\chi^{3/2}(2\pi/12)=3.346...$ $\ell^j=4$

$j=1/2$ $\chi^{1/2}(2\pi/12)=1.932...$ $\ell^j=2$

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* *D₂* of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Review 1. *Review of angular momentum cone geometry*
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Energy levels and RES of symmetric rotors: prolate vs. oblate cases
RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D₂ symmetry labels)
Asymmetric rotor is not Unsymmetric rotor

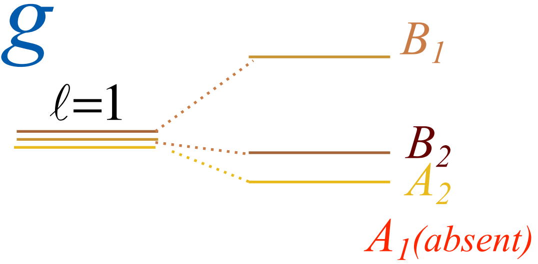
Polygonal algebra & geometry of U(2)⊃C_N character spectral function
Algebra of geometric series. *Geometry of algebraic series*
Molecular (2ℓ+1)-multiplet D₂-level splitting *Examples: ℓ=1, 2, 3,...*

j,m,n formulas for momentum operator matrix elements:Hamiltonian matrix for asymmetric rotor
(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*
Completing diagonalization from new D₂ basis:
J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group⊃Sub-group correlation

Molecular $(2\ell+1)$-multiplet D_2-level splitting

Example: (ℓ=1)



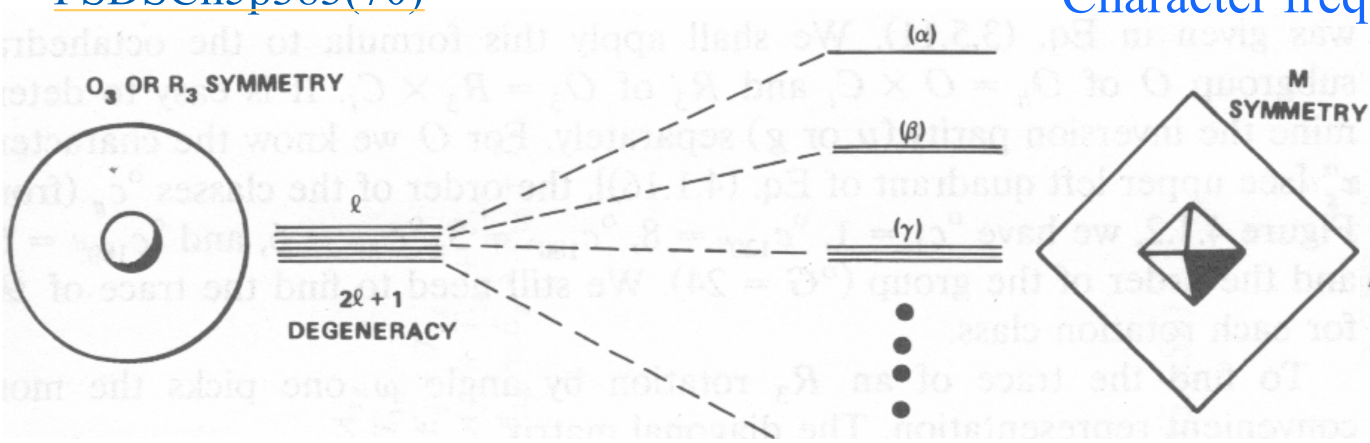
$$f^{(b)} = \frac{1}{{}^\circ D_2} \sum_{\substack{classes\\ \kappa_k \in D_2}} {}^\circ\kappa_k \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2}^{4} \chi_k^{(b)*} \chi_k^{(\ell)}$$

Characters QTCAtext p.69

Character frequency-f formula GrpTh Lect15 p.44.

f formula PSDStext p.38=187.

PSDSCh5p383(70)



$$D^\ell(R) = \begin{pmatrix} D^\ell_{\ell,\ell}(R) & \ldots\ldots D_{\ell,-\ell} \\ D_{\ell-1,\ell} & \\ D_{-\ell,\ell} & \ldots\ldots D_{-\ell,-\ell} \end{pmatrix} \Big\downarrow M \cong \begin{pmatrix} D^\alpha(R) & & \\ & D^\beta(R) & \\ & & D^\gamma(R) \end{pmatrix}$$

ℓ=0, s-singlet

$2\ell+1=1$

ℓ=1, p-triplet

$2\ell+1=3$

ℓ=2, d-quintet

$2\ell+1=5$

ℓ=3, f-septet

$2\ell+1=7$

ℓ=4, g-nonet

$2\ell+1=9$

ℓ=5, h-(11)-let

$2\ell+1=11$

…

U(2) characters
from Lecture 15 p.110 :

$$\chi^\ell\left(\frac{2\pi}{n}\right) = \frac{\sin\frac{(2\ell+1)\pi}{n}}{\sin\frac{\pi}{n}}$$

R(3) character
where: $2\ell+1$
is ℓ-orbital dimension

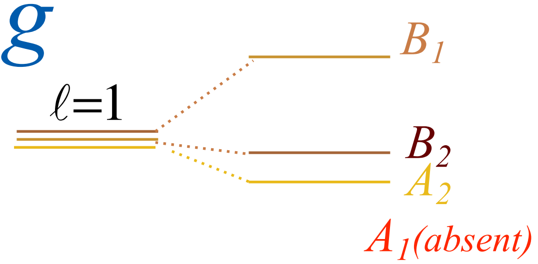
$$\chi^\ell(\Theta) = \frac{\sin(\ell+\frac{1}{2})\Theta}{\sin\frac{\Theta}{2}}$$

$\chi^\ell(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
1	3	-1	-1	-1
2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

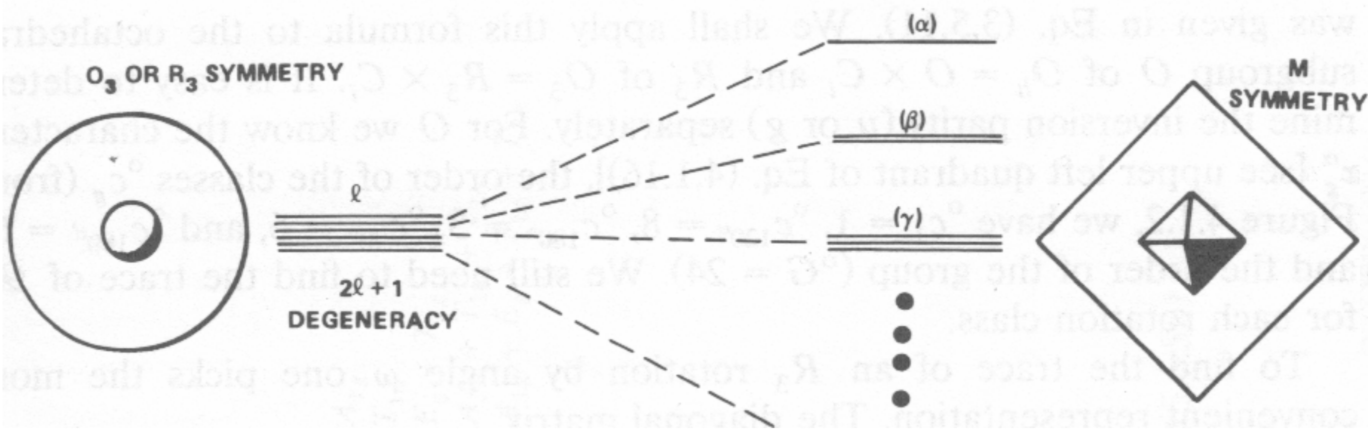
Molecular (2ℓ+1)-multiplet D_2-level splitting

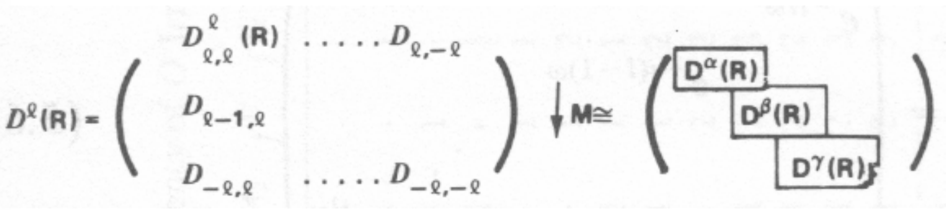
Example: (ℓ=1)

$$f^{(b)}=\frac{1}{{}^{\circ}D_2}\sum_{\substack{classes\\ \kappa_k\in D_2}} {}^{\circ}\kappa_k \chi_k^{(b)*}\chi_k^{(\ell)}=\frac{1}{4}\sum_{g\in D_2}^{4}\chi_k^{(b)*}\chi_k^{(\ell)}$$



ℓ=0, s-singlet
2ℓ+1=1
ℓ=1, p-triplet
2ℓ+1=3
ℓ=2, d-quintet
2ℓ+1=5
ℓ=3, f-septet
2ℓ+1=7
ℓ=4, g-nonet
2ℓ+1=9
ℓ=5, h-(11)-let
2ℓ+1=11
…





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4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

$$\chi^{\ell}\left(\frac{2\pi}{n}\right)=\frac{\sin\frac{(2\ell+1)\pi}{n}}{\sin\frac{\pi}{n}}$$

$$\chi^{\ell}(\Theta)=\frac{\sin(\ell+\frac{1}{2})\Theta}{\sin\frac{\Theta}{2}}$$

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

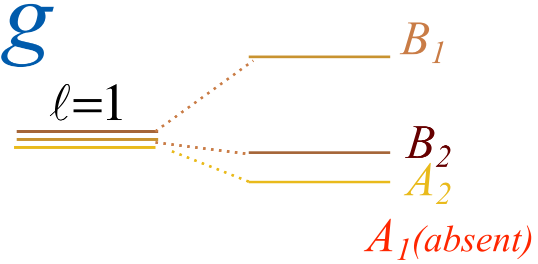
…this Lect.10 p.25
D_2 characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Molecular (2ℓ+1)-multiplet D_2-level splitting

Example: (ℓ=1)

$$f^{(b)}=\frac{1}{{}^{\circ}D_2}\sum_{\substack{classes\\ \kappa_k\in D_2}}{}^{\circ}\kappa_k\chi_k^{(b)*}\chi_k^{(\ell)}=\frac{1}{4}\sum_{g\in D_2}^{4}\chi_k^{(b)*}\chi_k^{(\ell)}$$



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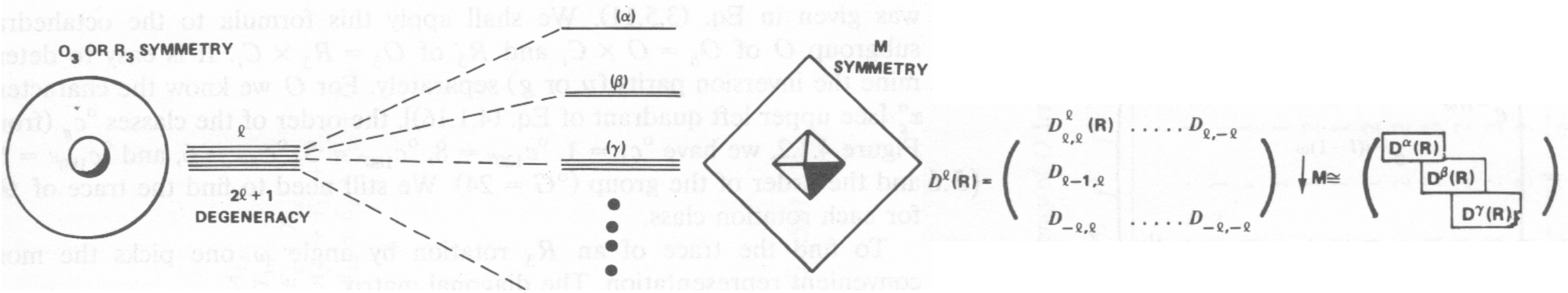
...



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where: 2ℓ+1
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$$\chi^{\ell}(\Theta)=\frac{\sin(\ell+\frac{1}{2})\Theta}{\sin\frac{\Theta}{2}}$$

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5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

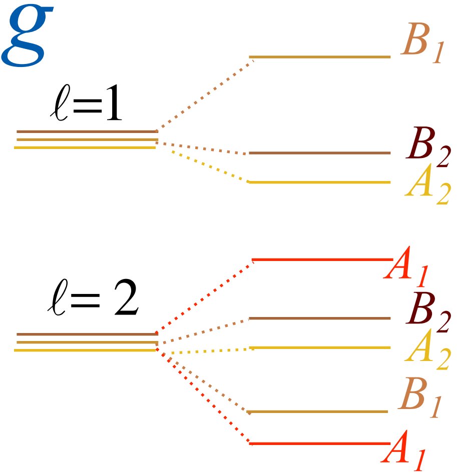
D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1\oplus A_2\oplus B_1\oplus B_2$

	3	-1	-1	-1
$0\chi^{A_1}(\mathbf{g})=$	1	1	1	1
$1\chi^{A_2}(\mathbf{g})=$	1	-1	1	-1
$1\chi^{B_1}(\mathbf{g})=$	1	1	-1	-1
$1\chi^{B_2}(\mathbf{g})=$	1	-1	-1	1

trial&error??

Molecular (2ℓ+1)-multiplet D_2-level splitting



ℓ=0, s-singlet
2ℓ+1=1
ℓ=1, p-triplet
2ℓ+1=3
ℓ=2, d-quintet
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ℓ=3, f-septet
2ℓ+1=7
ℓ=4, g-nonet
2ℓ+1=9
ℓ=5, h-(11)-let
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...

Example: (ℓ=1)

and: (ℓ=2)

$$f^{(b)} = \frac{1}{{}^\circ D_2}\sum_{\substack{\text{classes}\\ \kappa_k\in D_2}} {}^\circ\kappa_k\,\chi_k^{(b)*}\chi_k^{(\ell)} = \frac{1}{4}\sum_{g\in D_2}^{4}\chi_k^{(b)*}\chi_k^{(\ell)}$$

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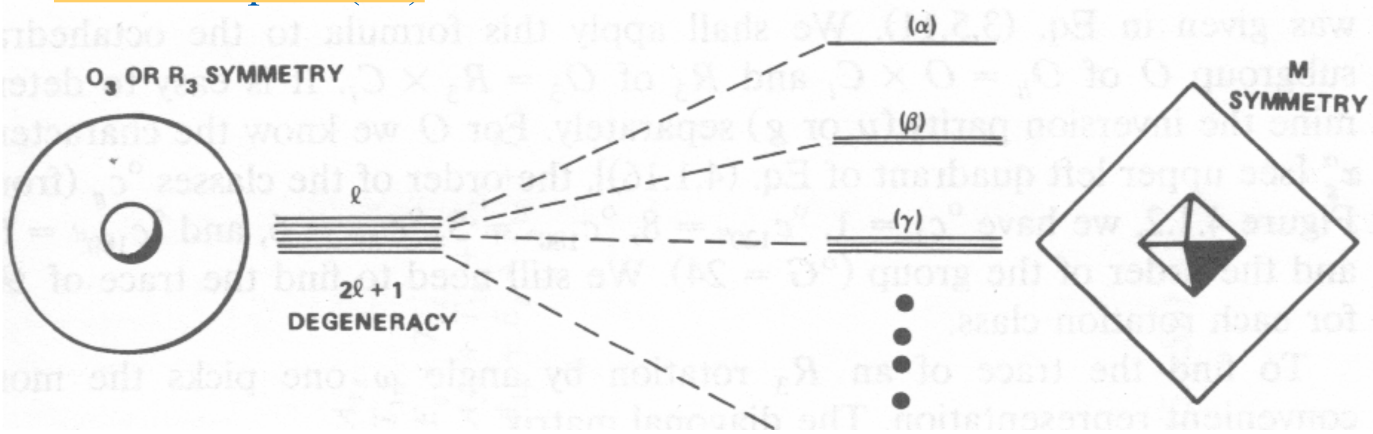

$$D^\ell(R) = \begin{pmatrix} D^\ell_{\ell,\ell}(R) & \cdots\cdots & D_{\ell,-\ell} \\ D_{\ell-1,\ell} & & \\ D_{-\ell,\ell} & \cdots\cdots & D_{-\ell,-\ell} \end{pmatrix} \downarrow M \cong \begin{pmatrix} \boxed{D^\alpha(R)} & & \\ & \boxed{D^\beta(R)} & \\ & & \boxed{D^\gamma(R)} \end{pmatrix}$$

$$\chi^\ell\left(\frac{2\pi}{n}\right) = \frac{\sin\frac{(2\ell+1)\pi}{n}}{\sin\frac{\pi}{n}}$$

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

$$\chi^\ell(\Theta) = \frac{\sin(\ell+\frac{1}{2})\Theta}{\sin\frac{\Theta}{2}}$$

$\chi^\ell(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
1	3	-1	-1	-1
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8	17	1	1	1

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
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B_2	1	-1	-1	1

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
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	5	1	1	1
$2\chi^{A_1}(\mathbf{g})=$	2	2	2	2
$1\chi^{A_2}(\mathbf{g})=$	1	-1	1	-1
$1\chi^{B_1}(\mathbf{g})=$	1	1	-1	-1
$1\chi^{B_2}(\mathbf{g})=$	1	-1	-1	1

trial&error??

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* *D*$_2$ of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Review 1. *Review of angular momentum cone geometry*

Review 2. *Review of Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions*

Review 3. *Review of RES and Multipole* $\mathbf{T}_q^k$ *tensor expansions*

Energy levels and RES of symmetric rotors: prolate vs. oblate cases

RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D$_2$ *symmetry labels)*

Asymmetric rotor is not Unsymmetric rotor

Polygonal algebra & geometry of U(2)$\supset$*C*$_N$ *character spectral function*

Algebra of geometric series. *Geometry of algebraic series*

Molecular (2ℓ+1)-multiplet D$_2$*-level splitting* *Examples: ℓ=1, 2, 3,…*

j,m,n formulas for momentum operator matrix elements:Hamiltonian matrix for asymmetric rotor

(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*

Completing diagonalization from new D$_2$ *basis:*

J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group$\supset$*Sub-group correlation*

Molecular (2ℓ+1)-multiplet D₂-level splitting

Example: (ℓ=1)

and: (ℓ=2)

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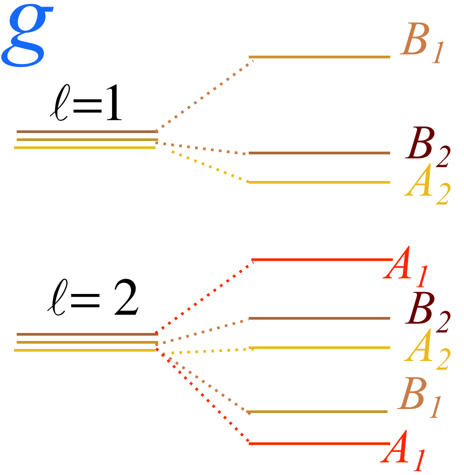

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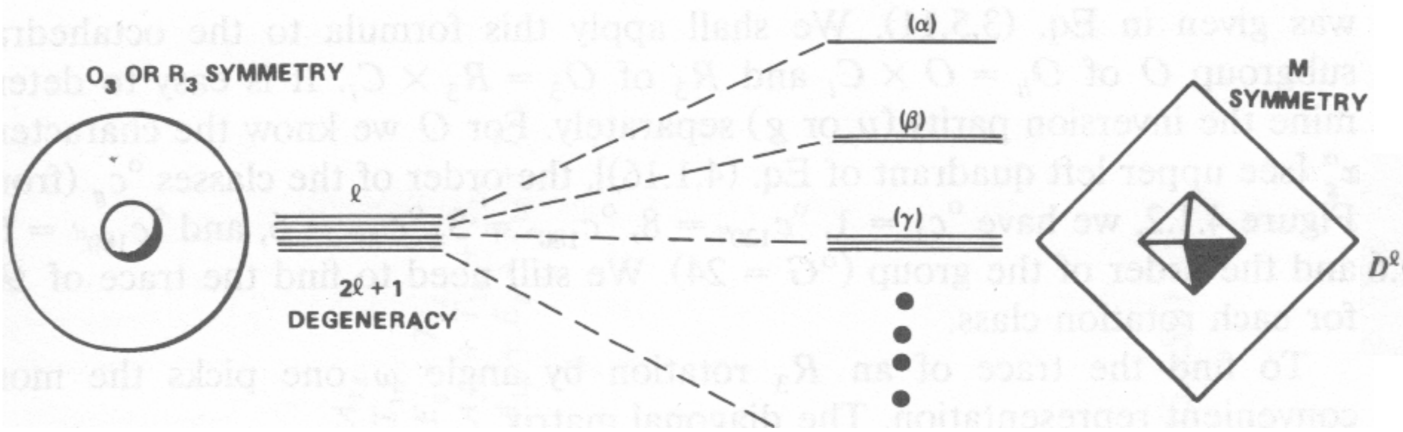

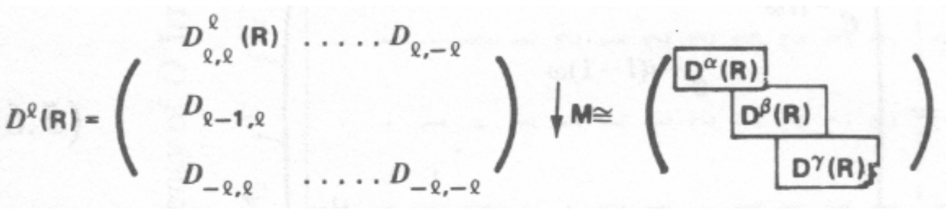

$$D^{\ell}(R) = \begin{pmatrix} D^{\ell}_{\ell,\ell}(R) & \ldots\ldots & D_{\ell,-\ell} \\ D_{\ell-1,\ell} & & \\ D_{-\ell,\ell} & \ldots\ldots & D_{-\ell,-\ell} \end{pmatrix} \Big\downarrow M \cong \begin{pmatrix} D^{\alpha}(R) & & \\ & D^{\beta}(R) & \\ & & D^{\gamma}(R) \end{pmatrix}$$

U(2) characters
from Lecture 15 p.110 :

$\chi^{\ell}(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
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...this Lect.10 p.25
D₂ characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
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where: 2ℓ+1
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$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
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f-formula better than trial&error

$$\frac{1}{4}\begin{array}{|cc|cc|} 1 & 1 & 1 & 1 \\ \hline 5 & 1 & 1 & 1 \end{array} = \frac{5+1+1+1}{4} = 2$$

$$\frac{1}{4}\begin{array}{|cc|cc|} 1 & -1 & 1 & -1 \\ \hline 5 & 1 & 1 & 1 \end{array} = \frac{5-1+1-1}{4} = 1$$

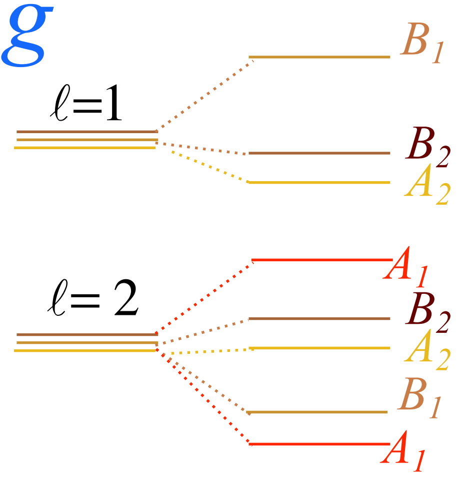
Molecular (2ℓ+1)-multiplet D_2-level splitting

Example: (ℓ=1)

and: (ℓ=2)

and: (ℓ=3)

$$f^{(b)}=\frac{1}{{}^{\circ}D_2}\sum_{\substack{\text{classes}\\ \kappa_k\in D_2}} {}^{\circ}\kappa_k\,\chi_k^{(b)*}\chi_k^{(\ell)}=\frac{1}{4}\sum_{g\in D_2}^{4}\chi_k^{(b)*}\chi_k^{(\ell)}$$



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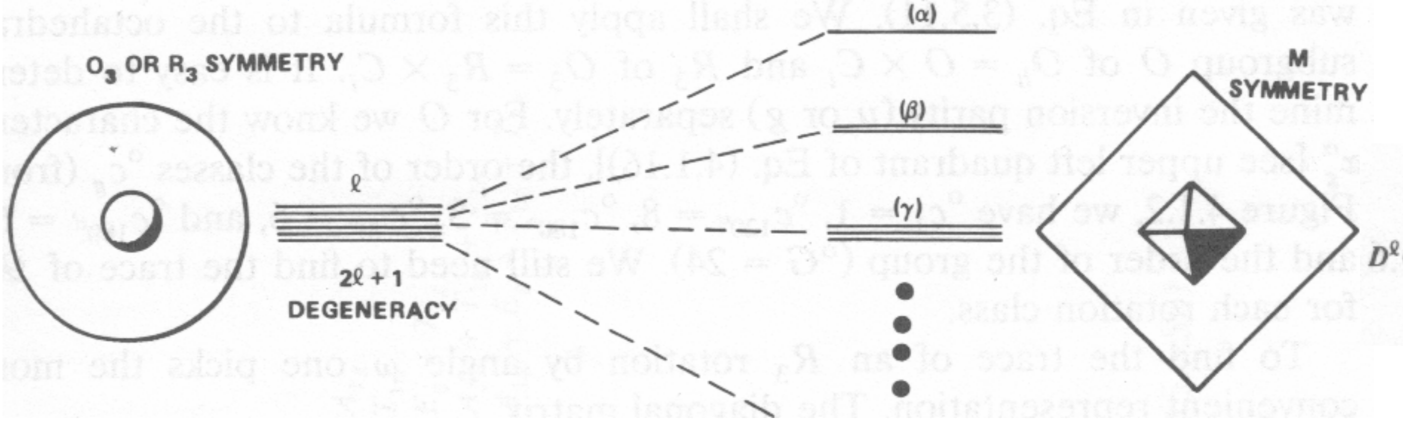

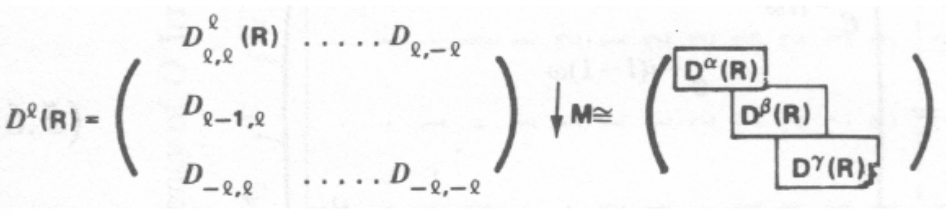

$$\chi^{\ell}\left(\frac{2\pi}{n}\right)=\frac{\sin\frac{(2\ell+1)\pi}{n}}{\sin\frac{\pi}{n}}$$

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where: 2ℓ+1

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$$\frac{1}{4}\begin{array}{|cc|cc|}\hline 1 & -1 & 1 & -1\\ \hline 7 & -1 & -1 & -1\\ \hline\end{array}=\frac{7+1-1+1}{4}=2$$

Molecular (2ℓ+1)-multiplet D₂-level splitting

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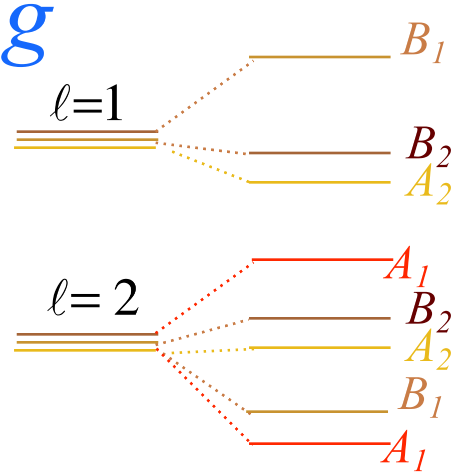
and: (ℓ=3) etc.



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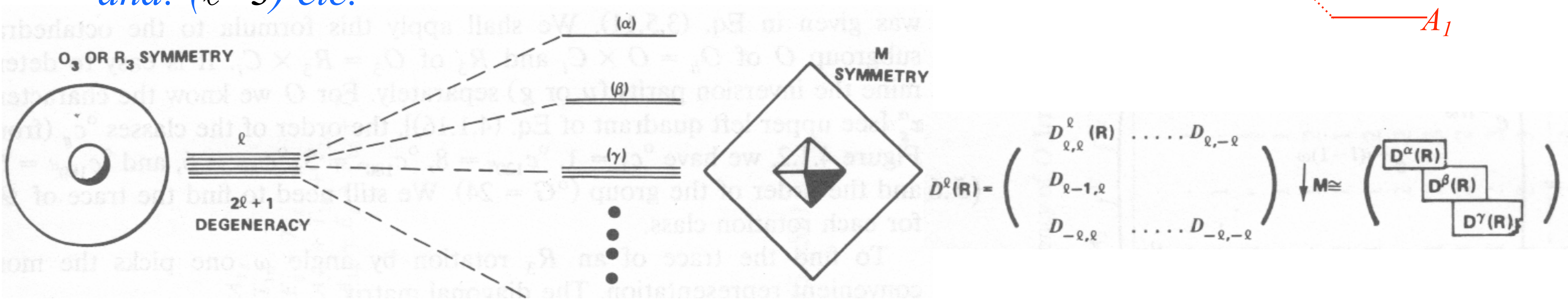

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…this Lect.10 p.25
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6	4	3	3	3	$4A_1 \oplus 3A_2 \oplus 3B_1 \oplus 3B_2$
7	3	4	4	4	$3A_1 \oplus 4A_2 \oplus 4B_1 \oplus 4B_2$

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* D_2 of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 *symmetry labels)*

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Completing diagonalization from new D_2 *basis:*

J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group⊃Sub-group correlation

j,*m*,*n* formulas for momentum operator matrix elements

$$n_\uparrow = j+m \quad , \quad n_\downarrow = j-m$$

$$\left|\begin{smallmatrix} j \\ m \end{smallmatrix}\right\rangle = \frac{(\mathbf{a}^\dagger_\uparrow)^{j+m}(\mathbf{a}^\dagger_\downarrow)^{j-m}}{\sqrt{(j+m)!}\sqrt{(j-m)!}}\left|0,0\right\rangle = \frac{\left|n_\uparrow,n_\downarrow\right\rangle}{\sqrt{(n_\uparrow)!}\sqrt{(n_\downarrow)!}}$$

$$\begin{array}{l} \mathbf{a}^\dagger_\uparrow\mathbf{a}_\downarrow\left|n_\uparrow,n_\downarrow\right\rangle=\sqrt{n_\uparrow+1}\sqrt{n_\downarrow}\left|n_\uparrow+1\ n_\downarrow-1\right\rangle \\ \mathbf{a}^\dagger_\downarrow\mathbf{a}_\uparrow\left|n_\uparrow,n_\downarrow\right\rangle=\sqrt{n_\uparrow}\sqrt{n_\downarrow+1}\left|n_\uparrow-1\ n_\downarrow+1\right\rangle \end{array} \boxed{\begin{array}{l} \Rightarrow \mathbf{J}_+\left|\begin{smallmatrix} j \\ m \end{smallmatrix}\right\rangle=\sqrt{j+m+1}\sqrt{j-m}\left|\begin{smallmatrix} j \\ m+1 \end{smallmatrix}\right\rangle \\ \Rightarrow \mathbf{J}_-\left|\begin{smallmatrix} j \\ m \end{smallmatrix}\right\rangle=\sqrt{j+m}\sqrt{j-m+1}\left|\begin{smallmatrix} j \\ m-1 \end{smallmatrix}\right\rangle \end{array}}$$

$$\mathbf{a}^\dagger_\uparrow\mathbf{a}_\downarrow = \mathbf{J}_+ = \mathbf{J}_X + i\mathbf{J}_Y$$

$$\mathbf{a}^\dagger_\downarrow\mathbf{a}_\uparrow = \mathbf{J}_- = \mathbf{J}_X - i\mathbf{J}_Y = \mathbf{J}^\dagger_+$$

$$\mathbf{J}_X = \tfrac{1}{2}[\mathbf{J}_+ + \mathbf{J}_-]$$

$$\mathbf{J}_Y = \tfrac{-i}{2}[\mathbf{J}_+ - \mathbf{J}_-]$$

LAB matrix elements use the usual atomic formula:

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_X\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = D^J_{m',m}\ (\mathbf{J}_X)\delta_{n'n} = \tfrac{1}{2}\ \left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)}+\delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\ \delta_{n'n}$$

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_Y\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = D^J_{m',m}\ (\mathbf{J}_Y)\delta_{n'n} = \tfrac{-i}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)}-\delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\ \delta_{n'n}$$

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_Z\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = D^J_{m',m}\ (\mathbf{J}_Z)\delta_{n'n} = \delta_{m'm}m\ \delta_{n'n}$$

BOD matrix elements are the same after switching *m's* into *n's*

and changing sign of $\mathbf{J}_Y$ matrix (*-conjugation)

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_{\bar{X}}\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = \delta_{m'm}D^J_{n',n}{}^*(\mathbf{J}_{\bar{X}}) = \tfrac{1}{2}\ \ \delta_{m'm}\left[\sqrt{(j-n)(j+n+1)}\delta_{n'n+1}+\sqrt{(j+n)(j-n+1)}\delta_{n'n-1}\right]$$

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_{\bar{Y}}\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = \delta_{m'm}D^J_{n',n}{}^*(\mathbf{J}_{\bar{Y}}) = \tfrac{+i}{2}\ \delta_{m'm}\left[\sqrt{(j-n)(j+n+1)}\delta_{n'n+1}-\sqrt{(j+n)(j-n+1)}\delta_{n'n-1}\right]$$

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_{\bar{Z}}\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = \delta_{m'm}D^J_{n',n}{}^*(\mathbf{J}_{\bar{Z}}) = \delta_{m'm}n\ \delta_{n'n}$$

(Go to Lecture 26 p. 26 to 29 to…)

Hamiltonian matrix for asymmetric rotor

$$\mathbf{H}=\tfrac{1}{2}\left(\frac{\mathbf{J}_{\bar{X}}^{\ 2}}{I_{\bar{X}}}+\frac{\mathbf{J}_{\bar{Y}}^{\ 2}}{I_{\bar{Y}}}+\frac{\mathbf{J}_{\bar{Z}}^{\ 2}}{I_{\bar{Z}}}\right)=A\mathbf{J}_{\bar{X}}^{2}+B\mathbf{J}_{\bar{Y}}^{2}+C\mathbf{J}_{\bar{Z}}^{2}$$

First are matrix formulas for BOD J^2 components.

$$\mathbf{J}_{\bar{X}}^{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle=\tfrac{1}{2}\sqrt{(j-n)(j+n+1)}\,\mathbf{J}_{\bar{X}}\left|\begin{smallmatrix}J\\ m,n+1\end{smallmatrix}\right\rangle \qquad =\tfrac{1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle+\tfrac{1}{4}(j-n)(j+n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

$$+\tfrac{1}{2}\sqrt{(j+n)(j-n+1)}\,\mathbf{J}_{\bar{X}}\left|\begin{smallmatrix}J\\ m,n-1\end{smallmatrix}\right\rangle \qquad +\tfrac{1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle+\tfrac{1}{4}(j+n)(j-n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

$$=\frac{\sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle+\frac{j(j+1)-n^2}{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle+\frac{\sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle$$

$$\mathbf{J}_{\bar{Y}}^{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle=\tfrac{i}{2}\sqrt{(j-n)(j+n+1)}\,\mathbf{J}_{\bar{Y}}\left|\begin{smallmatrix}J\\ m,n+1\end{smallmatrix}\right\rangle \qquad =\tfrac{-1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle+\tfrac{1}{4}(j-n)(j+n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

$$-\tfrac{i}{2}\sqrt{(j+n)(j-n+1)}\,\mathbf{J}_{\bar{Y}}\left|\begin{smallmatrix}J\\ m,n-1\end{smallmatrix}\right\rangle \qquad \tfrac{-1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle+\tfrac{1}{4}(j+n)(j-n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

$$=-\frac{\sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle+\frac{j(j+1)-n^2}{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle-\frac{\sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle$$

$$\mathbf{J}_{\bar{Z}}^{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle=n^2\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

This gives the rigid asymmetric-top matrix formula for general *A*, *B*, *C* and *J*,*n*.:

$$(A\mathbf{J}_{\bar{X}}^{2}+B\mathbf{J}_{\bar{Y}}^{2}+C\mathbf{J}_{\bar{Z}}^{2})\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle=$$

$$=(A\text{-}B)\frac{\sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle+\left[(A+B)\frac{j(j+1)-n^2}{2}+Cn^2\right]\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle+(A\text{-}B)\frac{\sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle$$

(Go to Lecture 26 p. 26 to 29 to…)

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* *D₂* of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Review 1. *Review of angular momentum cone geometry*

Review 2. *Review of Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions*

Review 3. *Review of RES and Multipole $\mathbf{T}_q^k$ tensor expansions*

Energy levels and RES of symmetric rotors: prolate vs. oblate cases

RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 symmetry labels)

Asymmetric rotor is not Unsymmetric rotor

Polygonal algebra & geometry of $U(2)\supset C_N$ character spectral function

Algebra of geometric series. *Geometry of algebraic series*

Molecular $(2\ell+1)$-multiplet D_2-level splitting *Examples: $\ell=1, 2, 3,\ldots$*

j,m,n formulas for momentum operator matrix elements:Hamiltonian matrix for asymmetric rotor

(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*

Completing diagonalization from new D_2 basis:

J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group$\supset$Sub-group correlation

(*J=1*)-Matrix for *A=1*, *B=2*, *C=3*.

$$\left\langle \begin{smallmatrix}1\\ m,n'\end{smallmatrix} \middle| \mathbf{J}_{\bar{X}} \middle| \begin{smallmatrix}1\\ m,n\end{smallmatrix} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle \begin{smallmatrix}1\\ m,n'\end{smallmatrix} \middle| \mathbf{J}_{\bar{Y}} \middle| \begin{smallmatrix}1\\ m,n\end{smallmatrix} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle \begin{smallmatrix}1\\ m,n'\end{smallmatrix} \middle| \mathbf{J}_{\bar{Z}} \middle| \begin{smallmatrix}1\\ m,n\end{smallmatrix} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle \begin{smallmatrix}1\\ m,n'\end{smallmatrix} \middle| \mathbf{J}^2_{\bar{X}} \middle| \begin{smallmatrix}1\\ m,n\end{smallmatrix} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle \begin{smallmatrix}1\\ m,n'\end{smallmatrix} \middle| \mathbf{J}^2_{\bar{Y}} \middle| \begin{smallmatrix}1\\ m,n\end{smallmatrix} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle \begin{smallmatrix}1\\ m,n'\end{smallmatrix} \middle| \mathbf{J}^2_{\bar{Z}} \middle| \begin{smallmatrix}1\\ m,n\end{smallmatrix} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

(J=1)-Matrix for A=1, B=2, C=3.

$$\left\langle {1 \atop m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {1 \atop m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {1 \atop m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {1 \atop m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {1 \atop m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {1 \atop m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {1 \atop m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {1 \atop m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

($J=1$)-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle {1 \atop m,n'} \right| \mathbf{J}_{\bar{X}} \left| {1 \atop m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \right| \mathbf{J}_{\bar{Y}} \left| {1 \atop m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \right| \mathbf{J}_{\bar{Z}} \left| {1 \atop m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {1 \atop m,n'} \right| \mathbf{J}^2_{\bar{X}} \left| {1 \atop m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \right| \mathbf{J}^2_{\bar{Y}} \left| {1 \atop m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {1 \atop m,n'} \right| \mathbf{J}^2_{\bar{Z}} \left| {1 \atop m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

eigen-values: $(B+C=5,\quad A+B=3,\quad A+C=4)$

eigen-vectors:
$$\begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & +1/\sqrt{2} \end{pmatrix}$$

(*J*=*1*)-Matrix for *A*=*1*, *B*=*2*, *C*=*3*.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ -\frac{i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & -\frac{i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

eigen-values: $(B+C=5, \quad A+B=3, \quad A+C=4)$

eigen-vectors:
$$\begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & +1/\sqrt{2} \end{pmatrix}$$

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

(*J*=*1*)-Matrix for *A*=*1*, *B*=*2*, *C*=*3*.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

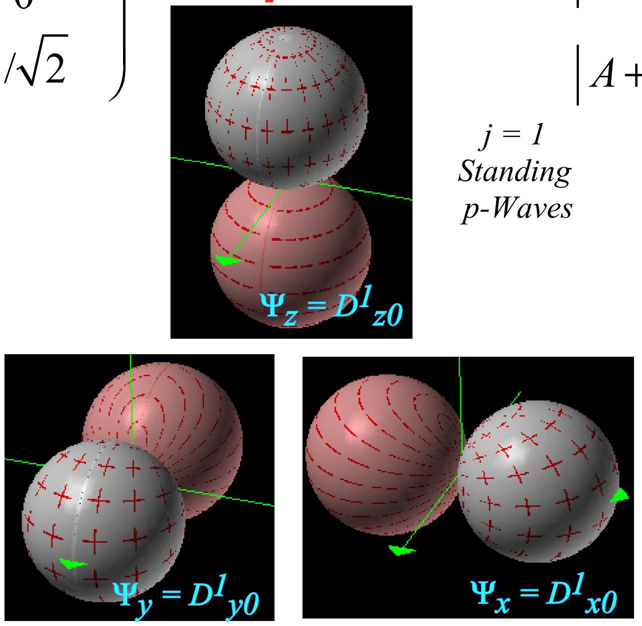
eigen-values: $(B+C=5, \quad A+B=3, \quad A+C=4)$

eigen-vectors: $\begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & +1/\sqrt{2} \end{pmatrix}$

$\left|B+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \quad -1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$ *y-like*

$\left|A+B\right\rangle = \quad +\left|{}^{1}_{m,0}\right\rangle$ *z-like*

$\left|A+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \quad +1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$ *x-like*



j = 1
Standing
p-Waves

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Body-based J=1
vector-like eigenfunctions

($J=1$)-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ -\frac{i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & -\frac{i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

eigen-values: $(B+C=5,\quad A+B=3,\quad A+C=4)$

eigen-vectors: $\begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & +1/\sqrt{2} \end{pmatrix}$

$$\left|B+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \quad - 1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$$

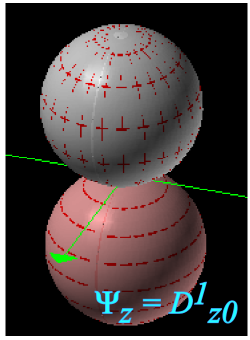
y-like

$$\left|A+B\right\rangle = \quad +\left|{}^{1}_{m,0}\right\rangle$$

z-like

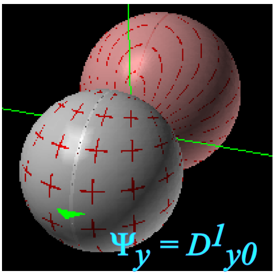
$$\left|A+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \quad +1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$$

x-like

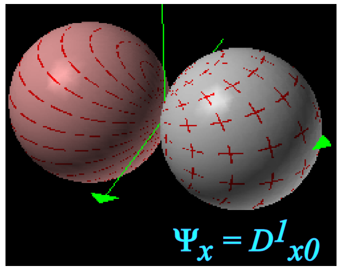


B_2

j = 1
Standing
p-Waves



A_2



B_1

Body-based J=1
vector-like eigenfunctions

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Rotational Energy Surfaces (RES) and Lab vs Body molecular rotor states, levels, and spectra: Body symmetry *R(2)* of prolate & oblate rotors *vs.* D_2 of asymmetric rotor $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Review 1. *Review of angular momentum cone geometry*
Review 2. *Review of Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions*
Review 3. *Review of RES and Multipole $\mathbf{T}_q^k$ tensor expansions*

Energy levels and RES of symmetric rotors: prolate vs. oblate cases
RES of prolate and oblate rotor vs. asymmetric rotor (Introducing D_2 symmetry labels)
Asymmetric rotor is not Unsymmetric rotor

Polygonal algebra & geometry of $U(2)\supset C_N$ character spectral function
Algebra of geometric series. *Geometry of algebraic series*
Molecular $(2\ell+1)$-multiplet D_2-level splitting *Examples: $\ell=1, 2, 3,\ldots$*

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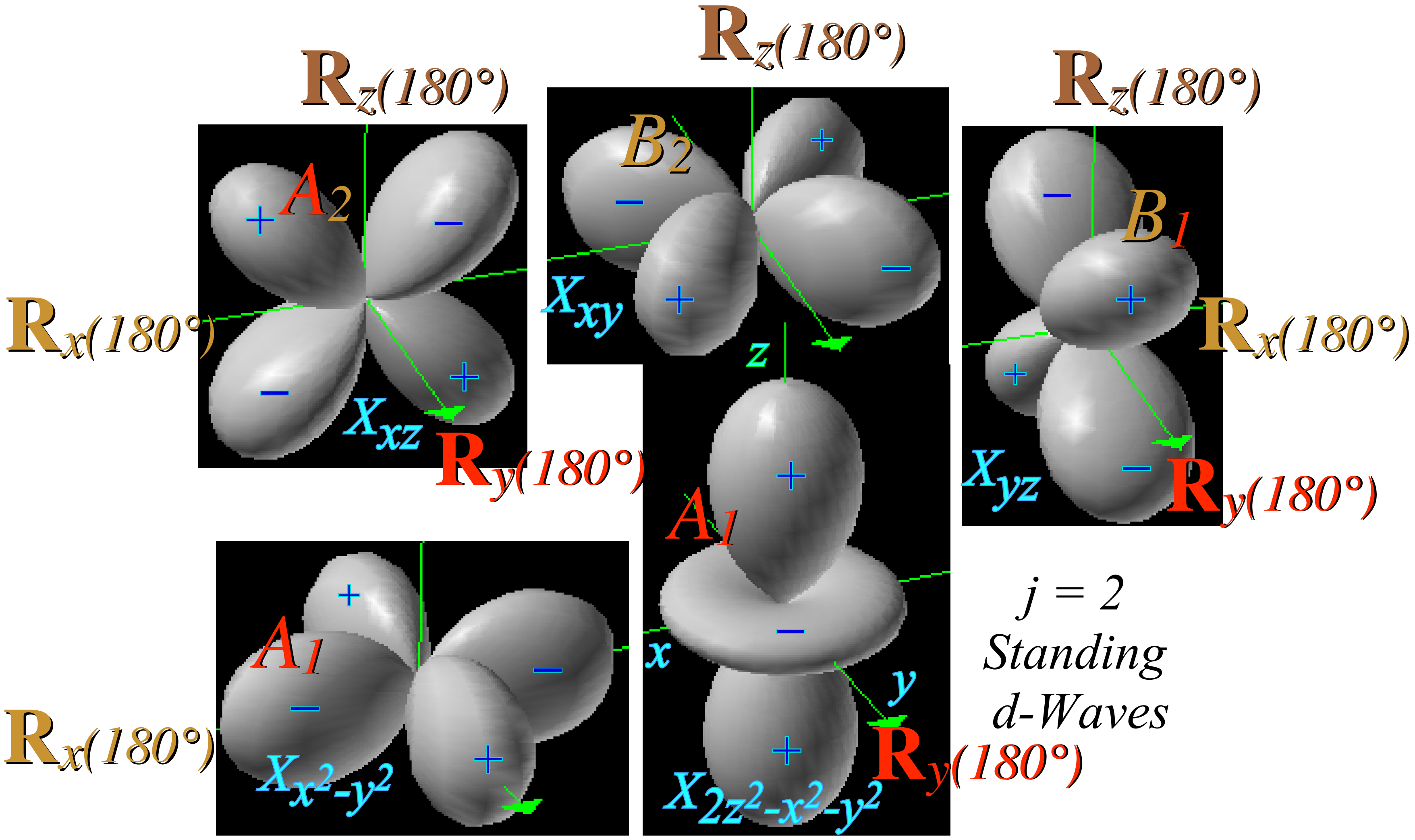
Completing diagonalization from new D_2 basis:
J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

Examples of Group$\supset$Sub-group correlation

(*J*=2)-Matrix for *A*=*1*, *B*=*2*, *C*=*3*.

$$\left\langle A\mathbf{J}_{\bar{X}}^2 + B\mathbf{J}_{\bar{Y}}^2 + C\mathbf{J}_{\bar{Z}}^2 \right\rangle^{J=2} = \begin{pmatrix} (A+B)+4C & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & \cdot \\ \cdot & \frac{5}{2}(A+B)+C & \cdot & \frac{3}{2}(A-B) & \cdot \\ \frac{\sqrt{6}}{2}(A-B) & \cdot & 3(A+B) & \cdot & \frac{\sqrt{6}}{2}(A-B) \\ \cdot & \frac{3}{2}(A-B) & \cdot & \frac{5}{2}(A+B)+C & \cdot \\ \cdot & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & (A+B)+4C \end{pmatrix} = \begin{pmatrix} 15 & & \frac{-\sqrt{6}}{2} & & \\ & \frac{15}{2} & & \frac{-3}{2} & \\ \frac{-\sqrt{6}}{2} & & 6 & & \frac{-\sqrt{6}}{2} \\ & \frac{-3}{2} & & \frac{15}{2} & \\ & & \frac{-\sqrt{6}}{2} & & 15 \end{pmatrix}$$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1



j = 2
Standing
d-Waves

$(J=2)$-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle A\mathbf{J}^2_{\bar{X}}+B\mathbf{J}^2_{\bar{Y}}+C\mathbf{J}^2_{\bar{Z}}\right\rangle^{J=2}=\begin{pmatrix} (A+B)+4C & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & \cdot \\ \cdot & \frac{5}{2}(A+B)+C & \cdot & \frac{3}{2}(A-B) & \cdot \\ \frac{\sqrt{6}}{2}(A-B) & \cdot & 3(A+B) & \cdot & \frac{\sqrt{6}}{2}(A-B) \\ \cdot & \frac{3}{2}(A-B) & \cdot & \frac{5}{2}(A+B)+C & \cdot \\ \cdot & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & (A+B)+4C \end{pmatrix}=\begin{pmatrix} 15 & & \frac{-\sqrt{6}}{2} & & \\ & \frac{15}{2} & & \frac{-3}{2} & \\ -\frac{\sqrt{6}}{2} & & 6 & & -\frac{\sqrt{6}}{2} \\ & \frac{-3}{2} & & \frac{15}{2} & \\ & & -\frac{\sqrt{6}}{2} & & 15 \end{pmatrix}$$

Matrix is nearly diagonalized in standing-wave D_2-symmetry basis

$$\left|A_1 2^+\right\rangle=\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+2\end{matrix}\right\rangle+\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-2\end{matrix}\right\rangle,\quad \left|B_1 1^+\right\rangle=\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+1\end{matrix}\right\rangle+\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-1\end{matrix}\right\rangle,\quad \left|A_1 0\right\rangle=\left|\begin{matrix}2\\0\end{matrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle=\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+2\end{matrix}\right\rangle-\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-2\end{matrix}\right\rangle,\quad \left|A_2 1^-\right\rangle=\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+1\end{matrix}\right\rangle-\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-1\end{matrix}\right\rangle$$

The following basis transformation "almost diagonalizes" $\langle\mathbf{H}\rangle^{J=2}$ by reducing it to block form.

Let: $\Sigma=A+B$ and $\Delta=A-B$ to shorten expressions.

$(J=2)$-Matrix for general A, B, C.

$$\left(\tfrac{1}{\sqrt{2}}\right)\begin{pmatrix} 1 & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & -1 \\ \cdot & 1 & \cdot & 1 & \cdot \\ \cdot & 1 & \cdot & -1 & \cdot \\ \cdot & \cdot & \sqrt{2} & \cdot & \cdot \end{pmatrix}\begin{pmatrix} 4C-\Sigma & \cdot & \frac{\sqrt{6}\Delta}{2} & \cdot & \cdot \\ \cdot & C+\frac{\Sigma}{2} & \cdot & \frac{3\Delta}{2} & \cdot \\ \frac{\sqrt{6}\Delta}{2} & \cdot & \Sigma & \cdot & \frac{\sqrt{6}\Delta}{2} \\ \cdot & \frac{3\Delta}{2} & \cdot & C+\frac{\Sigma}{2} & \cdot \\ \cdot & \cdot & \frac{\sqrt{6}\Delta}{2} & \cdot & 4C-\Sigma \end{pmatrix}\begin{pmatrix} 1 & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \sqrt{2} \\ \cdot & \cdot & 1 & -1 & \cdot \\ 1 & -1 & \cdot & \cdot & \cdot \end{pmatrix}\left(\tfrac{1}{\sqrt{2}}\right)+2\Sigma\mathbf{1}$$

$$=\begin{pmatrix} 4C+\Sigma & \cdot & \cdot & \cdot & \sqrt{3}\Delta \\ \cdot & 4C+\Sigma & \cdot & \cdot & \cdot \\ \cdot & \cdot & C+\frac{5\Sigma}{2}+\frac{3\Delta}{2} & \cdot & \cdot \\ \cdot & \cdot & \cdot & C+\frac{5\Sigma}{2}-\frac{3\Delta}{2} & \cdot \\ \sqrt{3}\Delta & \cdot & \cdot & \cdot & 3\Sigma \end{pmatrix}=\begin{pmatrix} 4C+A+B & \cdot & \cdot & \cdot & \sqrt{3}(A-B) \\ \cdot & 4C+A+B & \cdot & \cdot & \cdot \\ \cdot & \cdot & C+4A+B & \cdot & \cdot \\ \cdot & \cdot & \cdot & C+A+4B & \cdot \\ \sqrt{3}(A-B) & \cdot & \cdot & \cdot & 3A+3B \end{pmatrix}$$

New D_2 basis:

$$\left|A_1 2^+\right\rangle=\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+2\end{matrix}\right\rangle+\frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-2\end{matrix}\right\rangle$$

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$$\left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2$^+$)

$$\begin{pmatrix} 4C+A+B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & 3A+3B \end{pmatrix} \begin{matrix} \left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle \\ \left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle \end{matrix}$$

$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

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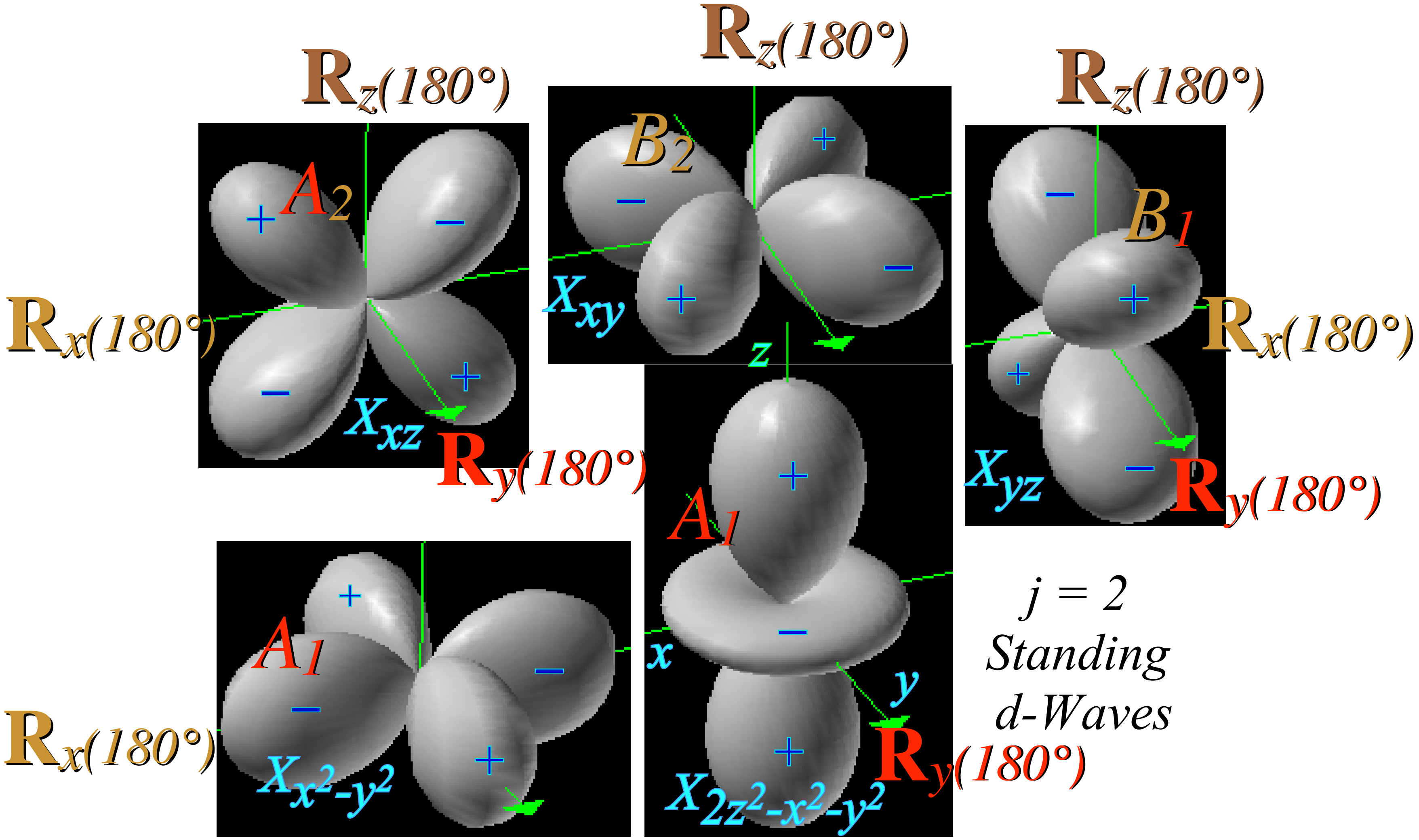

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Standing
d-Waves

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$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

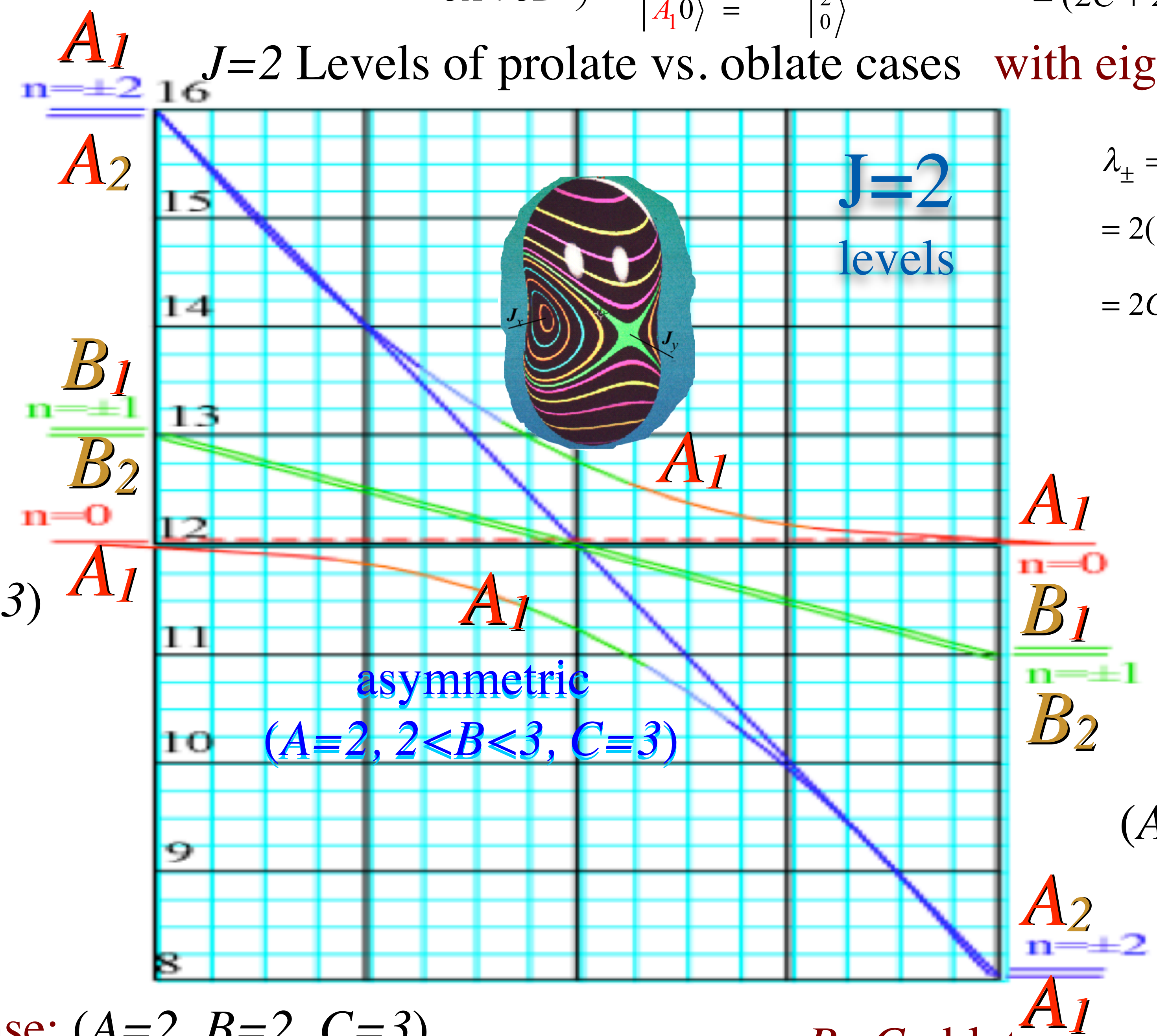
with eigenvalues:

$$\lambda_{\pm} = 2C+2A+2B \pm \sqrt{(2C-A-B)^2 + 3(A-B)^2}$$

$$= 2(A+B+C) \pm 2\sqrt{C^2 - (A+B)C + A^2 - AB + B^2}$$

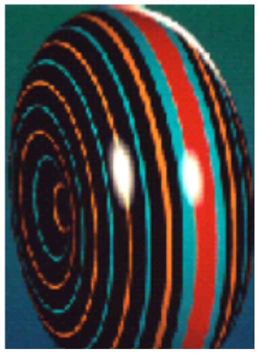
$$= 2C+4B \pm 2(C-B) = \begin{cases} 4C+2B \\ 6B \end{cases} \text{if: } A=B$$

J=2 Levels of prolate vs. oblate cases



prolate
(*A*=2, *B*=2, *C*=3)

oblate
(*A*=2, *B*=3, *C*=3



A=*B* prolate case: (*A*=2, *B*=2, *C*=3)

B(*J*(*J*+1) +(*C*-*B*)n^2=2*B*+4*C*=4+12=16 (*n*=±2)

5*B*+*C*=10+3=13 (*n*=±1) , 6*B*=12 (*n*=0)

B=*C* oblate case: (*A*=1, *B*=2, *C*=2)

B(*J*(*J*+1) +(*A*-*B*)n^2=2*B*+4*A*=4+4=8 (*n*=±2)

5*B*+*A*=10+1=11 (*n*=±1) , 6*B*=12 (*n*=0)

Completing diagonalization from new D_2 basis:

$$\begin{pmatrix} 4C+A+B & \cdot & \cdot & \cdot & \sqrt{3}(A-B) \\ \cdot & 4C+A+B & \cdot & \cdot & \cdot \\ \cdot & \cdot & C+4A+B & \cdot & \cdot \\ \cdot & \cdot & \cdot & C+A+4B & \cdot \\ \sqrt{3}(A-B) & \cdot & \cdot & \cdot & 3A+3B \end{pmatrix}$$

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$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

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Need only diagonalize the two A_1's:

(It is n=0 versus n=2^+)

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$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

with eigenvalues:

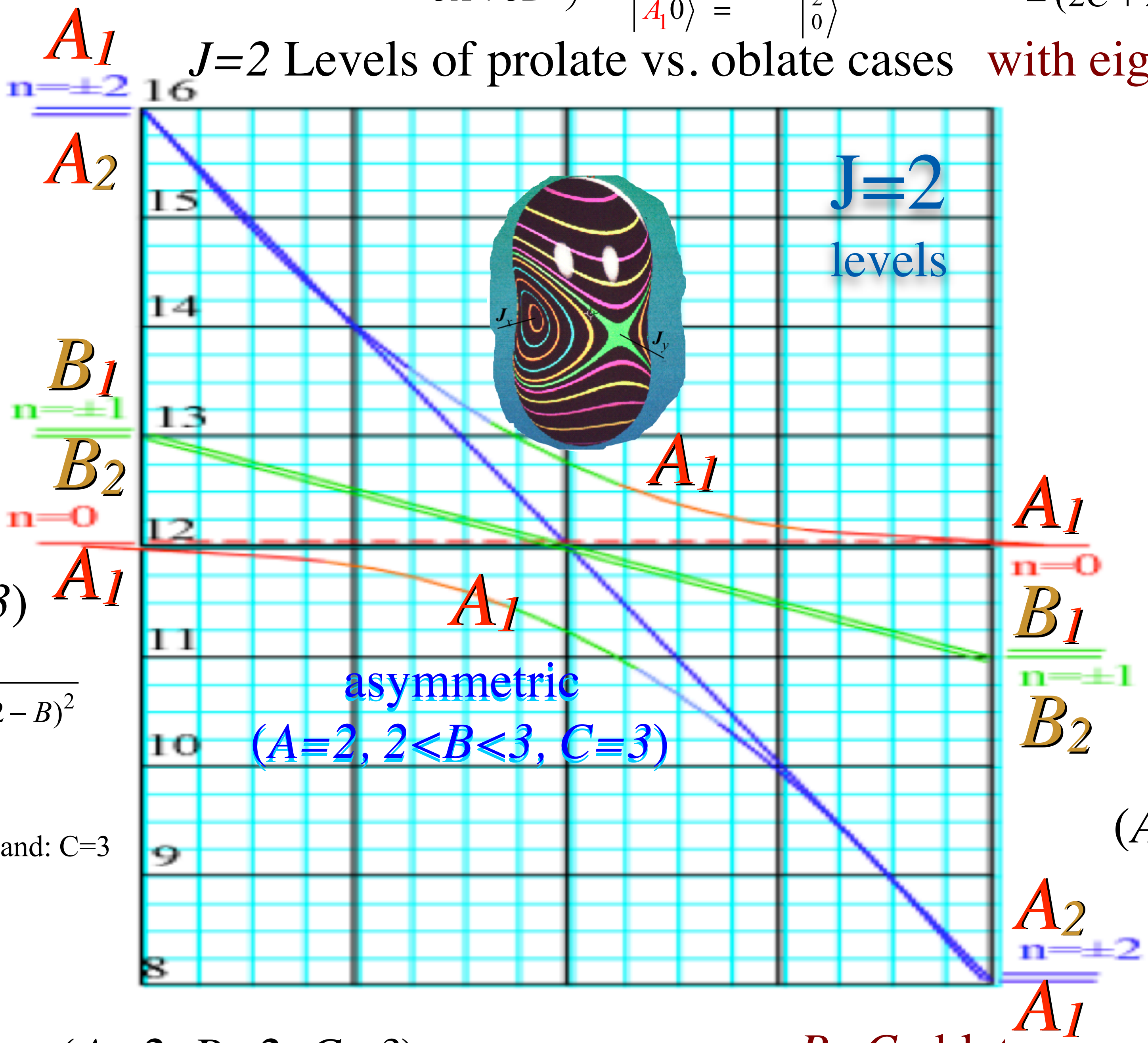
$$\begin{pmatrix} 14+B & \sqrt{3}(2-B) \\ \sqrt{3}(2-B) & 6+3B \end{pmatrix} =$$

$$(10+2B)\cdot\mathbf{1} + \begin{pmatrix} 4-B & \sqrt{3}(2-B) \\ \sqrt{3}(2-B) & -(4-B) \end{pmatrix}$$

J=2 Levels of prolate vs. oblate cases

prolate

(*A*=2, *B*=2, *C*=3)



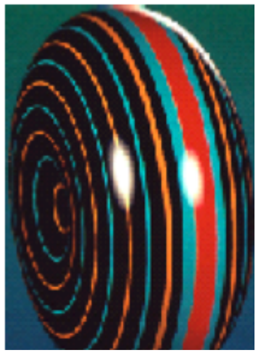
$$\lambda_\pm = 10+2B \pm \sqrt{(4-B)^2+3(2-B)^2}$$

$$= 2(5+B) \pm 2\sqrt{7-5B+B^2}$$

$$= 14 \pm 2 = \begin{cases} 16 & \text{if: } A=B=2 \text{ and: C=3} \\ 12 & \end{cases}$$

oblate

(*A*=2, *B*=3, *C*=3



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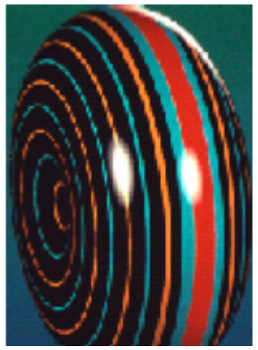
$J=20$ example of asymmetry levels

C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

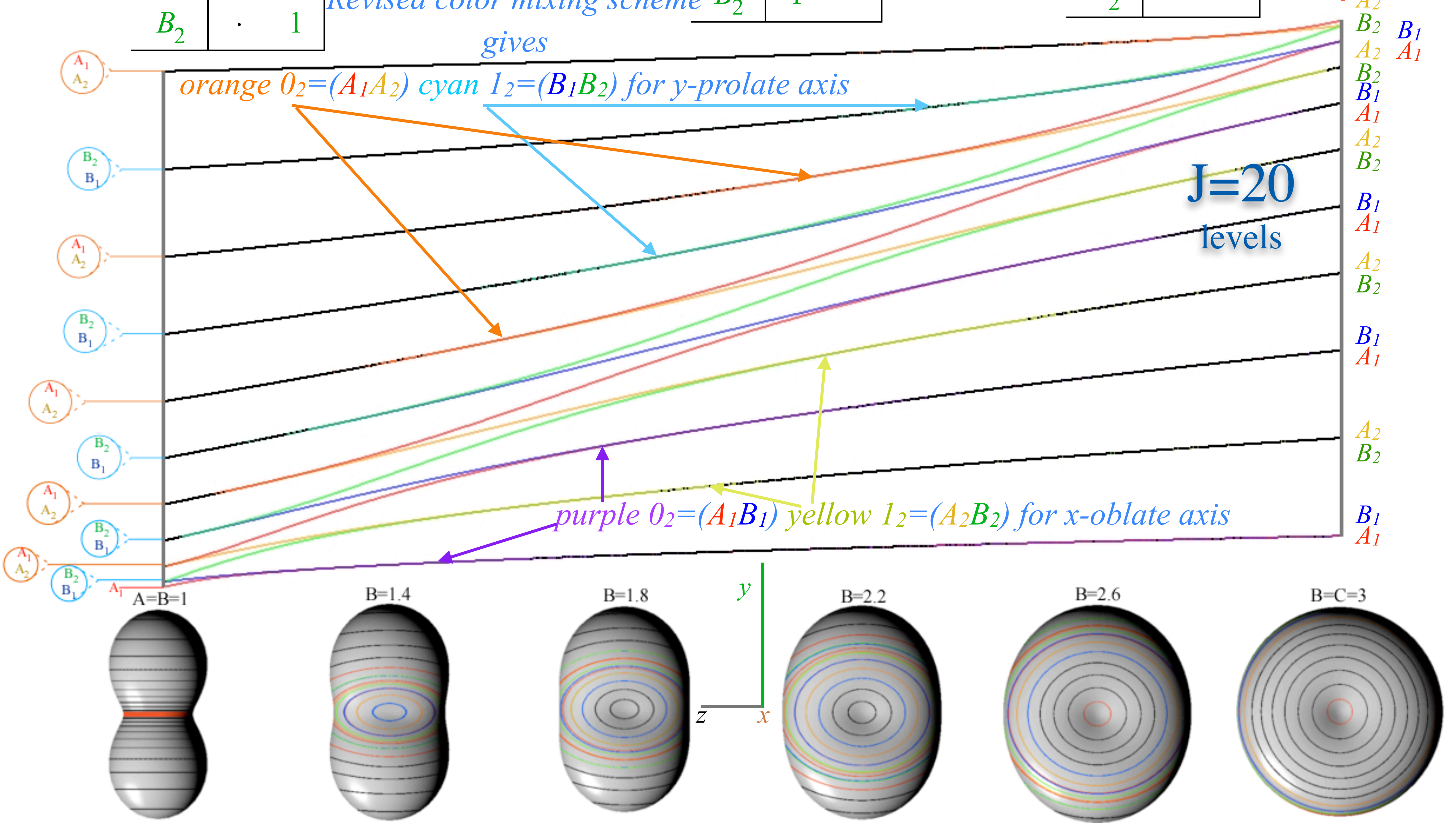
D_2	**1**	**R_x**	**R_y**	**R_z**
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1



Revised color mixing scheme gives



orange $0_2=(A_1A_2)$ cyan $1_2=(B_1B_2)$ for y-prolate axis

purple $0_2=(A_1B_1)$ yellow $1_2=(A_2B_2)$ for x-oblate axis

(Revised color mixing scheme used here)

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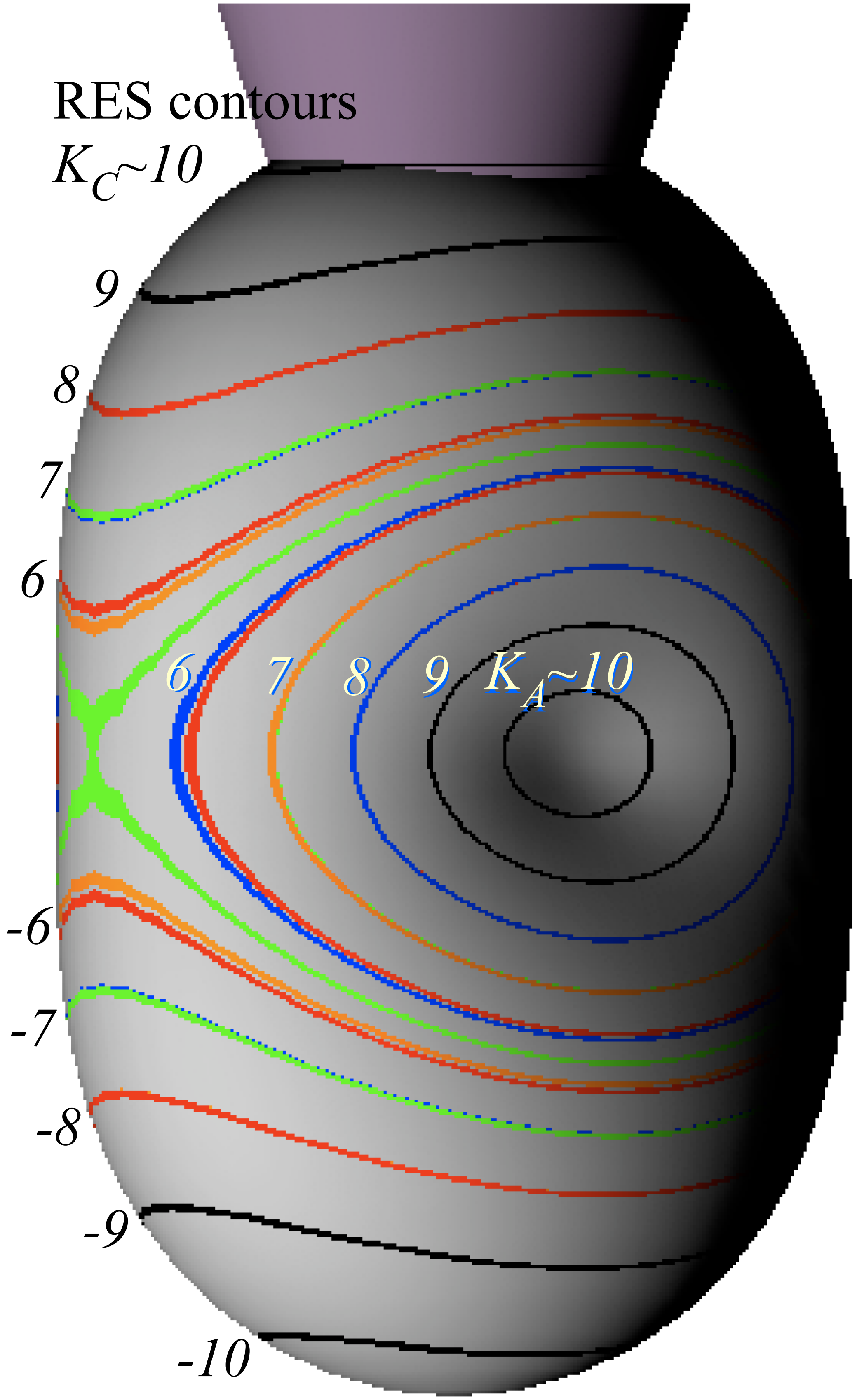
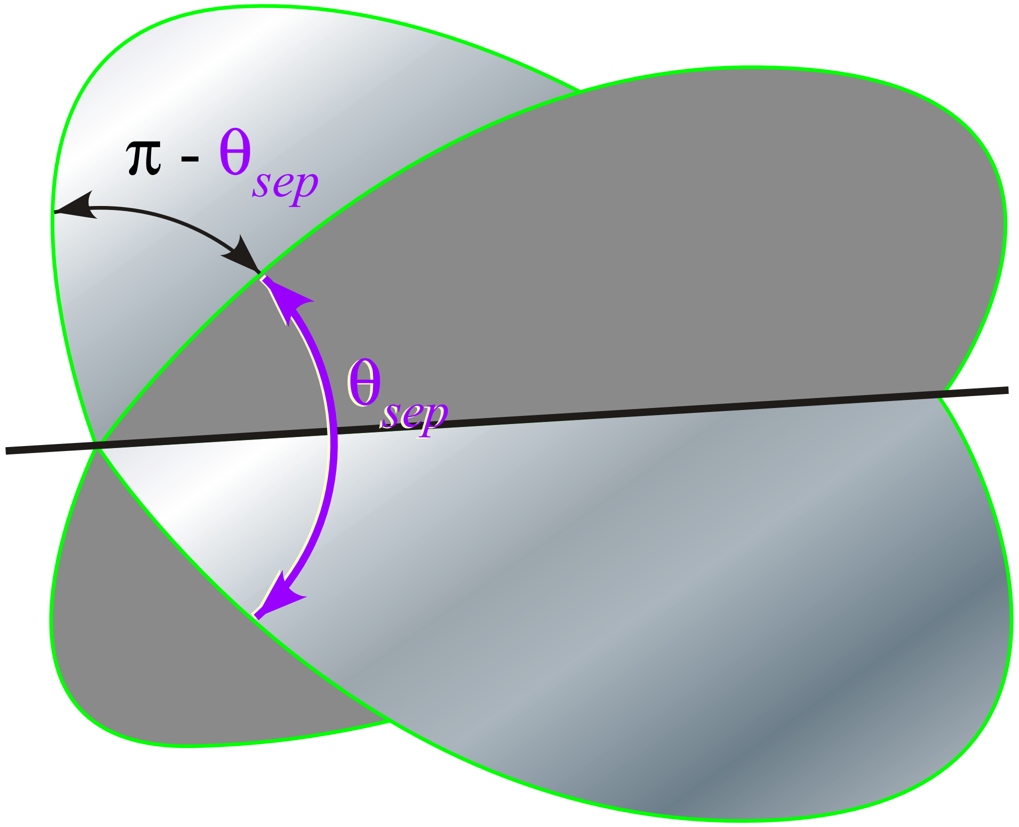


RES contours K_C~10

Separatrix circle pair
dihedral angle

$$\theta_{sep} = \text{atan}\left(\frac{A-B}{B-C}\right)$$



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Algebra of geometric series. *Geometry of algebraic series*

Molecular (2ℓ+1)-multiplet D$_2$*-level splitting* *Examples: ℓ=1, 2, 3,…*

j,m,n formulas for momentum operator matrix elements:Hamiltonian matrix for asymmetric rotor

(J=1)-Matrix for A=1, B=2, C=3. *(J=2)-Matrix for A=1, B=2, C=3*

Completing diagonalization from new D$_2$ *basis:*

J=2 example of asymmetry levels. *J=20 example of asymmetry levels*

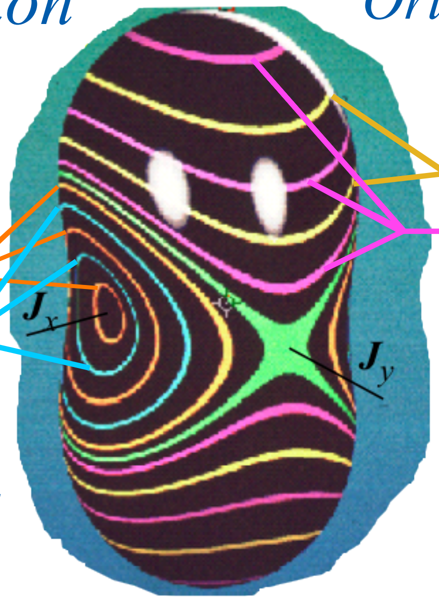
Examples of Group⊃Sub-group correlation (J=10 levels and RES)

Examples of Group⊃Sub-group correlation

$D_2 \supset C_2(x)$ $D_2 \supset C_2(y)$ $D_2 \supset C_2(z)$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Original color mixing scheme
gives



yellow $1_2=(A_2B_1)$

orange $0_2=(A_1B_1)$

purple $0_2=(A_1B_2)$

cyan $1_2=(A_2B_2)$

for x-oblate axis

for z-prolate axis

D_2

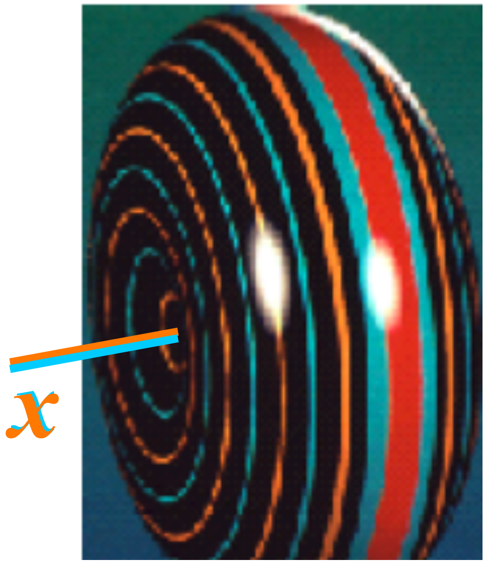
C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

D_2

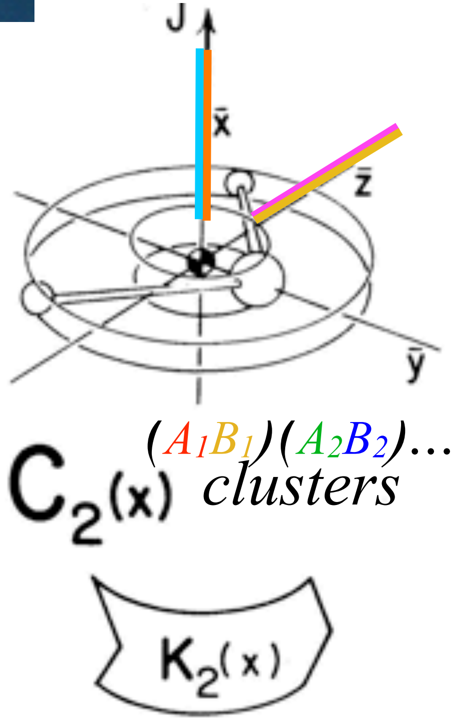
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

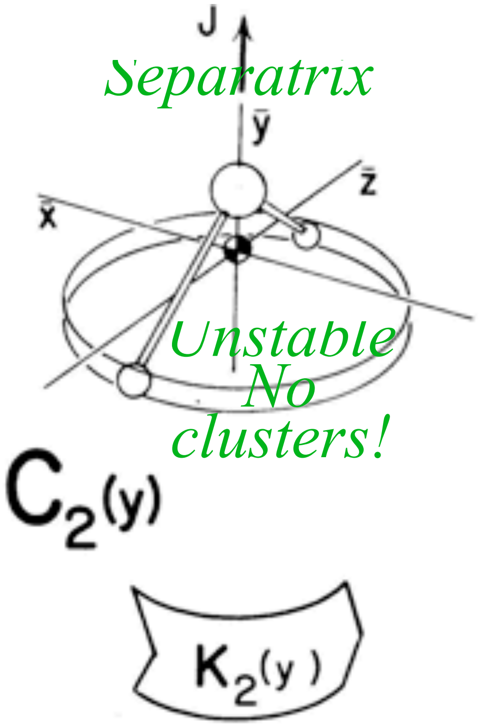
D_2

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·



Review:
Asymmetric
vs
Symmetric
rotor levels





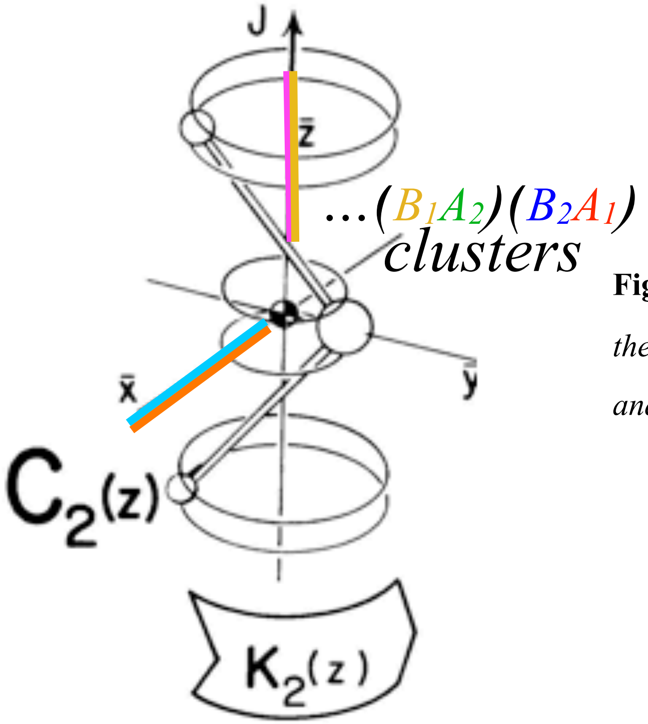
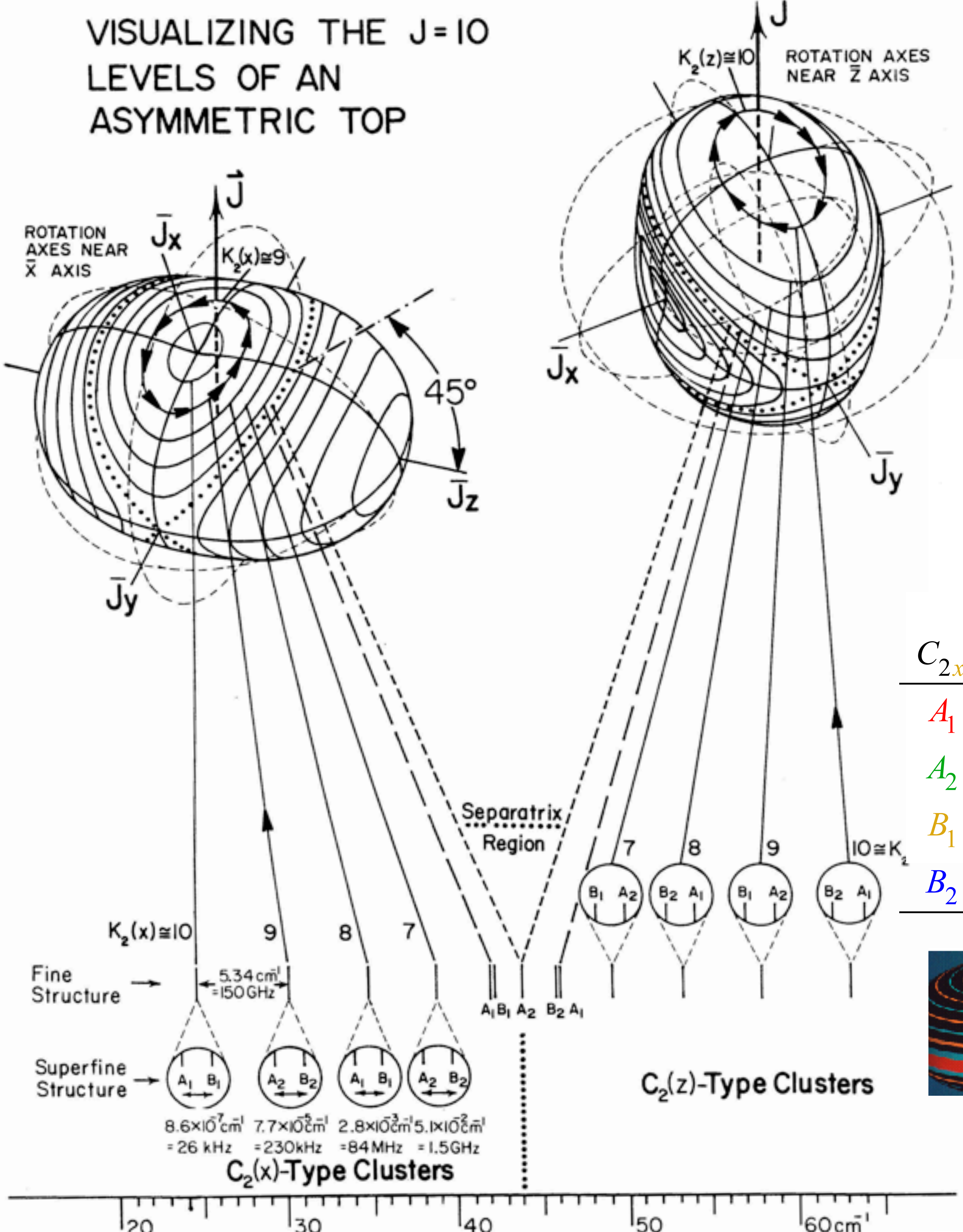


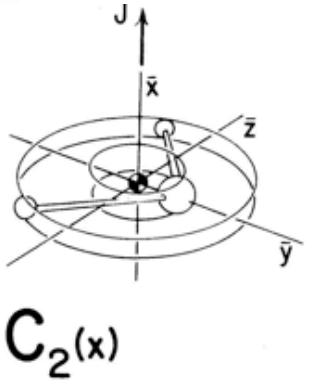
Fig. 25.4.3 *Correlations between the asymmetric top symmetry D_2 and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$.*

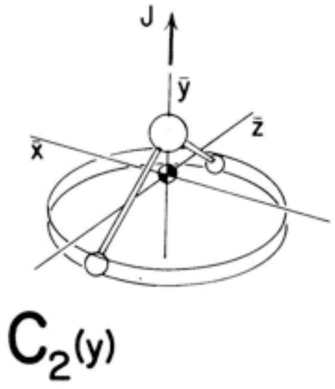


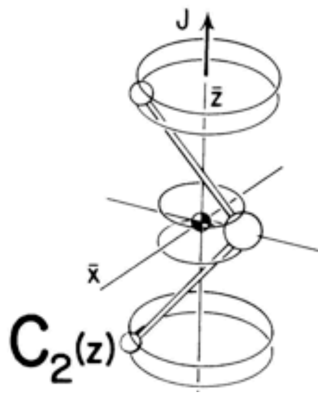
D_2	1	R_x	R_y	R_z
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Examples of Group⊃Sub-group correlation

$D_2 \supset C_2(x)$ *$D_2 \supset C_2(y)$* *$D_2 \supset C_2(z)$*



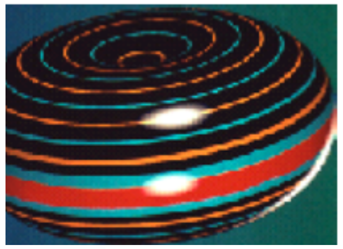




C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·



after QTforCA Unit 8. Ch. 25 Fig. 25.4.2

Fig. 25.4.2 *$J = 10$ asymmetric top energy levels and related RE surface paths ($A = 0.2$, $B = 0.4$, $C = 0.6$). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.*

Springer Handbook
of
Atomic, Molecular, and Optical
Physics (2005)
Fig.32.2 and 32.3 p. 495-497

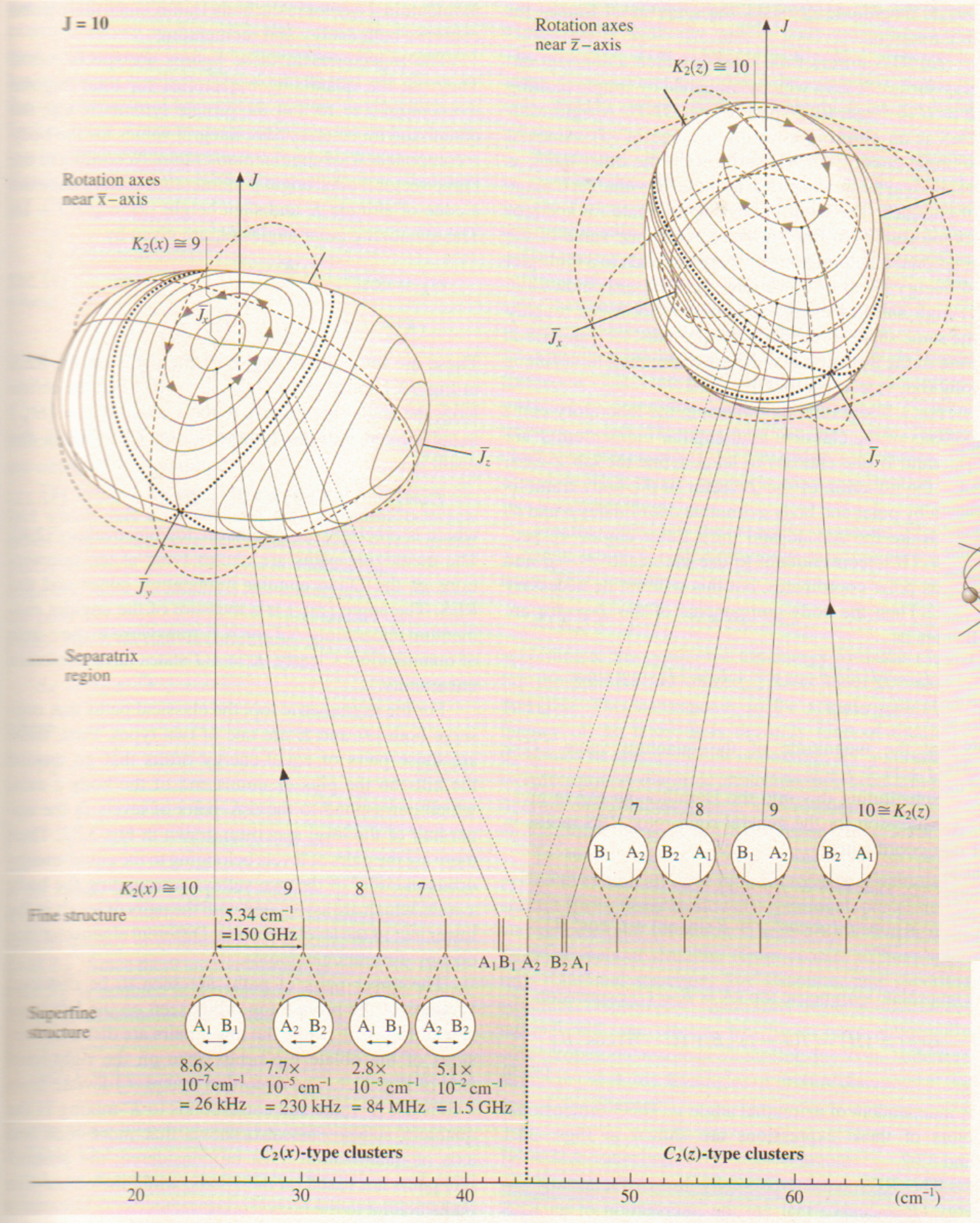
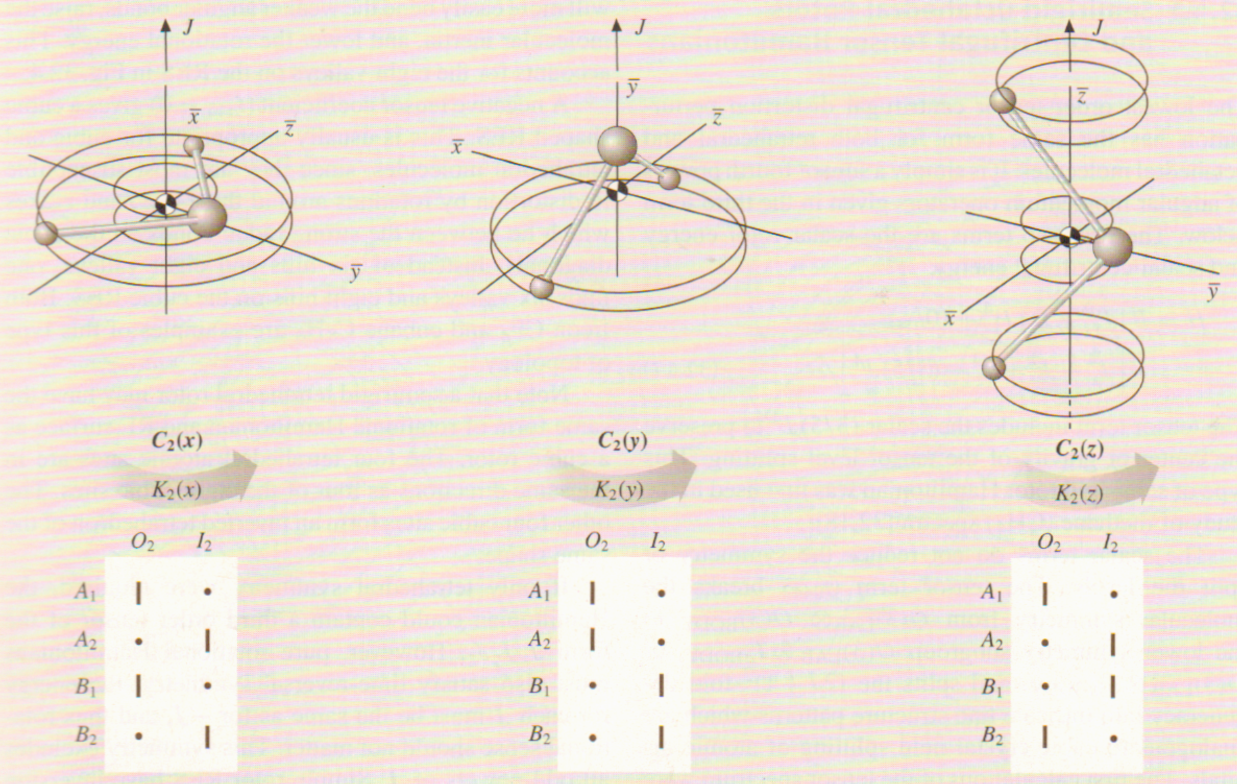


Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator ($A = 0.2$, $B = 0.4$, $C = 0.6\,\mathrm{cm}^{-1}$)

Examples of Group⊃Sub-group correlation

$D_2 \supset C_2(x)$ *$D_2 \supset C_2(y)$* *$D_2 \supset C_2(z)$*



	O_2	I_2
A_1	|	•
A_2	•	|
B_1	|	•
B_2	•	|

	O_2	I_2
A_1	|	•
A_2	|	•
B_1	•	|
B_2	•	|

	O_2	I_2
A_1	|	•
A_2	•	|
B_1	•	|
B_2	|	•

after QTforCA Unit 8. Ch. 25 Fig. 25.4.2