AMOP reference links on following page

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral *(T_d)* or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^{E} irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O

R(3)⊃O character analysis. *O⊃D_4⊃D_2 and O⊃D_4⊃C_4 level correlations s*

Applecations of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

Appendix: O⊃D_4⊃D_2 irrep table very similar to our irreps on p.48

QTCALect.21p.77

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
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 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. This bad boy will be a sure force multiplier.*

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor **H***-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia **H** ?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor **H***-expansions*

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors {**x,y,z**} of *p-wave $D^{\ell=1}_{\{x,y,z\}}$*

D^{T2} irreps derived from standing d-wave $D^{\ell=2}_{\{x,y,z\}}$. *D^{E} irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O

$R(3)\supset O$ character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group$\supset$Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

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

2^k-pole expansion of an N-by-N matrix **H**

2-by-2 case: $\mathbf{H} = \begin{pmatrix} A & B-iC \\ B+iC & D \end{pmatrix} = \frac{A+D}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + B\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + C\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{A-D}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$= \frac{A+D}{2}\,\mathbf{1} + B\,\boldsymbol{\sigma}_x + C\,\boldsymbol{\sigma}_y + \frac{A-D}{2}\,\boldsymbol{\sigma}_z$$

$$= \frac{A+D}{2}\,\mathbf{T}^0_0 + (B-iC)\,\mathbf{T}^1_1 + (B+iC)\,\mathbf{T}^1_{-1} + \frac{A-D}{2}\,\mathbf{T}^1_0$$

$$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

U(2) generators *(spin J=1/2)*

$\mathbf{u}^1_{+1} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ $\mathbf{u}^1_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{1}{\sqrt{2}}$ $\mathbf{u}^1_{-1} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$ rank-1 (vector)

$\mathbf{u}^0_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\frac{1}{\sqrt{2}}$ rank-0 (scalar)

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

2^k-pole expansion of an N-by-N matrix $\mathbf{H}$

2-by-2 case:

$$\mathbf{H}=\begin{pmatrix} A & B-iC \\ B+iC & D \end{pmatrix} = \frac{A+D}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + B\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + C\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{A-D}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \frac{A+D}{2}\,\mathbf{1} + B\,\boldsymbol{\sigma}_x + C\,\boldsymbol{\sigma}_y + \frac{A-D}{2}\,\boldsymbol{\sigma}_z$$

$$= \frac{A+D}{2}\,\mathbf{T}_0^0 + (B-iC)\,\mathbf{T}_1^1 + (B+iC)\,\mathbf{T}_{-1}^1 + \frac{A-D}{2}\,\mathbf{T}_0^1$$

$$\mathbf{T}_1^1 = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \mathbf{T}_{-1}^1 = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

U(2) generators *(spin J=1/2)*

$$\mathbf{u}_{+1}^1=\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \mathbf{u}_0^1=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}_{-1}^1=\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$ rank-1 (vector)

$$\mathbf{u}_0^0=\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\frac{1}{\sqrt{2}}$$ rank-0 (scalar)

Generalization of U(2) spinor analysis to U(3)⊂U(4)⊂U(5)... (Introduced in this and following lectures)

3-by-3 case:

$$\mathbf{H}=\begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} = B\,\mathbf{T}_0^0 + \ldots + t_2\,\mathbf{T}_2^2 + \ldots$$

U(3) generators *(spin J=1)*

$$\mathbf{u}_{+2}^2=\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathbf{u}_{+1}^2=\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}_0^2=\begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix}\frac{1}{\sqrt{6}} \quad \mathbf{u}_{-1}^2=\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}_{-2}^2=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$ rank-2 (tensor)

$$\mathbf{u}_{+1}^1=\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}_0^1=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}_{-1}^1=\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}\frac{1}{\sqrt{2}}$$ rank-1 (vector)

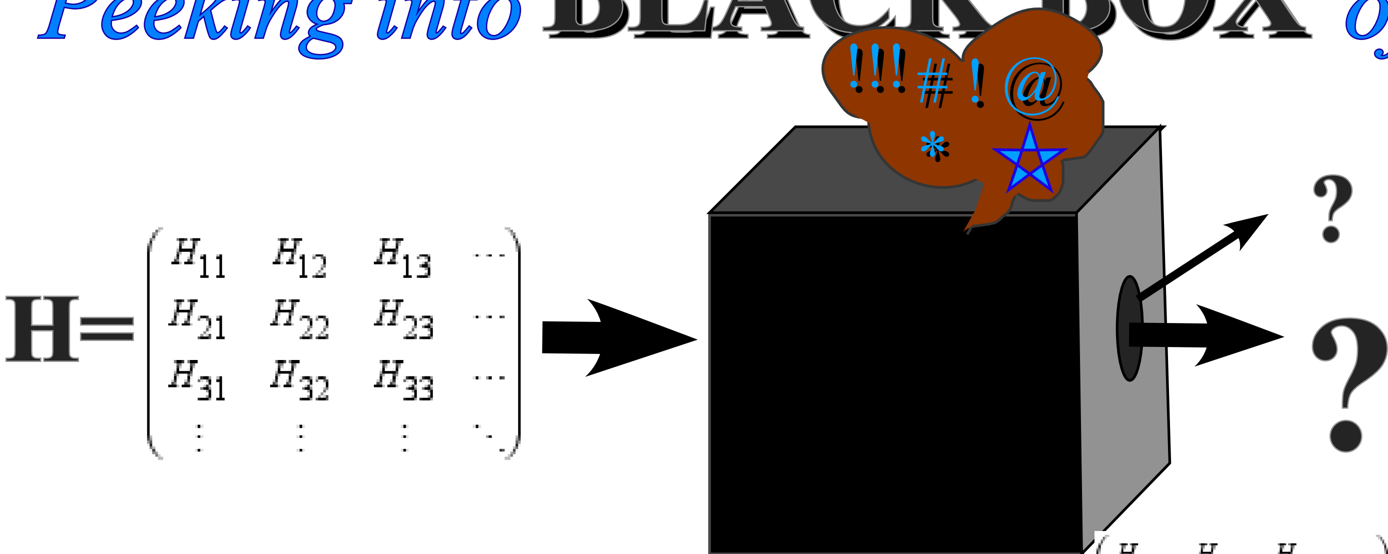
$$\mathbf{u}_0^0=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\frac{1}{\sqrt{3}}$$ rank-0 (scalar)

Mutually commuting diagonal operators

Tensor matrices in IJMS-2013 (p9) Ch.7 p592 Tensor matrices in PSDS Ch.7 p589

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* **H**-*expansions*

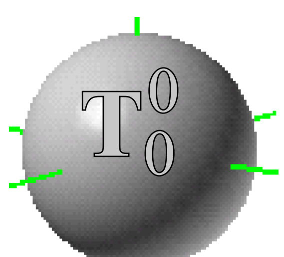
Peeking into **BLACK BOX** *of matrix diagonalization:*



Plotting 2^k*-pole expansion of* $\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$ *into Fano-Racah tensors*

scalar+ *+ vector+* *+* 2^2*-tensor +...* *+* 2^k*-tensor +..*

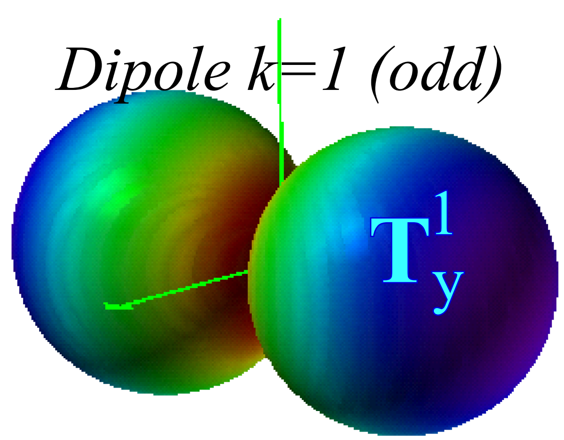
$$\mathbf{H}= a\mathbf{T}^0_0+b\mathbf{T}^1_0+c\mathbf{T}^1_1+\ldots+d\mathbf{T}^2_0+e\mathbf{T}^2_1+\ldots=\Sigma c^k_q\,\mathbf{T}^k_q$$



Monopole
k=0 (even)

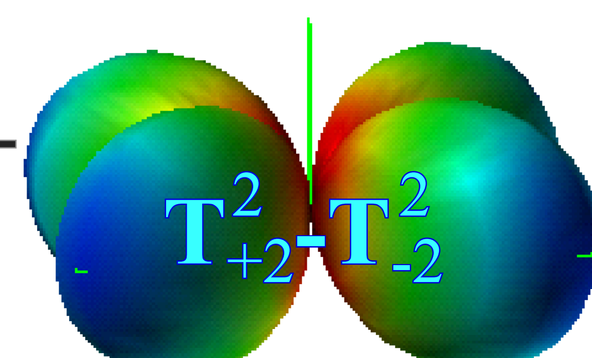
+

Dipole k=1 (odd)



anti-symmetric to time reversal (Not present unless "gyros" are on board)

+

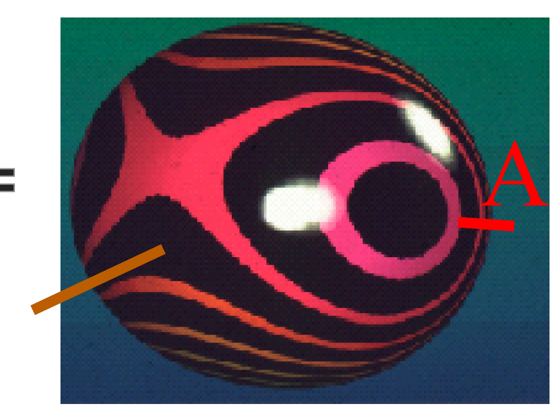


Quadrupole k=2 (even)

spherical rotor, prolate, oblate, or asymmetric rotor.

+... =

mixed-k



Tensors of higher rank-k=3,4,5,6... describe *__deformable__* *rotors such as* CF_4, SF_6, C_8H_8, C_{60}, ...

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h *multipole* $\mathbf{T}_q^{[4]}$ *and* $\mathbf{T}_q^{[2,2]}$ *tensor* $\mathbf{H}$*-expansions*

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, *and* D^{A1}, *irreducible representations (irreps) of O*

Finding O_h *group products.* *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} *irreps derived visually using unit vectors* {**x**,**y**,**z**} of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} *irreps derived from standing d-wave* $D^{\ell=2}{}_{\{x,y,z\}}$. D^{E} *irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, *and* χ^{A1} *of O*

R(3)⊃O character analysis. $O\supset D_4\supset D_2$ *and* $O\supset D_4\supset C_4$ *level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

$$\mathbf{H} = B[(\mathbf{J}_x)^2+(\mathbf{J}_y)^2+(\mathbf{J}_z)^2]+ t_0^{[3]}[(\mathbf{J}_x)^3+(\mathbf{J}_y)^3+(\mathbf{J}_z)^3]+ t_0^{[4]}[(\mathbf{J}_x)^4+(\mathbf{J}_y)^4+(\mathbf{J}_z)^4]+\ldots$$

spherical rotor 2nd rank kinetic term with $B=1/2I$

Odd k=3 is anti-symmetric to time reversal ($\mathbf{J}_q = -\mathbf{J}_x$)

4th rank centrifugal distortion term for T_d *or* O_h *symmetric rotor*

**Multipole function D-definition* Class 9 p93

$$X_q^k = r^k D_{q,0}^{k*} = \sqrt{\frac{4\pi}{2k+1}} r^k Y_q^k$$

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

$$\mathbf{H} = B[(\mathbf{J}_x)^2+(\mathbf{J}_y)^2+(\mathbf{J}_z)^2]+ t_0^{[3]}[(\mathbf{J}_x)^3+(\mathbf{J}_y)^3+(\mathbf{J}_z)^3]+ t_0^{[4]}[(\mathbf{J}_x)^4+(\mathbf{J}_y)^4+(\mathbf{J}_z)^4]+\ldots$$

spherical rotor 2nd rank kinetic term with $B=1/2I$

Odd $k=3$ *is anti-symmetric to time reversal* ($\mathbf{J}_q = -\mathbf{J}_x$)

4th rank centrifugal distortion term for T_d *or* O_h *symmetric rotor*

For now we reject the forbidden [$k=3$] term and rewrite the 4^{th}-rank [$k=4$] term.

*Multipole function D-definition Class 9 p93

$$X_q^k = r^k D_{q,0}^{k*} = \sqrt{\frac{4\pi}{2k+1}} r^k Y_q^k$$

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h *multipole* $\mathbf{T}_q^{[4]}$ *and* $\mathbf{T}_q^{[2,2]}$ *tensor* $\mathbf{H}$*-expansions*

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, *and* D^{A1}, *irreducible representations (irreps) of O*

Finding O_h *group products.* *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} *irreps derived visually using unit vectors* $\{\mathbf{x,y,z}\}$ of *p-wave* $D^{\ell=1}_{\{x,y,z\}}$

D^{T2} *irreps derived from standing d-wave* $D^{\ell=2}_{\{x,y,z\}}$. D^{E} *irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, *and* χ^{A1} *of O*

R(3)⊃O character analysis. *O⊃D_4⊃D_2 and O⊃D_4⊃C_4 level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

$$\mathbf{H} = B[(\mathbf{J}_x)^2+(\mathbf{J}_y)^2+(\mathbf{J}_z)^2]+ t_0^{[3]}[(\mathbf{J}_x)^3+(\mathbf{J}_y)^3+(\mathbf{J}_z)^3]+ t_0^{[4]}[(\mathbf{J}_x)^4+(\mathbf{J}_y)^4+(\mathbf{J}_z)^4]+\ldots$$

spherical rotor 2nd rank kinetic term with $B=1/2I$

Odd k=3 is anti-symmetric to time reversal $(\mathbf{J}_q = -\mathbf{J}_x)$

4th rank centrifugal distortion term for T_d *or* O_h *symmetric rotor*

For now we reject the forbidden $[k=3]$ term and rewrite the 4^{th}-rank $[k=4]$ term.

4^{th}-rank multipole* functions $X_q^{[4]}(x,y,z)$: (listed in PSDS Apps F p793)

$$X_4^{\{4\}}=\sqrt{\tfrac{35}{128}}(x+iy)^4$$

$$X_3^{\{4\}}=\tfrac{-\sqrt{35}}{4}z(x+iy)^3$$

$$X_2^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x+iy)^2$$

$$X_1^{\{4\}}=-\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x+iy)$$

$$X_0^{\{4\}}=-\sqrt{\tfrac{1}{64}}(35z^4-30z^2r^2+3r^4)$$

$$X_{-1}^{\{4\}}=\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x-iy)$$

$$X_{-2}^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x-iy)^2$$

$$X_{-3}^{\{4\}}=\tfrac{\sqrt{35}}{4}z(x-iy)^3$$

$$X_{-4}^{\{4\}}=\sqrt{\tfrac{35}{128}}(x-iy)^4$$

*Multipole function D-definition Class 9 p93

$$X_q^k = r^k D_{q,0}^{k*} = \sqrt{\frac{4\pi}{2k+1}}\, r^k Y_q^k$$

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

$$\mathbf{H} = B[(\mathbf{J}_x)^2+(\mathbf{J}_y)^2+(\mathbf{J}_z)^2]+ t_0^{[3]}[(\mathbf{J}_x)^3+(\mathbf{J}_y)^3+(\mathbf{J}_z)^3]+ t_0^{[4]}[(\mathbf{J}_x)^4+(\mathbf{J}_y)^4+(\mathbf{J}_z)^4]+\ldots$$

spherical rotor 2nd rank kinetic term with B=1/2I

Odd k=3 is anti-symmetric to time reversal ($\mathbf{J}_q = -\mathbf{J}_x$)

4th rank centrifugal distortion term for T_d or O_h symmetric rotor

For now we reject the forbidden [*k=3*] term and rewrite the *4th*-rank [*k=4*] term.

4th-rank multipole* functions $X_q^{[4]}(x,y,z)$: *(listed in PSDS Apps F p793)*

Partially inverted into monomials:

$$X_4^{\{4\}}=\sqrt{\tfrac{35}{128}}(x+iy)^4$$
$$X_3^{\{4\}}=\tfrac{-\sqrt{35}}{4}z(x+iy)^3$$
$$X_2^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x+iy)^2$$
$$X_1^{\{4\}}=-\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x+iy)$$
$$X_0^{\{4\}}=-\sqrt{\tfrac{1}{64}}(35z^4-30z^2r^2+3r^4)$$
$$X_{-1}^{\{4\}}=\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x-iy)$$
$$X_{-2}^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x-iy)^2$$
$$X_{-3}^{\{4\}}=\tfrac{\sqrt{35}}{4}z(x-iy)^3$$
$$X_{-4}^{\{4\}}=\sqrt{\tfrac{35}{128}}(x-iy)^4$$

$$x^4=\tfrac{1}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})-\tfrac{2}{7\sqrt{10}}(X_2^{[4]}+X_{-2}^{[4]})+\tfrac{3}{35}X_0^{[4]}+\tfrac{\sqrt{6}}{7}(X_2^{[2]}+X_{-2}^{[2]})r^2-\tfrac{2}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$
$$y^4=\tfrac{1}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})+\tfrac{2}{7\sqrt{10}}(X_2^{[4]}+X_{-2}^{[4]})+\tfrac{3}{35}X_0^{[4]}-\tfrac{\sqrt{6}}{7}(X_2^{[2]}+X_{-2}^{[2]})r^2-\tfrac{2}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$
$$z^4=\tfrac{8}{35}X_0^{[4]}+\tfrac{4}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$

**Multipole function D-definition* Class 9 p93

$$X_q^k=r^kD_{q,0}^{k*}=\sqrt{\frac{4\pi}{2k+1}}r^kY_q^k$$

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

$$\mathbf{H} = B[(\mathbf{J}_x)^2+(\mathbf{J}_y)^2+(\mathbf{J}_z)^2]+ t_0^{[3]}[(\mathbf{J}_x)^3+(\mathbf{J}_y)^3+(\mathbf{J}_z)^3]+ t_0^{[4]}[(\mathbf{J}_x)^4+(\mathbf{J}_y)^4+(\mathbf{J}_z)^4]+\ldots$$

spherical rotor 2nd rank kinetic term with $B=1/2I$

Odd k=3 is anti-symmetric to time reversal $(\mathbf{J}_q = -\mathbf{J}_x)$

4th rank centrifugal distortion term for T_d *or* O_h *symmetric rotor*

For now we reject the forbidden $[k=3]$ term and rewrite the 4^{th}-rank $[k=4]$ term.

4^{th}-rank multipole* functions $X_q^{[4]}(x,y,z)$:

(listed in PSDS Apps F p793)

$$X_4^{\{4\}}=\sqrt{\tfrac{35}{128}}(x+iy)^4$$
$$X_3^{\{4\}}=\tfrac{-\sqrt{35}}{4}z(x+iy)^3$$
$$X_2^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x+iy)^2$$
$$X_1^{\{4\}}=-\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x+iy)$$
$$X_0^{\{4\}}=-\sqrt{\tfrac{1}{64}}(35z^4-30z^2r^2+3r^4)$$
$$X_{-1}^{\{4\}}=\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x-iy)$$
$$X_{-2}^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x-iy)^2$$
$$X_{-3}^{\{4\}}=\tfrac{\sqrt{35}}{4}z(x-iy)^3$$
$$X_{-4}^{\{4\}}=\sqrt{\tfrac{35}{128}}(x-iy)^4$$

Partially inverted into monomials:

$$x^4=\tfrac{1}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})-\tfrac{2}{7\sqrt{10}}(X_2^{[4]}+X_{-2}^{[4]})+\tfrac{3}{35}X_0^{[4]}+\tfrac{\sqrt{6}}{7}(X_2^{[2]}+X_{-2}^{[2]})r^2-\tfrac{2}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$
$$y^4=\tfrac{1}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})+\tfrac{2}{7\sqrt{10}}(X_2^{[4]}+X_{-2}^{[4]})+\tfrac{3}{35}X_0^{[4]}-\tfrac{\sqrt{6}}{7}(X_2^{[2]}+X_{-2}^{[2]})r^2-\tfrac{2}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$
$$z^4=\tfrac{8}{35}X_0^{[4]}+\tfrac{4}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$

$$x^4+y^4+z^4=\tfrac{2}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})+\tfrac{2}{5}X_0^{[4]}+\tfrac{3}{5}r^4$$

*Multipole function D-definition Class 9 p93

$$X_q^k=r^kD_{q,0}^{k*}=\sqrt{\frac{4\pi}{2k+1}}r^kY_q^k$$

2.19.18 class 11.0: *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 O of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h *multipole* $\mathbf{T}_q^{[4]}$ *and* $\mathbf{T}_q^{[2,2]}$ *tensor* $\mathbf{H}$*-expansions*

Matrix D^{T1}, D^{T2}, D^E, D^{A2}, *and* D^{A1}, *irreducible representations (irreps) of O*

Finding O_h *group products.* *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} *irreps derived visually using unit vectors* {**x**,**y**,**z**} of *p-wave* $D^{\ell=1}_{\{x,y,z\}}$

D^{T2} *irreps derived from standing d-wave* $D^{\ell=2}_{\{x,y,z\}}$. D^E *irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^E, χ^{A2}, *and* χ^{A1} *of O*

R(3)⊃O character analysis. $O\supset D_4\supset D_2$ *and* $O\supset D_4\supset C_4$ *level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

$$\mathbf{H} = B[(\mathbf{J}_x)^2+(\mathbf{J}_y)^2+(\mathbf{J}_z)^2]+ t_0^{[3]}[(\mathbf{J}_x)^3+(\mathbf{J}_y)^3+(\mathbf{J}_z)^3]+ t_0^{[4]}[(\mathbf{J}_x)^4+(\mathbf{J}_y)^4+(\mathbf{J}_z)^4]+\ldots$$

spherical rotor 2nd rank kinetic term with $B=1/2I$

Odd k=3 is anti-symmetric to time reversal $(\mathbf{J}_q = -\mathbf{J}_x)$

4th rank centrifugal distortion term for T_d *or* O_h *symmetric rotor*

For now we reject the forbidden $[k=3]$ term and rewrite the 4^{th}-rank $[k=4]$ term.

4^{th}-rank multipole* functions $X_q^{[4]}(x,y,z)$:

(listed in PSDS Apps F p793)

$$X_4^{\{4\}}=\sqrt{\tfrac{35}{128}}(x+iy)^4$$
$$X_3^{\{4\}}=\tfrac{-\sqrt{35}}{4}z(x+iy)^3$$
$$X_2^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x+iy)^2$$
$$X_1^{\{4\}}=-\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x+iy)$$
$$X_0^{\{4\}}=-\sqrt{\tfrac{1}{64}}(35z^4-30z^2r^2+3r^4)$$
$$X_{-1}^{\{4\}}=\sqrt{\tfrac{5}{16}}(7z^3-3zr^2)(x-iy)$$
$$X_{-2}^{\{4\}}=\sqrt{\tfrac{5}{32}}(7z^2-r^2)(x-iy)^2$$
$$X_{-3}^{\{4\}}=\tfrac{\sqrt{35}}{4}z(x-iy)^3$$
$$X_{-4}^{\{4\}}=\sqrt{\tfrac{35}{128}}(x-iy)^4$$

Partially inverted into monomials:

$$x^4=\tfrac{1}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})-\tfrac{2}{7\sqrt{10}}(X_2^{[4]}+X_{-2}^{[4]})+\tfrac{3}{35}X_0^{[4]}+\tfrac{\sqrt{6}}{7}(X_2^{[2]}+X_{-2}^{[2]})r^2-\tfrac{2}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$
$$y^4=\tfrac{1}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})+\tfrac{2}{7\sqrt{10}}(X_2^{[4]}+X_{-2}^{[4]})+\tfrac{3}{35}X_0^{[4]}-\tfrac{\sqrt{6}}{7}(X_2^{[2]}+X_{-2}^{[2]})r^2-\tfrac{2}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$
$$z^4=\tfrac{8}{35}X_0^{[4]}+\tfrac{4}{7}X_0^{[2]}r^2+\tfrac{1}{5}r^4$$

$$x^4+y^4+z^4=\tfrac{2}{\sqrt{70}}(X_4^{[4]}+X_{-4}^{[4]})+\tfrac{2}{5}X_0^{[4]}+\tfrac{3}{5}r^4$$

Sum gives O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

$$\mathbf{T}^{\{4\}}=\mathbf{J}_x^4+\mathbf{J}_y^4+\mathbf{J}_z^4=\tfrac{2}{\sqrt{70}}(\mathbf{T}_4^{[4]}+\mathbf{T}_{-4}^{[4]})+\tfrac{2}{5}\mathbf{T}_0^{[4]}+\tfrac{3}{5}(\mathbf{J}\cdot\mathbf{J})^2$$

**Multipole function D-definition* Class 9 p93

$$X_q^k=r^kD_{q,0}^{k*}=\sqrt{\frac{4\pi}{2k+1}}r^kY_q^k$$

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* **H**-*expansions*

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia **H** ?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h *multipole* $\mathbf{T}_q^{[4]}$ *and* $\mathbf{T}_q^{[2,2]}$ *tensor* **H**-*expansions*

Matrix D^{T1}, D^{T2}, D^E, D^{A2}, *and* D^{A1}, *irreducible representations (irreps) of O*

Finding O_h *group products.* *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} *irreps derived visually using unit vectors* {**x**,**y**,**z**} of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} *irreps derived from standing d-wave* $D^{\ell=2}{}_{\{x,y,z\}}$. D^E *irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^E, χ^{A2}, *and* χ^{A1} *of O*

R(3)⊃O character analysis. $O\supset D_4\supset D_2$ *and* $O\supset D_4\supset C_4$ *level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

RES and matrix irreps of O_h multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

Alternative 4th-rank O_h tensors found by squaring r^2:

$r^4 =$	x^2	y^2	z^2
x^2	x^4	x^2y^2	x^2z^2
y^2	y^2x^2	y^4	y^2z^2
z^2	z^2x^2	z^2y^2	z^4

A second rank-4 tensor (dependent on r^4 and first one)

$$x^2y^2 + x^2z^2 + y^2z^2 = r^4 - \tfrac{1}{2}(x^4 + y^4 + z^4)$$

$$r^4 = x^4 + y^4 + z^4 + 2(x^2y^2 + x^2z^2 + y^2z^2)$$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

Alternative 4th-rank O_h tensors found by squaring r^2:

$r^4 =$	x^2	y^2	z^2
x^2	x^4	x^2y^2	x^2z^2
y^2	y^2x^2	y^4	y^2z^2
z^2	z^2x^2	z^2y^2	z^4

A second rank-4 tensor (dependent on r^4 and first one)

$$x^2y^2 + x^2z^2 + y^2z^2 = r^4 - \tfrac{1}{2}(x^4 + y^4 + z^4) \qquad r^4 = x^4 + y^4 + z^4 + 2(x^2y^2 + x^2z^2 + y^2z^2)$$

Operator version: $\mathbf{T}^{[2\cdot 2]} = (\mathbf{J}_x)^2 \cdot (\mathbf{J}_y)^2 + (\mathbf{J}_x)^2 \cdot (\mathbf{J}_z)^2 + (\mathbf{J}_y)^2 \cdot (\mathbf{J}_z)^2$

is not so simply related to: $\mathbf{T}^{[4]} = (\mathbf{J}_x)^4 + (\mathbf{J}_x)^4 + (\mathbf{J}_y)^4$ since $(\mathbf{J}_x)^2$,$(\mathbf{J}_y)^2$, and $(\mathbf{J}_z)^2$ do not commute.

For semi-classical RES approximations commutation is not an issue.

RES and matrix irreps of O_h multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

Alternative 4th-rank O_h tensors found by squaring r^2:

$r^4 =$	x^2	y^2	z^2
x^2	x^4	x^2y^2	x^2z^2
y^2	y^2x^2	y^4	y^2z^2
z^2	z^2x^2	z^2y^2	z^4

A second rank-4 tensor (dependent on r^4 and first one)

$$x^2y^2 + x^2z^2 + y^2z^2 = r^4 - \tfrac{1}{2}(x^4 + y^4 + z^4) \qquad r^4 = x^4 + y^4 + z^4 + 2(x^2y^2 + x^2z^2 + y^2z^2)$$

Operator version: $\mathbf{T}^{[2\cdot 2]} = (\mathbf{J}_x)^2\cdot(\mathbf{J}_y)^2 + (\mathbf{J}_x)^2\cdot(\mathbf{J}_z)^2 + (\mathbf{J}_y)^2\cdot(\mathbf{J}_z)^2$

is not so simply related to: $\mathbf{T}^{[4]} = (\mathbf{J}_x)^4 + (\mathbf{J}_x)^4 + (\mathbf{J}_y)^4$ since $(\mathbf{J}_x)^2, (\mathbf{J}_y)^2$, and $(\mathbf{J}_z)^2$ do not commute.

For semi-classical RES approximations commutation is not an issue. Instead, we simply plug in the J-coordinates ($J_x = |J|\sin\beta\cos\gamma$, $J_y = |J|\sin\beta\sin\gamma$, $J_z = |J|\cos\beta$) into Hamiltonian $\mathbf{H}(\mathbf{J})$.

For $\mathbf{H}(\mathbf{J}) = B\mathbf{J}^2 + t^{[4]}(\mathbf{J}_x{}^4 + \mathbf{J}_x{}^4 + \mathbf{J}_y{}^4)$

plot RES:

$E = B|J|^2 + t^{[4]}|J|^4(\sin^4\beta\cos^4\gamma + \sin^4\beta\sin^4\gamma + \cos^4\beta)$.

RES and matrix irreps of O_h multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

Alternative 4^{th}-rank O_h tensors found by squaring r^2:

$r^4 =$	x^2	y^2	z^2
x^2	x^4	x^2y^2	x^2z^2
y^2	y^2x^2	y^4	y^2z^2
z^2	z^2x^2	z^2y^2	z^4

A second rank-4 tensor (dependent on r^4 and first one)

$$x^2y^2+x^2z^2+y^2z^2=r^4-\tfrac{1}{2}(x^4+y^4+z^4) \qquad r^4=x^4+y^4+z^4+2(x^2y^2+x^2z^2+y^2z^2)$$

Operator version: $\mathbf{T}^{[2\cdot 2]}=(\mathbf{J}_x)^2\cdot(\mathbf{J}_y)^2+(\mathbf{J}_x)^2\cdot(\mathbf{J}_z)^2+(\mathbf{J}_y)^2\cdot(\mathbf{J}_z)^2$

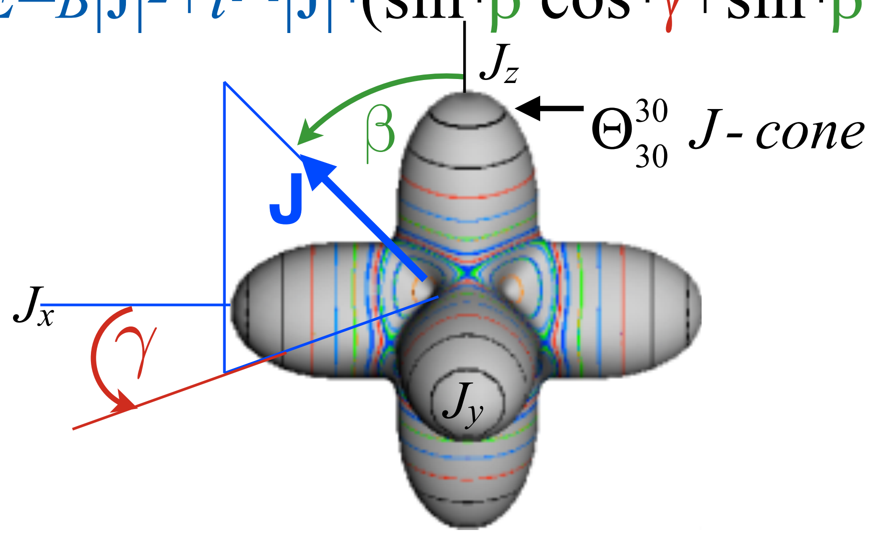
is not so simply related to: $\mathbf{T}^{[4]}=(\mathbf{J}_x)^4+(\mathbf{J}_x)^4+(\mathbf{J}_y)^4$ since $(\mathbf{J}_x)^2$,$(\mathbf{J}_y)^2$, and $(\mathbf{J}_z)^2$ do not commute.

For semi-classical RES approximations commutation is not an issue. Instead, we simply plug in the J-coordinates ($J_x=|J|\sin\beta\cos\gamma$, $J_y=|J|\sin\beta\sin\gamma$, $J_z=|J|\cos\beta$) into Hamiltonian $\mathbf{H}(\mathbf{J})$.

For $\mathbf{H}(\mathbf{J})=B\mathbf{J}^2+t^{[4]}(\mathbf{J}_x{}^4+\mathbf{J}_x{}^4+\mathbf{J}_y{}^4)$

plot RES:

$E=B|J|^2+t^{[4]}|J|^4(\sin^4\beta\cos^4\gamma+\sin^4\beta\sin^4\gamma+\cos^4\beta)$.



*E(β,γ) plotted radially for fixed |**J**|=J=30*

RES and matrix irreps of O_h multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

Alternative 4th-rank O_h tensors found by squaring r^2:

$r^4=$	x^2	y^2	z^2
x^2	x^4	x^2y^2	x^2z^2
y^2	y^2x^2	y^4	y^2z^2
z^2	z^2x^2	z^2y^2	z^4

A second rank-4 tensor (dependent on r^4 and first one)

$$x^2y^2+x^2z^2+y^2z^2=r^4-\tfrac{1}{2}(x^4+y^4+z^4) \qquad r^4=x^4+y^4+z^4+2(x^2y^2+x^2z^2+y^2z^2)$$

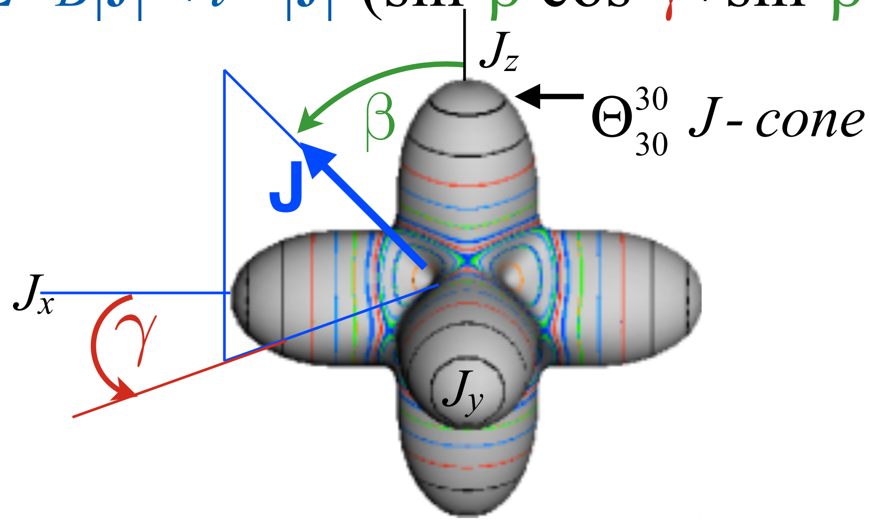
Operator version: $\mathbf{T}^{[2\cdot 2]}=(\mathbf{J}_x)^2\cdot(\mathbf{J}_y)^2+(\mathbf{J}_x)^2\cdot(\mathbf{J}_z)^2+(\mathbf{J}_y)^2\cdot(\mathbf{J}_z)^2$

is not so simply related to: $\mathbf{T}^{[4]}=(\mathbf{J}_x)^4+(\mathbf{J}_x)^4+(\mathbf{J}_y)^4$ since $(\mathbf{J}_x)^2$,$(\mathbf{J}_y)^2$, and $(\mathbf{J}_z)^2$ do not commute.

For semi-classical RES approximations commutation is not an issue. Instead, we simply plug in the J-coordinates ($J_x=|J|\sin\beta\cos\gamma$, $J_y=|J|\sin\beta\sin\gamma$, $J_z=|J|\cos\beta$) into Hamiltonian $\mathbf{H}(\mathbf{J})$.

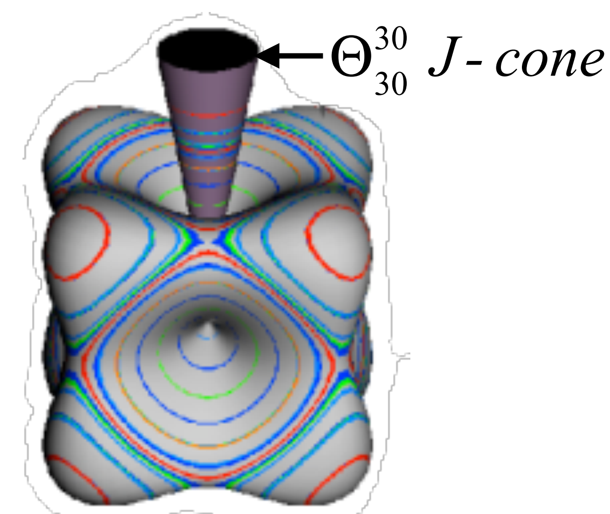
For $\mathbf{H}(\mathbf{J})=B\mathbf{J}^2+t^{[4]}(\mathbf{J}_x{}^4+\mathbf{J}_x{}^4+\mathbf{J}_y{}^4)$ plot RES:

$E=B|J|^2+t^{[4]}|J|^4(\sin^4\beta\cos^4\gamma+\sin^4\beta\sin^4\gamma+\cos^4\beta)$.



For $\mathbf{H}(\mathbf{J})=B\mathbf{J}^2+t^{[22]}(\mathbf{J}_x{}^2\mathbf{J}_y{}^2+\mathbf{J}_x{}^2\mathbf{J}_z{}^2+\mathbf{J}_y{}^2\mathbf{J}_z{}^2)$ plot RES:

$E=B|J|^2+t^{[22]}|J|^4(\sin^4\beta\cos^2\gamma\sin^2\gamma+\sin^2\beta\cos^2\beta)$



*E(β,γ) plotted radially for fixed |**J**|=J=30*

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* **H**-*expansions*

What tensors go in tetrahedral *(T_d)* or octahedral (O_h) free-rotor Hamiltonia **H** ?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h *multipole* $\mathbf{T}_q^{[4]}$ *and* $\mathbf{T}_q^{[2,2]}$ *tensor* **H**-*expansions*

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, *and* D^{A1}, *irreducible representations (irreps) of O*

Finding O_h *group products.* *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} *irreps derived visually using unit vectors* {**x,y,z**} of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} *irreps derived from standing d-wave* $D^{\ell=2}{}_{\{x,y,z\}}$. D^{E} *irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, *and* χ^{A1} *of O*

R(3)⊃O character analysis. $O\supset D_4\supset D_2$ *and* $O\supset D_4\supset C_4$ *level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

Here we begin to use the j=1 dipole or "vector" functions of R(3)

TABLE F.1.1 $R(3)$ Multiple Functions and SU(3) Harmonic Monomials

$$\mathrm{I}_1^{(1)} = -\frac{1}{\sqrt{2}}(x+iy) \qquad x = \frac{1}{\sqrt{2}}(\mathrm{I}_{-1}^{(1)} - \mathrm{I}_1^{(1)})$$

$$\mathrm{I}_{-1}^{(1)} = \frac{1}{\sqrt{2}}(x-iy) \qquad iy = -\frac{1}{\sqrt{2}}(\mathrm{I}_{-1}^{(1)} + \mathrm{I}_1^{(1)})$$

$$\mathrm{I}_0^{(1)} = z \qquad z = \mathrm{I}_0^{(1)}$$

$$\mathrm{II}_2^{(2)} = \sqrt{\frac{3}{8}}(x+iy)^2 \qquad x^2 = \frac{1}{6}(\mathrm{II}_2^{(2)} + \mathrm{II}_{-2}^{(2)}) - \frac{1}{3}\mathrm{II}_0^{(2)} + \frac{1}{3}r^2$$

$$\mathrm{II}_1^{(2)} = -\sqrt{\frac{3}{2}}z(x+iy) \qquad y^2 = -\frac{1}{6}(\mathrm{II}_2^{(2)} + \mathrm{II}_{-2}^{(2)}) - \frac{1}{3}\mathrm{II}_0^{(2)} + \frac{1}{3}r^2$$

$$\mathrm{II}_0^{(2)} = \frac{1}{2}(3z^2 - r^2) \qquad z^2 = -\frac{2}{3}\mathrm{II}_0^{(2)} + \frac{1}{3}r^2$$

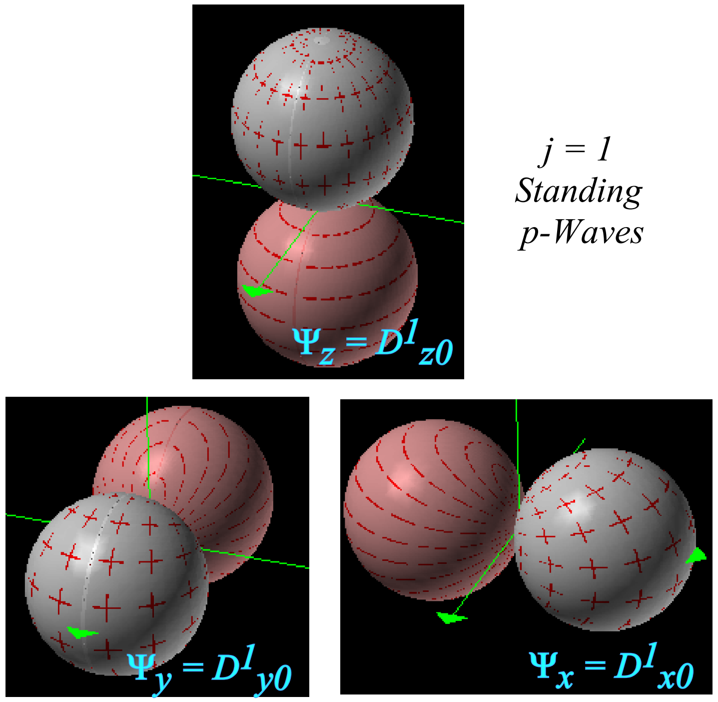
$$\mathrm{II}_{-1}^{(2)} = \sqrt{\frac{3}{2}}z(x-iy) \qquad xy = \frac{i}{\sqrt{6}}(\mathrm{II}_2^{(2)} - \mathrm{II}_{-2}^{(2)})$$

$$\mathrm{II}_{-2}^{(2)} = \sqrt{\frac{3}{8}}(x-iy)^2 \qquad xz = \frac{1}{\sqrt{6}}(\mathrm{II}_1^{(2)} - \mathrm{II}_{-1}^{(2)})$$

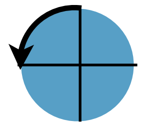
$$yz = \frac{i}{\sqrt{6}}(\mathrm{II}_1^{(2)} + \mathrm{II}_{-1}^{(2)})$$

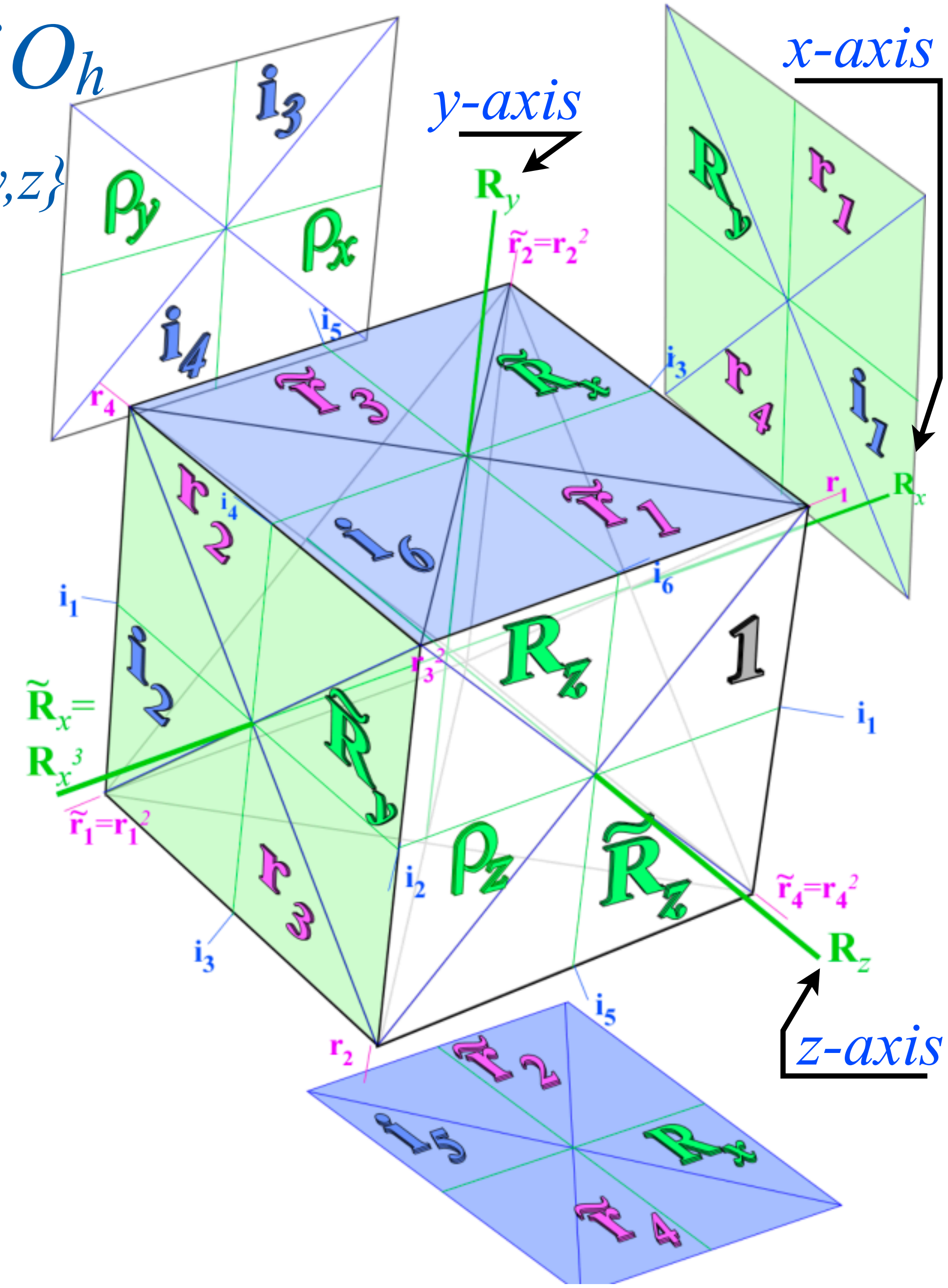
Matrix D^{T_1}, D^{T_2}, D^E, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



Locate x, y, z axes of


+90° rotations **R_x, R_y, R_z,**

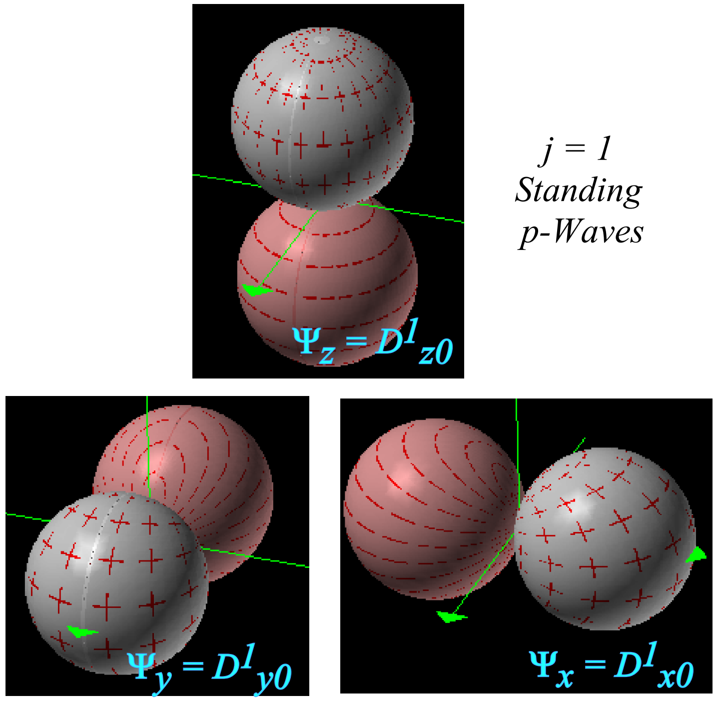


Finding O_h group products

**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^E, D^{A_2}, and D^{A_1}, irreps* of O_h

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$

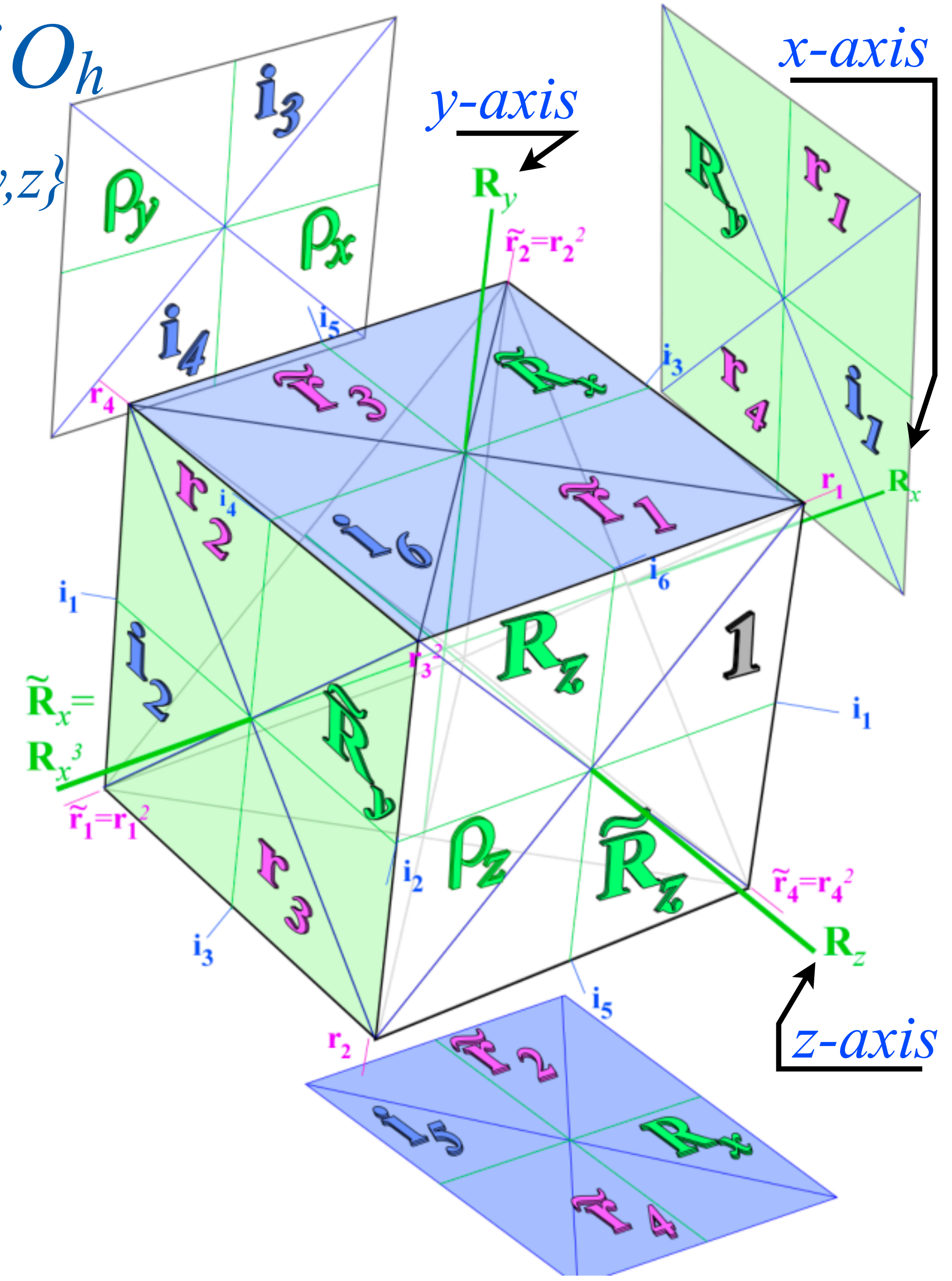


Locate x, y, z axes of

+90° rotations $\mathbf{R}_x$, $\mathbf{R}_y$, $\mathbf{R}_z$,

-90° rotations $\tilde{\mathbf{R}}_x$, $\tilde{\mathbf{R}}_y$, $\tilde{\mathbf{R}}_z$,

180° rotations $\boldsymbol{\rho}_x$, $\boldsymbol{\rho}_y$, $\boldsymbol{\rho}_z$,

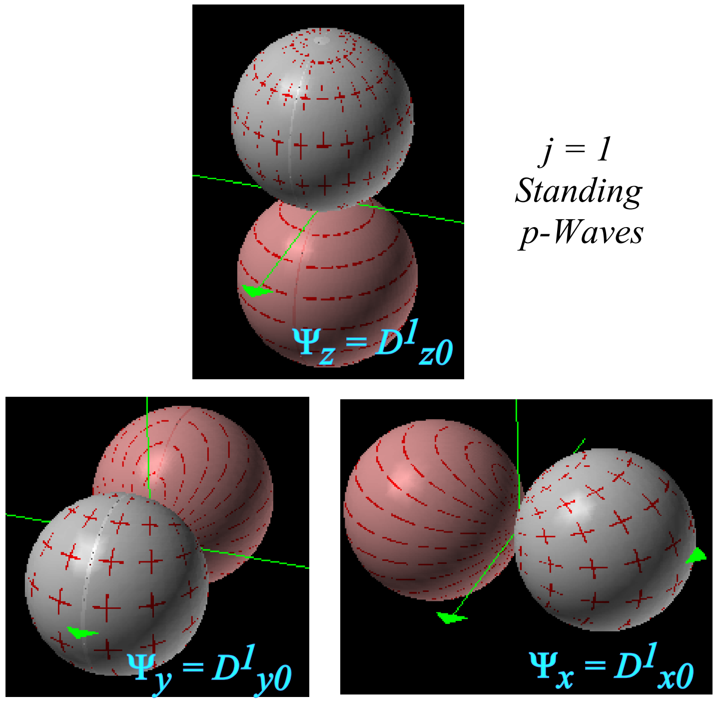


Finding O_h group products

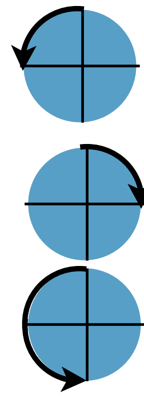
*(irrep=irreducible representations)

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



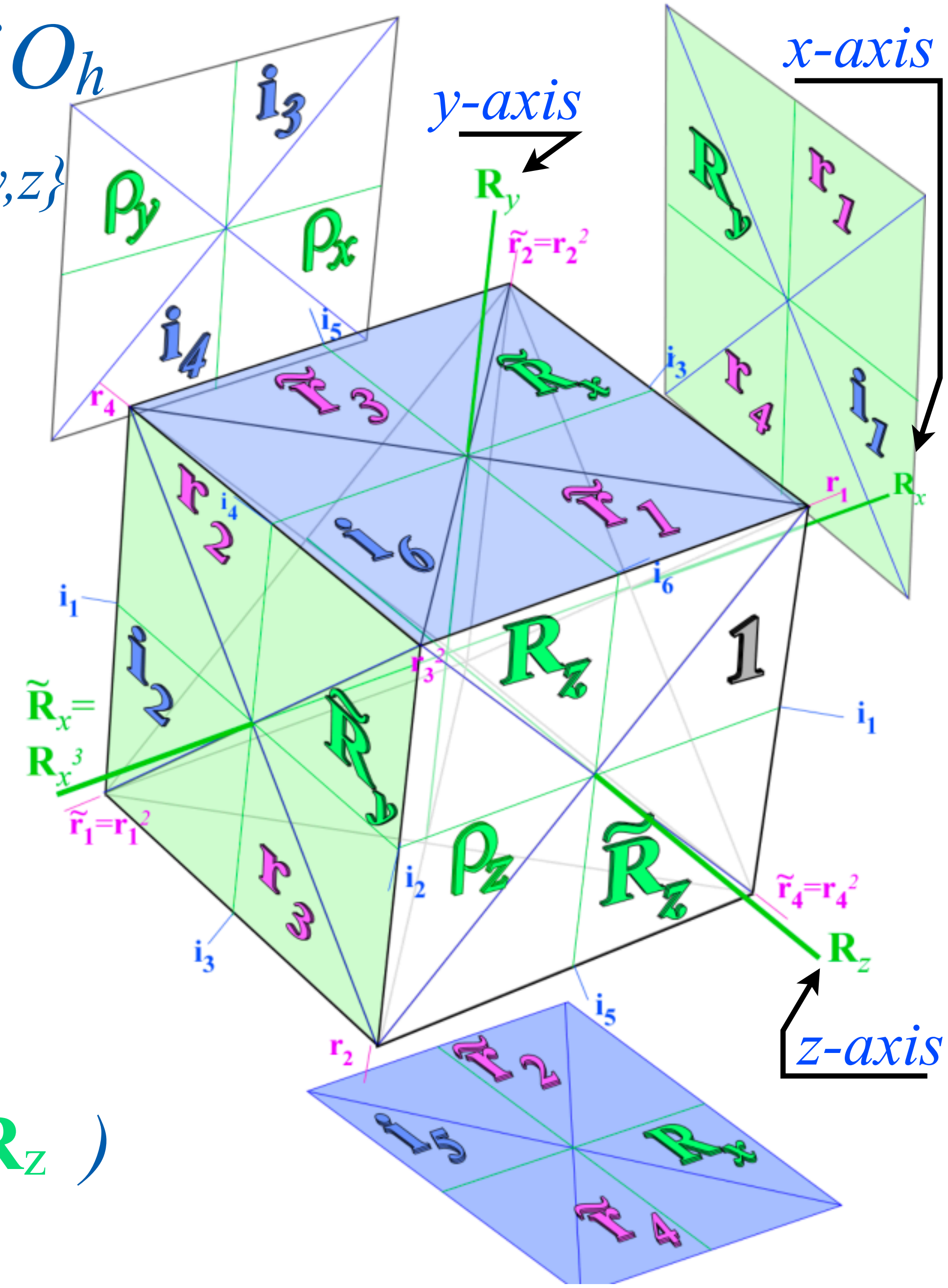
Locate x, y, z axes of



+90° rotations $\mathbf{R}_x$, $\mathbf{R}_y$, $\mathbf{R}_z$,

-90° rotations $\tilde{\mathbf{R}}_x$, $\tilde{\mathbf{R}}_y$, $\tilde{\mathbf{R}}_z$,

180° rotations $\boldsymbol{\rho}_x$, $\boldsymbol{\rho}_y$, $\boldsymbol{\rho}_z$,



Finding O_h group products

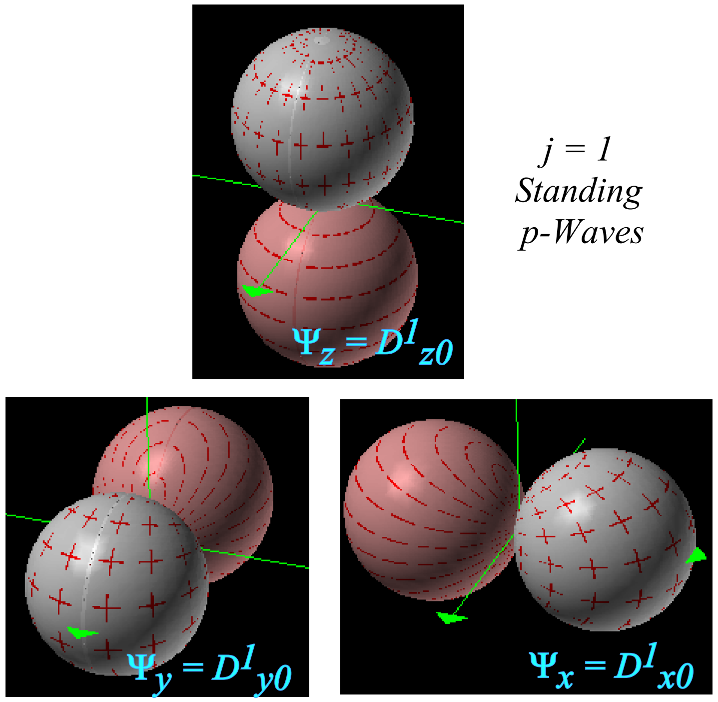
Note that $\tilde{\mathbf{R}}_z$ *is inverse (and third power of* $\mathbf{R}_z$ *)*

$$\tilde{\mathbf{R}}_z = (\mathbf{R}_z)^{-1} = (\mathbf{R}_z)^3$$

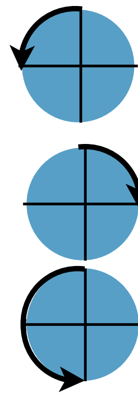
**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



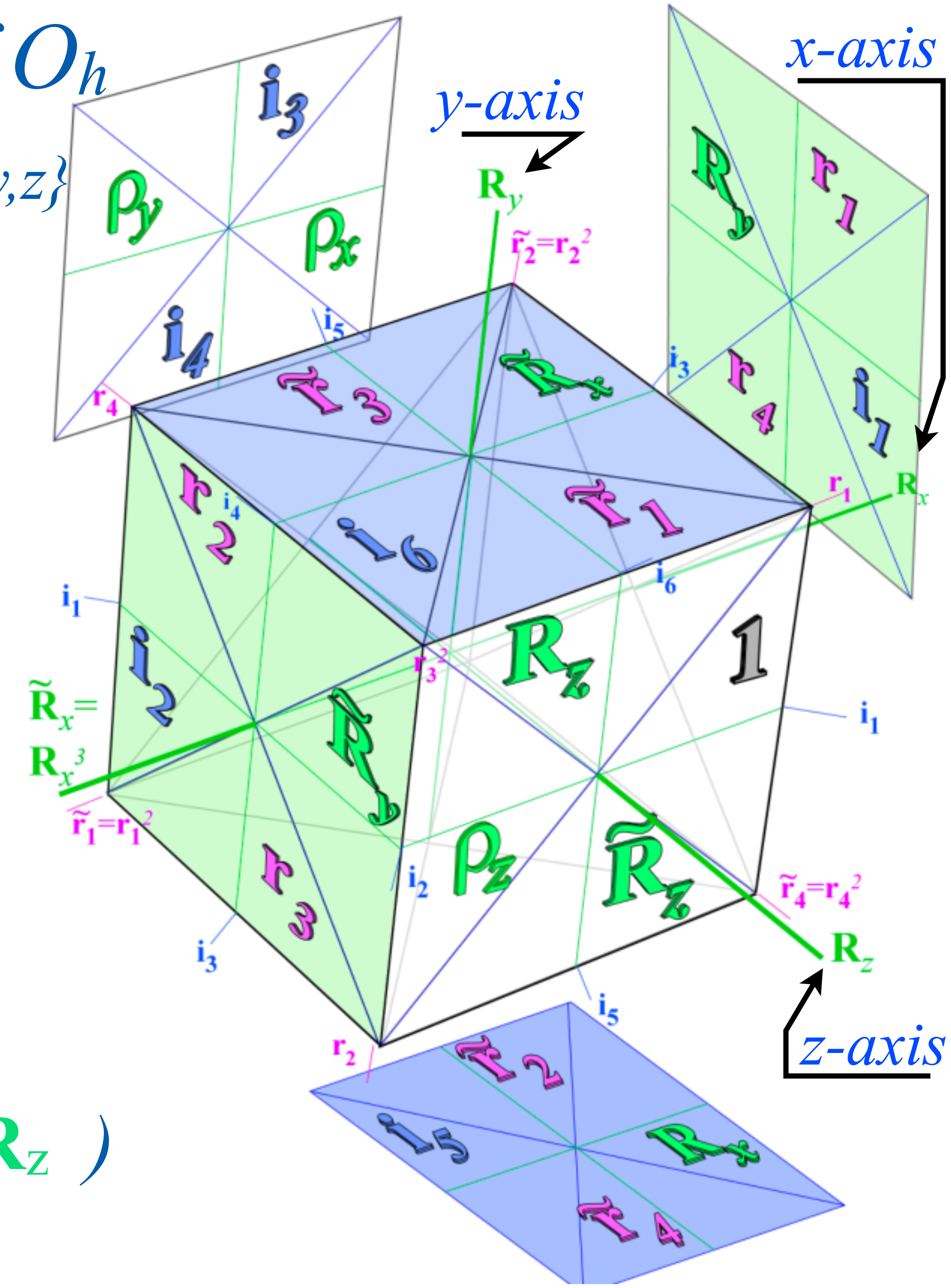
Locate x, y, z axes of



+90° rotations $\mathbf{R}_x$, $\mathbf{R}_y$, $\mathbf{R}_z$,

-90° rotations $\tilde{\mathbf{R}}_x$, $\tilde{\mathbf{R}}_y$, $\tilde{\mathbf{R}}_z$,

180° rotations $\boldsymbol{\rho}_x$, $\boldsymbol{\rho}_y$, $\boldsymbol{\rho}_z$,



Finding O_h group products

Note that $\tilde{\mathbf{R}}_z$ *is inverse (and third power of* $\mathbf{R}_z$ *)*

$$\tilde{\mathbf{R}}_z = (\mathbf{R}_z)^{-1} = (\mathbf{R}_z)^3$$

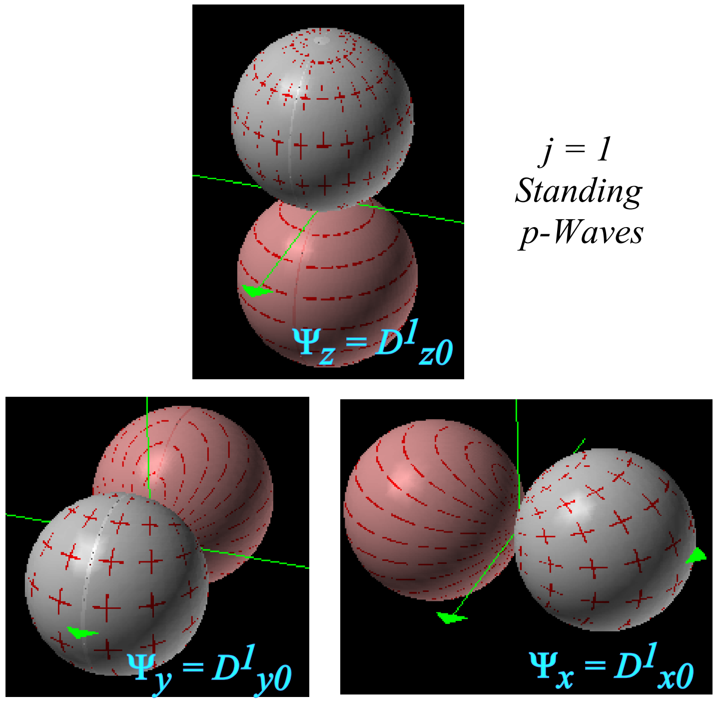
Note that $\boldsymbol{\rho}_z$ *is 2nd power of* $\mathbf{R}_z$ *(and its own inverse)*

$$\boldsymbol{\rho}_z = (\boldsymbol{\rho}_z)^{-1} = (\mathbf{R}_z)^2$$

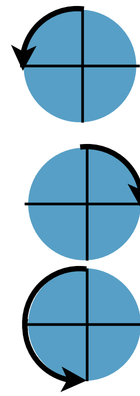
**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



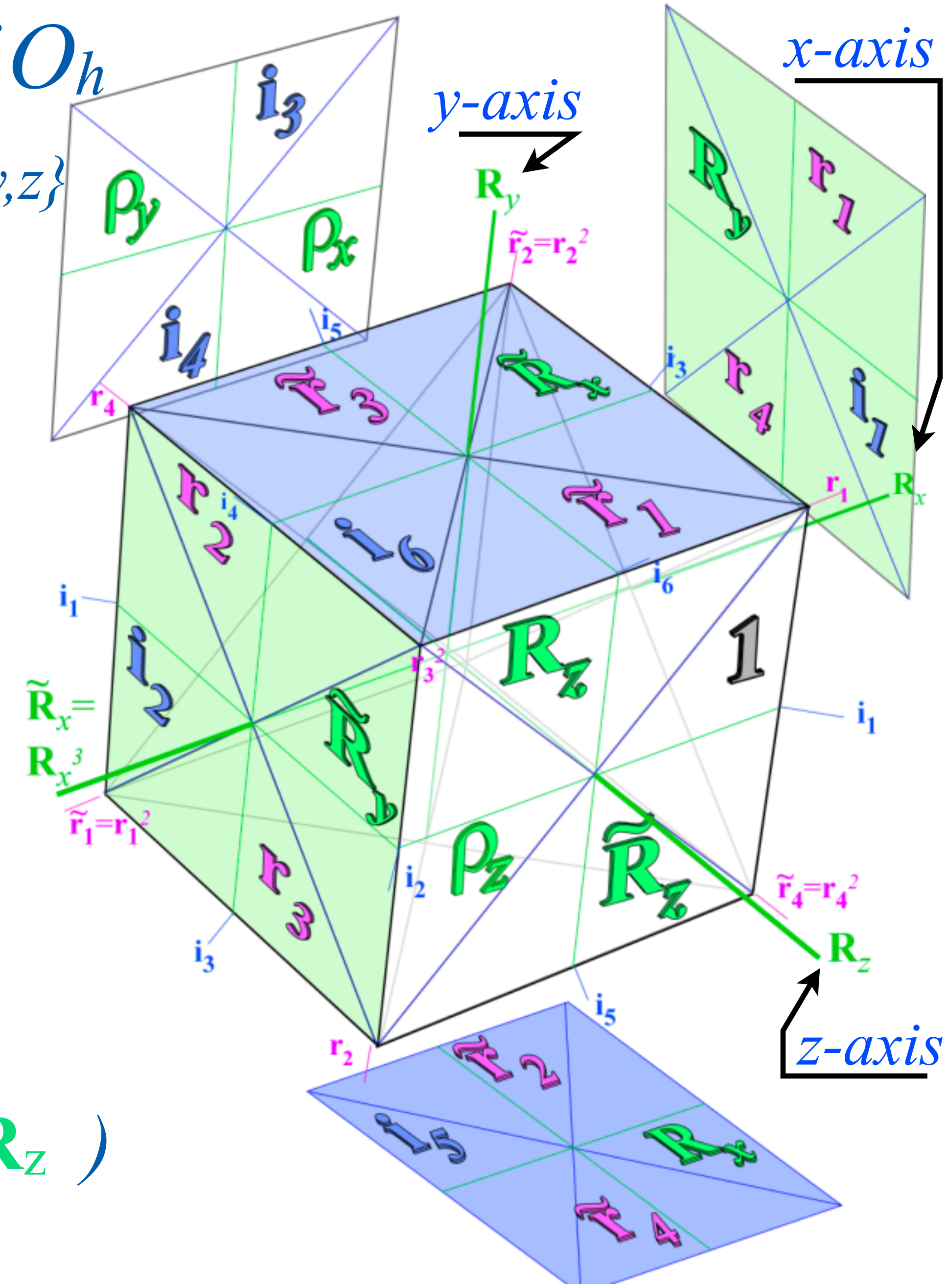
Locate x, y, z axes of



+90° rotations $\mathbf{R}_x$, $\mathbf{R}_y$, $\mathbf{R}_z$,

-90° rotations $\tilde{\mathbf{R}}_x$, $\tilde{\mathbf{R}}_y$, $\tilde{\mathbf{R}}_z$,

180° rotations $\boldsymbol{\rho}_x$, $\boldsymbol{\rho}_y$, $\boldsymbol{\rho}_z$,



Finding O_h group products

Note that $\tilde{\mathbf{R}}_z$ *is inverse (and third power of* $\mathbf{R}_z$ *)*

$$\tilde{\mathbf{R}}_z = (\mathbf{R}_z)^{-1} = (\mathbf{R}_z)^3$$

Note that $\boldsymbol{\rho}_z$ *is 2nd power of* $\mathbf{R}_z$ *(and its own inverse)*

$$\boldsymbol{\rho}_z = (\boldsymbol{\rho}_z)^{-1} = (\mathbf{R}_z)^2$$

The four operators $\{\mathbf{1}, \mathbf{R}_z, \boldsymbol{\rho}_z, \tilde{\mathbf{R}}_z\}$ *form an important C_4 subgroup of O.*

**(irrep=irreducible representations)*

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^{E} irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O

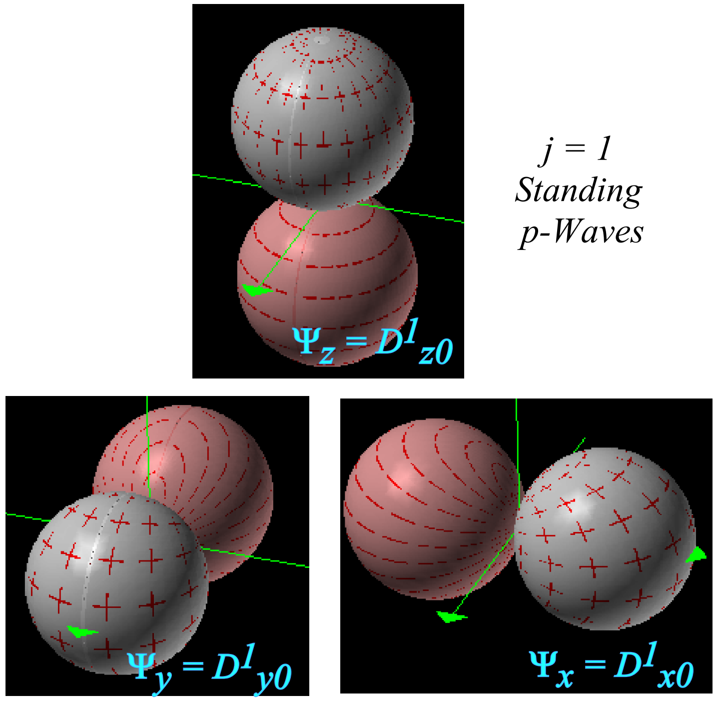
$R(3)\supset O$ character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group$\supset$Sub-group correlation

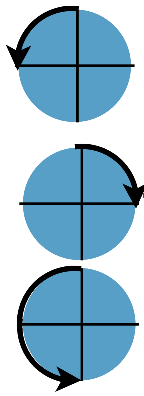
Comparing Octahedral and Asymmetric rotor states and level clusters at high J

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



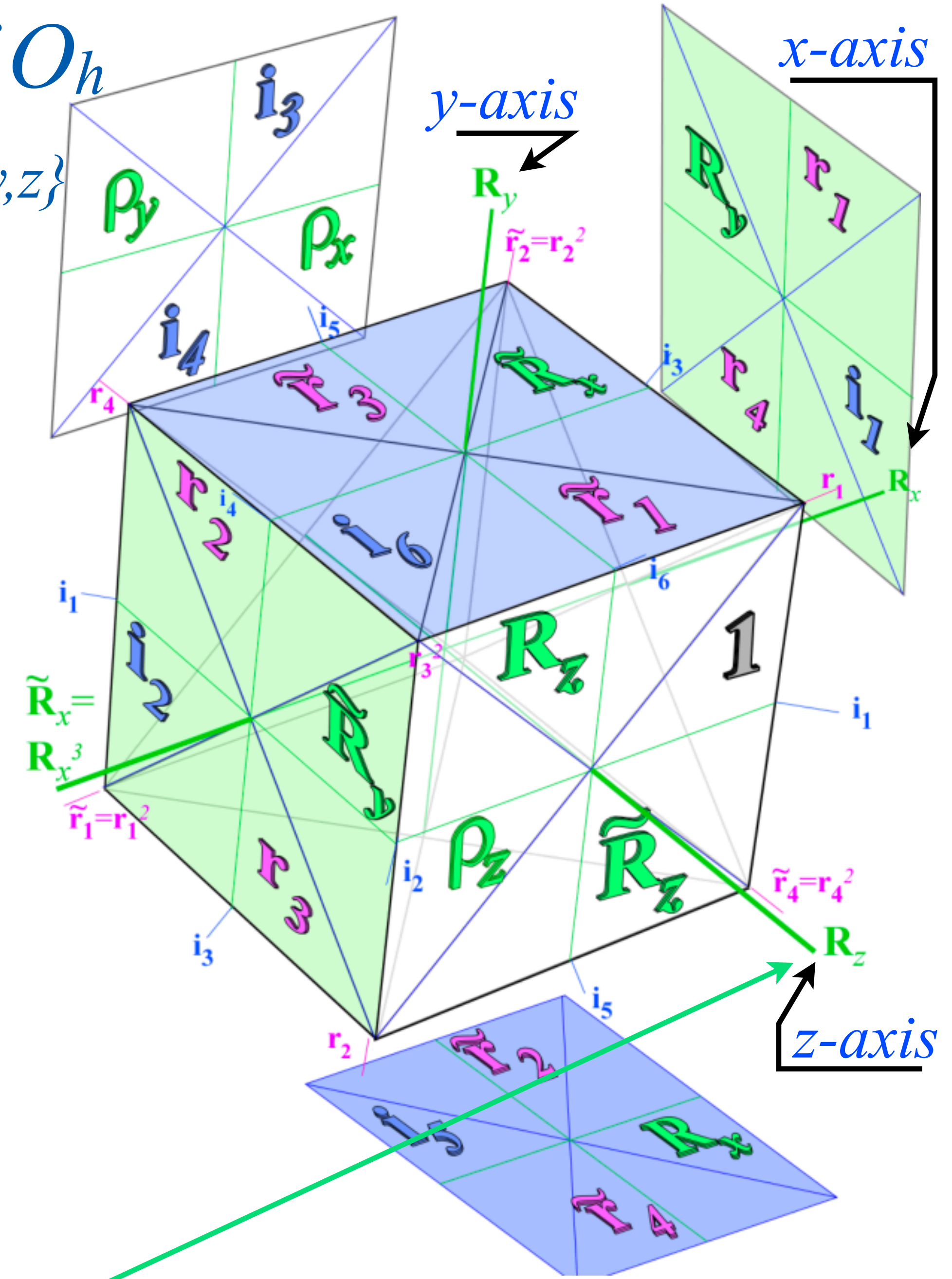
Locate x, y, z axes of



+90° rotations $\mathbf{R}_x$, $\mathbf{R}_y$, $\mathbf{R}_z$,

-90° rotations $\tilde{\mathbf{R}}_x$, $\tilde{\mathbf{R}}_y$, $\tilde{\mathbf{R}}_z$,

180° rotations $\boldsymbol{\rho}_x$, $\boldsymbol{\rho}_y$, $\boldsymbol{\rho}_z$,



Finding O_h group products

To calculate O products like $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *(easy) or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *(less easy)…* *or* $\mathbf{i}_6\mathbf{R}_z=\tilde{\mathbf{r}}_1$ *(even less easy)*

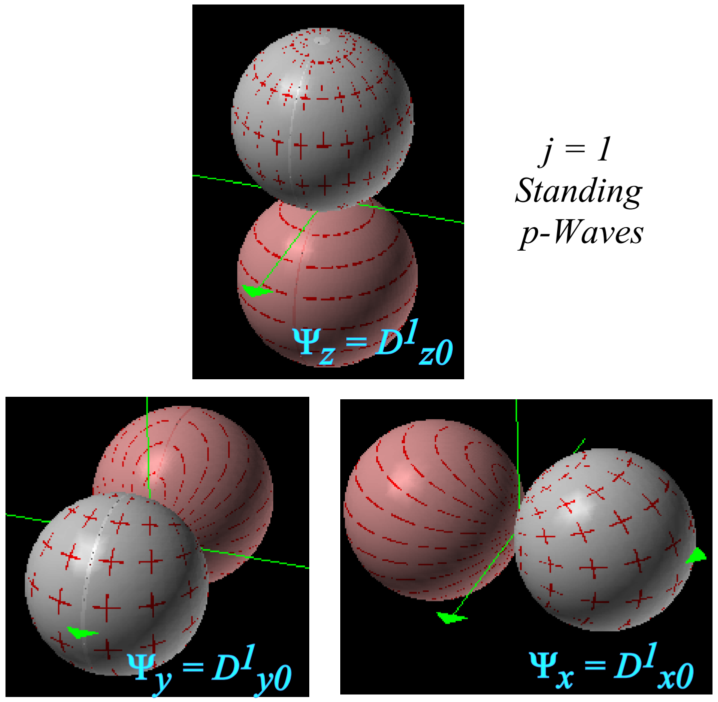
Find $\mathbf{R}_z$ *operator axis*

(line by small type R_z*)*

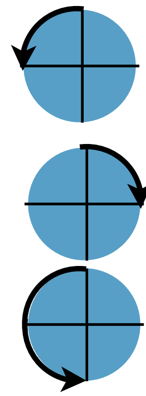
**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^E, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



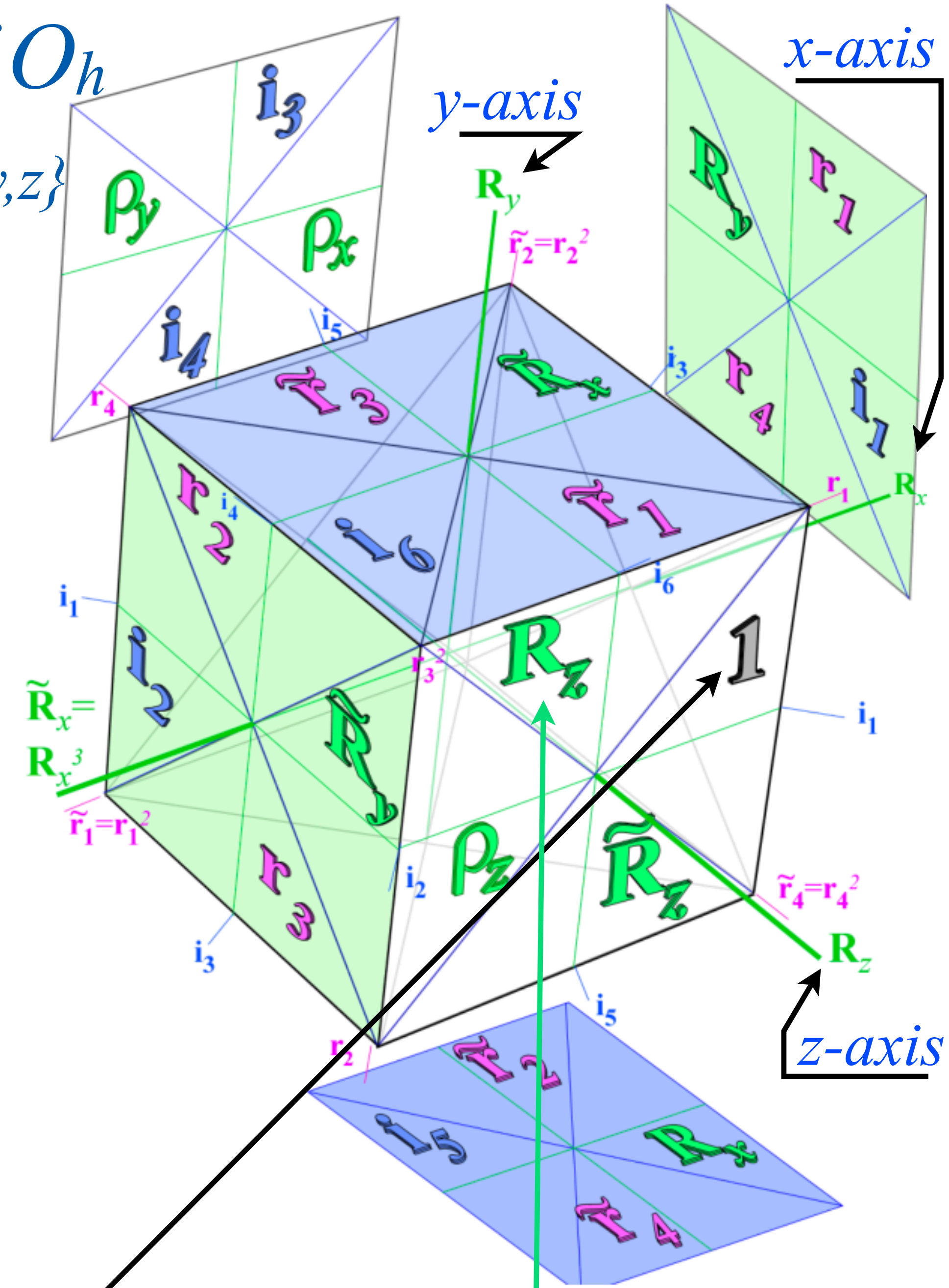
Locate x, y, z axes of



+90° rotations $\mathbf{R}_x$, $\mathbf{R}_y$, $\mathbf{R}_z$,

-90° rotations $\tilde{\mathbf{R}}_x$, $\tilde{\mathbf{R}}_y$, $\tilde{\mathbf{R}}_z$,

180° rotations ρ_x, ρ_y, ρ_z,



Finding O_h group products

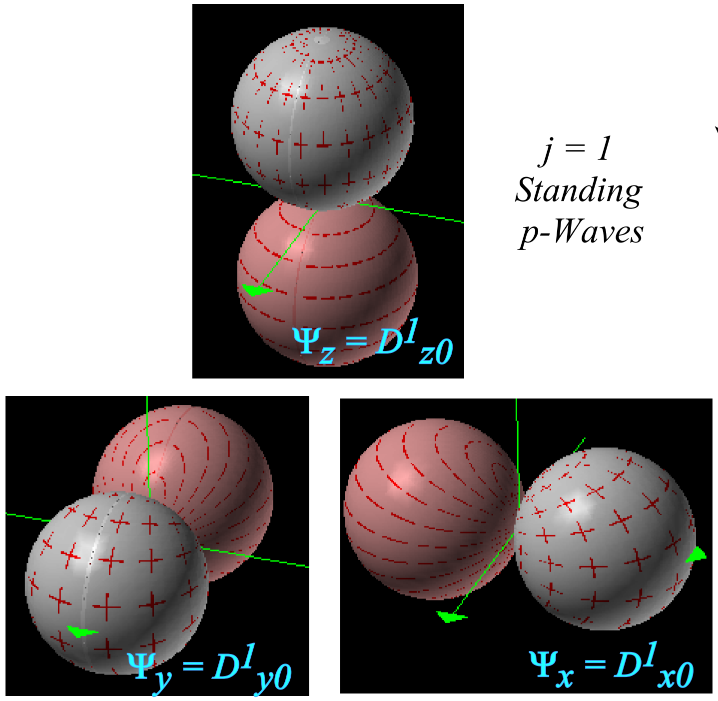
To calculate O products like $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *(easy) or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *(less easy)…* *or* $\mathbf{i}_6\mathbf{R}_z=\tilde{\mathbf{r}}_1$ *(even less easy)*

Find $\mathbf{R}_z$ *operator axis*
(line by small type R_z*)*
Imagine 90° rotation R_z
of "state triangle" **1** to the
triangle with result $\mathbf{R}_z=\mathbf{R}_z\mathbf{1}$

**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$

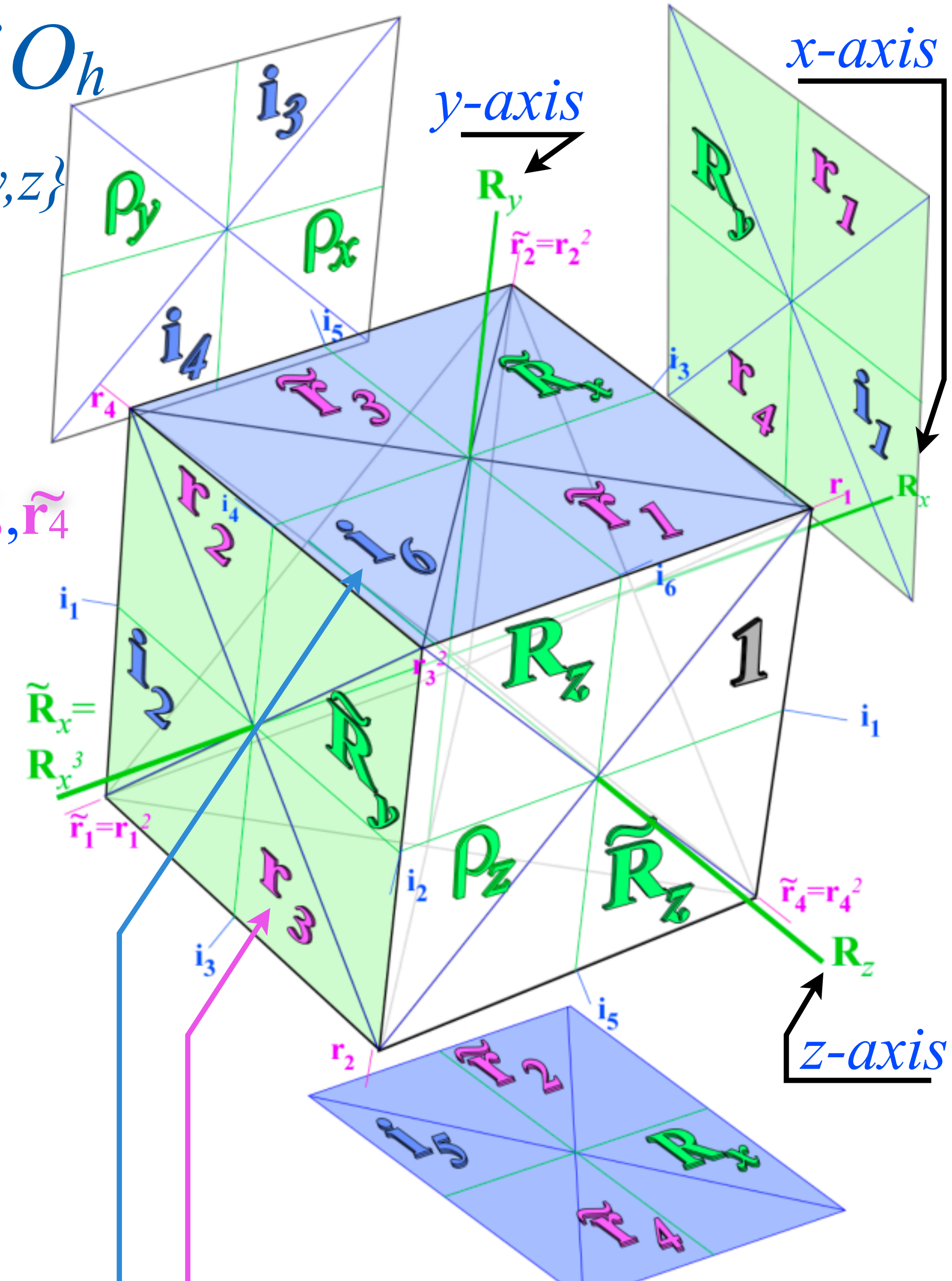


Locate x, y, z axes of

±90° *rotations* $\mathbf{R}_x,\mathbf{R}_y,\mathbf{R}_z,\tilde{\mathbf{R}}_x,\tilde{\mathbf{R}}_y,\tilde{\mathbf{R}}_z$

±120° *rotations* $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\tilde{\mathbf{r}}_1,\tilde{\mathbf{r}}_2,\tilde{\mathbf{r}}_3,\tilde{\mathbf{r}}_4$

±180° *rotations* $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$
$\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3,\mathbf{i}_4,\mathbf{i}_5,\mathbf{i}_6$



Finding O_h group products

To calculate O products like $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *(easy) or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *(less easy)…* *or* $\mathbf{i}_6\mathbf{R}_z=\tilde{\mathbf{r}}_1$ *(even less easy)*

Find $\mathbf{R}_z$ *operator axis*
(line by small type R_z)
Imagine 90° rotation R_z
of "state triangle" **1** to the
triangle with result $\mathbf{R}_z=\mathbf{R}_z\mathbf{1}$

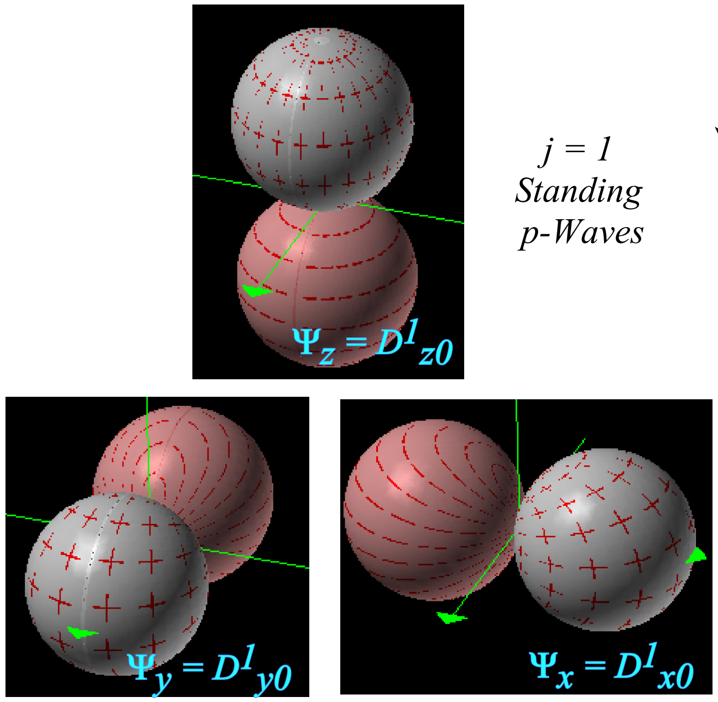
Find $\mathbf{R}_z$ *operator axis*
(line by small type R_z)
Imagine 90° rotation R_z
of "state triangle" $\mathbf{i}_6$ to
triangle with result $\mathbf{r}_3=\mathbf{R}_z\mathbf{i}_6$

$\mathbf{r}_3$ is a 120° rotation about [+1-1-1]

**(irrep=irreducible representations)*

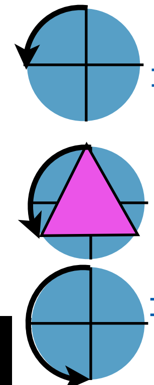
Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



j = 1 Standing p-Waves

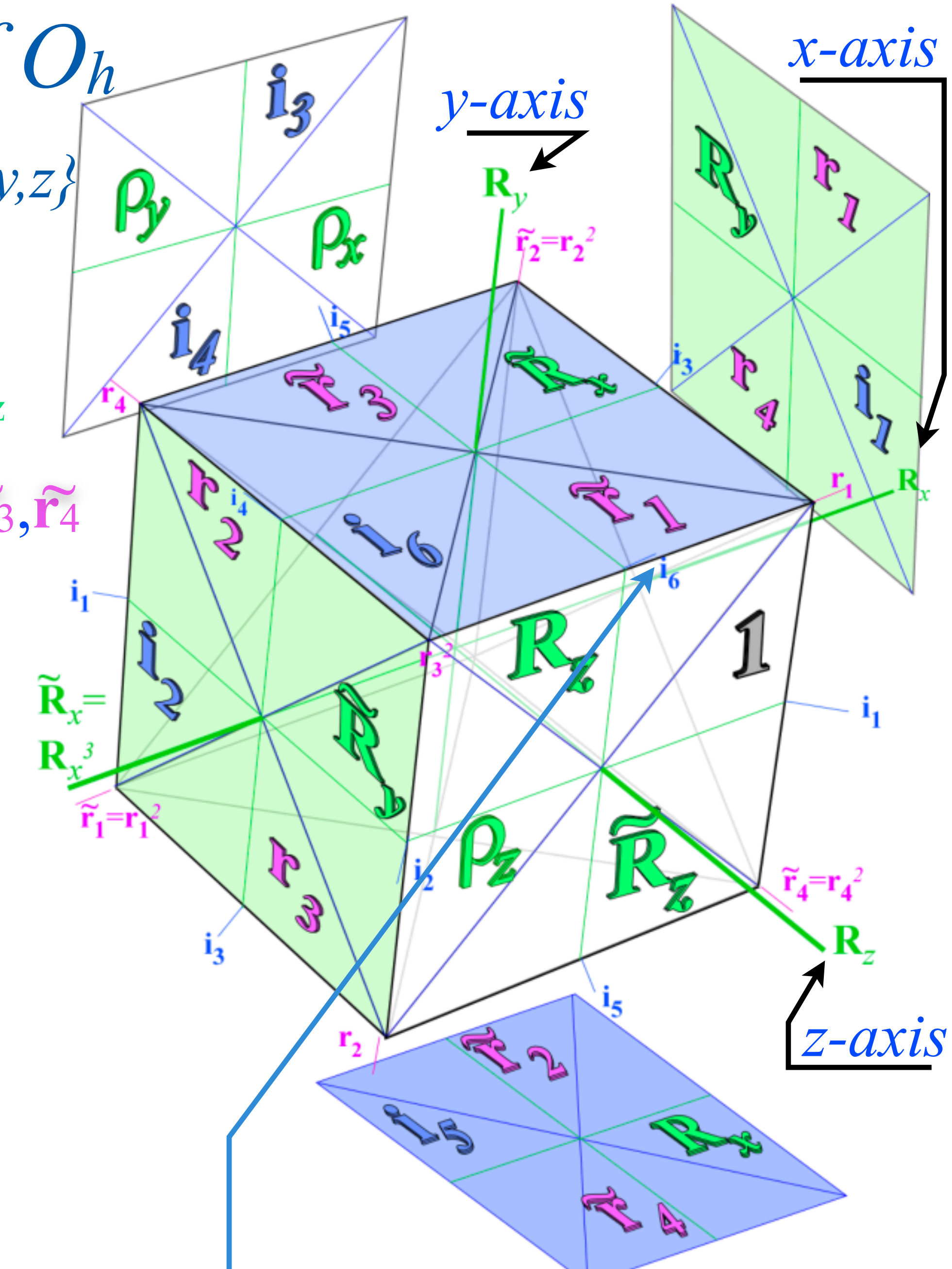
Locate x, y, z axes of



±90° *rotations* $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

±120° *rotations* $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \tilde{\mathbf{r}}_4$

±180° *rotations* $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z$, $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$



Finding O_h group products

To calculate O products like $\mathbf{R}_z\mathbf{1} = \mathbf{R}_z$ *(easy) or* $\mathbf{R}_z\mathbf{i}_6 = \mathbf{r}_3$ *(less easy)…* *or* $\mathbf{i}_6\mathbf{R}_z = \tilde{\mathbf{r}}_1$ *(even less easy)*

Find $\mathbf{R}_z$ *operator axis*
(*line by* small type R_z)
Imagine 90° rotation R_z
of "state triangle" **1** to the
triangle with result $\mathbf{R}_z = \mathbf{R}_z\mathbf{1}$

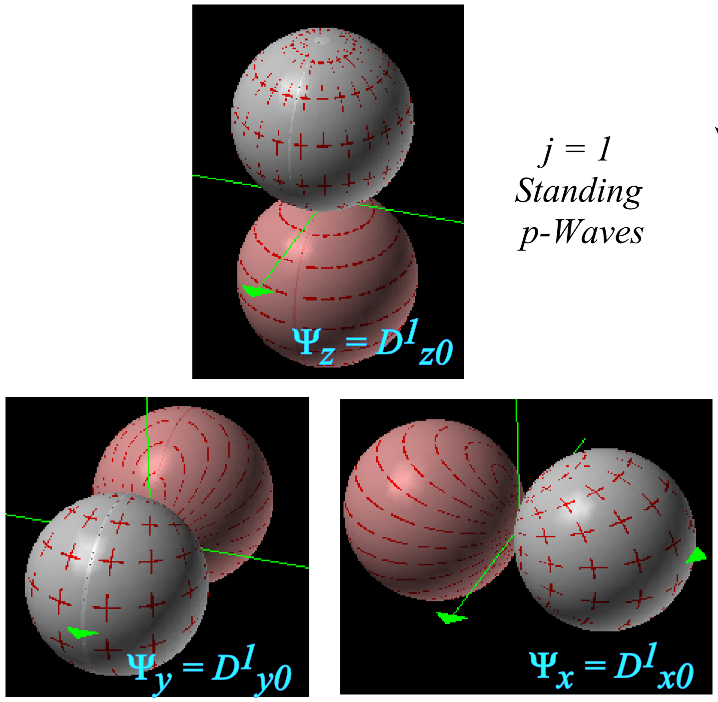
Find $\mathbf{R}_z$ *operator axis*
(*line by* small type R_z)
Imagine 90° rotation R_z
of "state triangle" $\mathbf{i}_6$ to
triangle with result $\mathbf{r}_3 = \mathbf{R}_z\mathbf{i}_6$
$\mathbf{r}_3$ is a 120° rotation about [+1-1-1]

Find $\mathbf{i}_6$ *operator axis*
(*line by* small type $\mathbf{i}_6$ on [011])
Imagine 180° rotation $\mathbf{i}_6$
of "state triangle" $\mathbf{R}_z$ to
triangle with result $\tilde{\mathbf{r}}_1 = \mathbf{i}_6\mathbf{R}_z$
$\tilde{\mathbf{r}}_1$ is a 120° rotation about [-1-1-1]
or a -120° rotation $(\mathbf{r}_1)^2$ about [111]

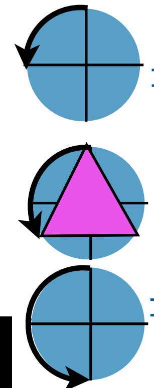
**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps* of O_h

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



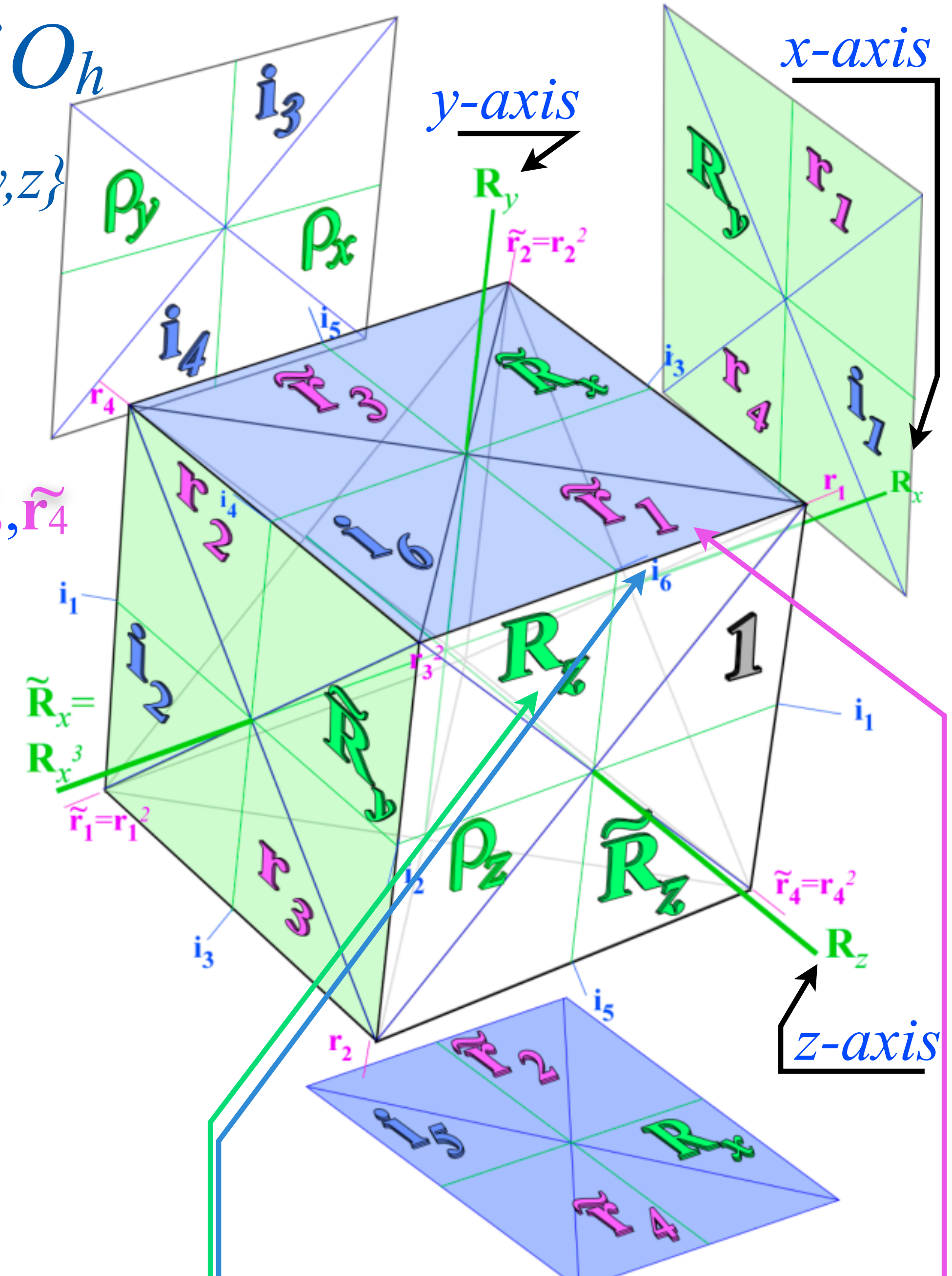
Locate x, y, z axes of



$\pm 90°$ *rotations* $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

$\pm 120°$ *rotations* $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \tilde{\mathbf{r}}_4$

$\pm 180°$ *rotations* $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$
$\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$



Finding O_h group products

To calculate O products like $\mathbf{R}_z\mathbf{1} = \mathbf{R}_z$ *(easy) or* $\mathbf{R}_z\mathbf{i}_6 = \mathbf{r}_3$ *(less easy)…* *or* $\mathbf{i}_6\mathbf{R}_z = \tilde{\mathbf{r}}_1$ *(even less easy)*

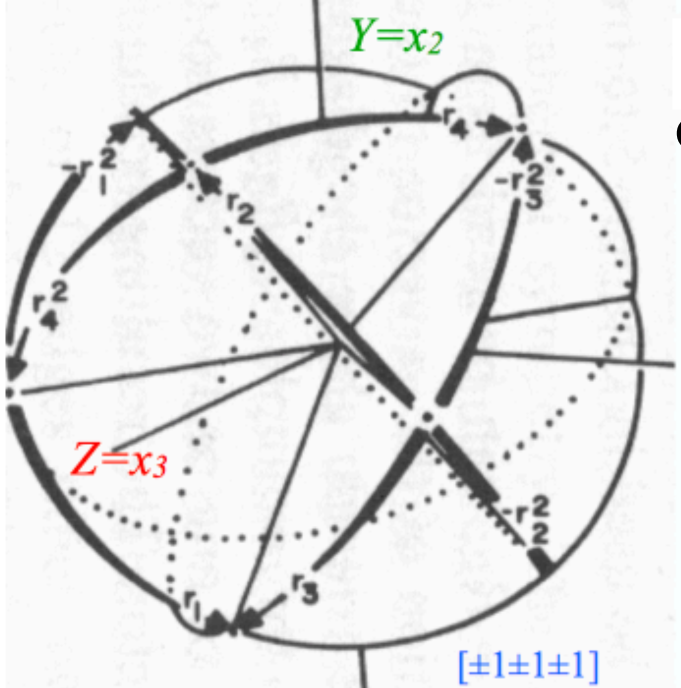
Find $\mathbf{R}_z$ *operator axis*
(*line by* small type R_z)
Imagine 90° rotation R_z
of "state triangle" **1** to the
triangle with result $\mathbf{R}_z = \mathbf{R}_z\mathbf{1}$

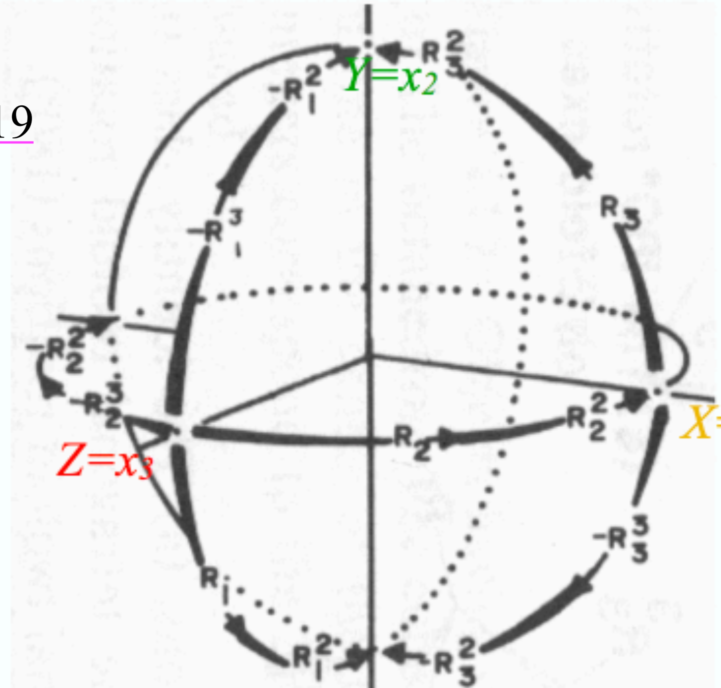
Find $\mathbf{R}_z$ *operator axis*
(*line by* small type R_z)
Imagine 90° rotation R_z
of "state triangle" $\mathbf{i}_6$ to
triangle with result $\mathbf{r}_3 = \mathbf{R}_z\mathbf{i}_6$
$\mathbf{r}_3$ is a 120° rotation about [+1-1-1]

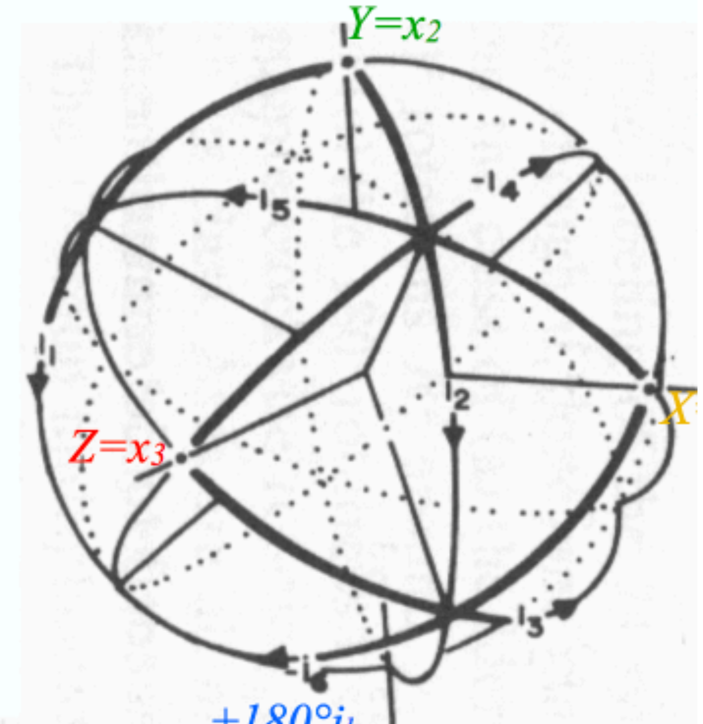
Find $\mathbf{i}_6$ *operator axis*
(*line by* small type $\mathbf{i}_6$ on [011])
Imagine 180° rotation $\mathbf{i}_6$
of "state triangle" $\mathbf{R}_z$ to
triangle with result $\tilde{\mathbf{r}}_1 = \mathbf{i}_6\mathbf{R}_z$
$\tilde{\mathbf{r}}_1$ is a 120° rotation about [-1-1-1]
or a -120° rotation $(\mathbf{r}_1)^2$ about [111]

*(*irrep=irreducible representations*)

O *products* GTh19p19







	+120°				-120°				±180° XYZ			+90° XYZ			-90° XYZ			±180°i_k					
	[1 1 1]	$[\bar{1}\,\bar{1}\,1]$	$[1\,\bar{1}\,\bar{1}]$	$[\bar{1}\,1\,\bar{1}]$	$[\bar{1}\,\bar{1}\,\bar{1}]$	$[1\,1\,\bar{1}]$	$[\bar{1}\,1\,1]$	$[1\,\bar{1}\,1]$	[1 0 0]	[0 1 0]	[0 0 1]	[1 0 0]	[0 1 0]	[0 0 1]	$[\bar{1}\,0\,0]$	$[0\,\bar{1}\,0]$	$[0\,0\,\bar{1}]$	[1 0 1]	$[1\,0\,\bar{1}]$	[1 1 0]	$[1\,\bar{1}\,0]$	$[0\,1\,\bar{1}]$	[0 1 1]
1	r_1	r_2	r_3	r_4	r_1^2	r_2^2	r_3^2	r_4^2	R_1^2	R_2^2	R_3^2	R_1	R_2	R_3	R_1^3	R_2^3	R_3^3	i_1	i_2	i_3	i_4	i_5	i_6
r_1	r_1^2	$-r_4^2$	$-r_2^2$	$-r_3^2$	-1	$-R_2^2$	$-R_3^2$	$-R_1^2$	$-r_2$	$-r_3$	$-r_4$	i_3	i_6	i_1	$-R_3$	$-R_1$	$-R_2$	R_1^3	i_5	R_2^3	i_2	$-i_4$	R_3^3
r_2	$-r_3^2$	r_2^2	$-r_4^2$	$-r_1^2$	R_2^2	-1	R_1^2	$-R_3^2$	r_1	r_4	$-r_3$	R_3	$-R_1^3$	i_2	i_3	$-i_5$	R_2^3	i_6	$-R_1$	R_2	$-i_1$	R_3^3	i_4
r_3	$-r_4^2$	$-r_1^2$	r_3^2	$-r_2^2$	R_3^2	$-R_1^2$	-1	R_2^2	$-r_4$	r_1	r_2	$-i_4$	R_1	$-R_2^3$	R_3^3	i_6	i_2	i_5	$-R_1^3$	i_1	R_2	$-i_3$	R_3
r_4	$-r_2^2$	$-r_3^2$	$-r_1^2$	r_4^2	R_1^2	R_3^2	$-R_2^2$	-1	r_3	$-r_2$	r_1	$-R_3^3$	$-i_5$	R_2	$-i_4$	R_1^3	i_1	R_1	i_6	$-i_2$	R_2^3	R_3	i_3
r_1^2	-1	R_1^2	R_2^2	R_3^2	$-r_1$	r_3	r_4	r_2	r_4^2	r_2^2	r_3^2	R_2^3	R_3^3	R_1^3	$-i_1$	$-i_3$	$-i_6$	$-R_3$	$-i_4$	$-R_1$	i_5	$-i_2$	$-R_2$
r_2^2	$-R_1^2$	-1	R_3^2	$-R_2^2$	r_4	$-r_2$	r_1	r_3	$-r_3^2$	$-r_1^2$	r_4^2	i_2	$-i_3$	$-R_1$	R_2	$-R_3^3$	$-i_5$	i_4	$-R_3$	$-R_1^3$	$-i_6$	R_2^3	$-i_1$
r_3^2	$-R_2^2$	$-R_3^2$	-1	R_1^2	r_2	r_4	$-r_3$	r_1	r_2^2	$-r_4^2$	$-r_1^2$	$-R_2$	$-i_4$	$-i_6$	i_2	R_3	$-R_1^3$	$-i_3$	$-R_3^3$	i_5	R_1	$-i_1$	$-R_2^3$
r_4^2	$-R_3^2$	R_2^2	$-R_1^2$	-1	r_3	r_1	r_2	$-r_4$	$-r_1^2$	r_3^2	$-r_2^2$	$-i_1$	$-R_3$	$-i_5$	$-R_2^3$	$-i_4$	R_1	$-R_3^3$	i_3	$-i_6$	R_1^3	R_2	$-i_2$
R_1^2	$-r_4$	r_3	$-r_2$	r_1	r_2^2	$-r_1^2$	r_4^2	$-r_3^2$	-1	R_3^2	$-R_2^2$	R_1^3	i_1	$-i_4$	$-R_1$	i_2	$-i_3$	$-R_2$	$-R_2^3$	R_3^3	R_3	$-i_6$	i_5
R_2^2	$-r_2$	r_1	r_4	$-r_3$	r_3^2	$-r_4^2$	$-r_1^2$	r_2^2	$-R_3^2$	-1	R_1^2	$-i_5$	R_2^3	i_3	$-i_6$	$-R_2$	$-i_4$	$-i_2$	i_1	$-R_3$	R_3^3	R_1	R_1^3
R_3^2	$-r_3$	$-r_4$	r_1	r_2	r_4^2	r_3^2	$-r_2^2$	$-r_1^2$	R_2^2	$-R_1^2$	-1	i_6	i_2	R_3^3	$-i_5$	$-i_1$	$-R_3$	R_2^3	$-R_2$	i_4	$-i_3$	R_1^3	$-R_1$
R_1	i_1	$-R_2^3$	$-i_2$	R_2	R_3^3	$-i_3$	$-R_3$	i_4	R_1^3	i_6	i_5	R_1^2	r_1	$-r_4^2$	-1	$-r_3$	r_2^2	$-r_4$	r_2	r_1^2	$-r_3^2$	$-R_2^2$	R_3^2
R_2	i_3	R_3	$-R_3^3$	i_4	R_1^3	i_5	$-i_6$	$-R_1$	$-i_2$	R_2^3	i_1	$-r_2^2$	R_2^2	r_1	r_3^2	-1	$-r_4$	R_1^2	R_3^2	$-r_2$	$-r_3$	$-r_4^2$	r_1^2
R_3	i_6	i_5	R_1	$-R_1^3$	R_2^3	$-R_2$	$-i_2$	$-i_1$	i_3	i_4	R_3^3	r_1	$-r_3^2$	R_3^2	$-r_2$	r_4^2	-1	r_1^2	r_2^2	R_2^2	$-R_1^2$	$-r_4$	$-r_3$
R_1^3	$-R_2$	$-i_2$	R_2^3	i_1	$-i_3$	$-R_3^3$	i_4	R_3	$-R_1$	i_5	$-i_6$	-1	$-r_4$	r_3^2	$-R_1^2$	r_2	$-r_1^2$	$-r_1$	r_3	r_2^2	$-r_4^2$	$-R_3^2$	$-R_2^2$
R_2^3	$-R_3$	i_3	i_4	R_3^3	$-i_6$	R_1	$-R_1^3$	i_5	$-i_1$	$-R_2$	$-i_2$	r_4^2	-1	$-r_2$	$-r_1^2$	$-R_2^2$	r_3	$-R_3^2$	R_1^2	$-r_1$	$-r_4$	$-r_2^2$	r_3^2
R_3^3	$-R_1$	R_1^3	i_6	i_5	$-i_1$	$-i_2$	R_2	$-R_2^3$	i_4	$-i_3$	$-R_3$	$-r_3$	r_2^2	-1	r_4	$-r_1^2$	$-R_3^2$	r_4^2	r_3^2	$-R_1^2$	$-R_2^2$	$-r_2$	$-r_1$
i_1	R_3^3	$-i_4$	i_3	R_3	$-R_1$	$-i_6$	$-i_5$	$-R_1^3$	R_2^3	i_2	$-R_2$	r_1^2	R_3^2	$-r_4$	r_4^2	$-R_1^2$	$-r_1$	-1	$-R_2^2$	$-r_3$	r_2	r_3^2	r_2^2
i_2	i_4	R_3^3	R_3	$-i_3$	$-i_5$	R_1^3	R_1	$-i_6$	R_2	$-i_1$	R_2^3	$-r_3^2$	$-R_1^2$	$-r_3$	$-r_2^2$	$-R_3^2$	$-r_2$	R_2^2	-1	r_4	$-r_1$	r_1^2	r_4^2
i_3	R_1^3	R_1	$-i_5$	i_6	$-R_2$	$-R_2^3$	$-i_1$	i_2	$-R_3$	R_3^3	$-i_4$	$-r_2$	r_1^2	R_1^2	$-r_1$	r_2^2	$-R_2^2$	r_3^2	$-r_4^2$	-1	R_3^2	r_3	$-r_4$
i_4	$-i_5$	i_6	$-R_1^3$	$-R_1$	$-i_2$	i_1	$-R_2^3$	$-R_2$	$-R_3^3$	$-R_3$	i_3	r_4	r_4^2	R_2^2	r_3	r_3^2	R_1^2	$-r_2^2$	r_1^2	$-R_3^3$	-1	r_1	$-r_2$
i_5	i_2	$-R_2$	i_1	$-R_2^3$	i_4	$-R_3$	i_3	$-R_3^3$	i_6	$-R_1^3$	$-R_1$	R_3^2	r_2	r_2^2	R_2^2	r_4	r_4^2	$-r_3$	$-r_1$	$-r_3^2$	$-r_1^2$	-1	$-R_1^2$
i_6	R_2^3	i_1	R_2	i_2	$-R_3$	$-i_4$	$-R_3^3$	$-i_3$	$-i_5$	$-R_1$	R_1^3	R_2^2	$-r_3$	r_1^2	$-R_3^2$	$-r_1$	r_3^2	$-r_2$	$-r_4$	r_4^2	r_2^2	R_1^2	-1

Octahedral O and spin-O⊂U(2) rotation product Table F.2.1 from Principles of Symmetry, Dynamics and Spectroscopy

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^E, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^E irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^E, χ^{A2}, and χ^{A1} of O

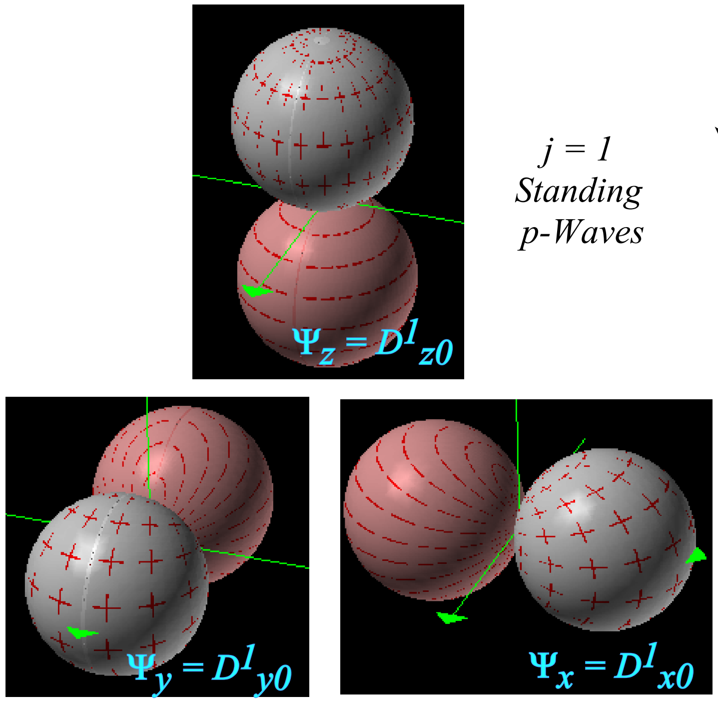
$R(3)\supset O$ character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group$\supset$Sub-group correlation

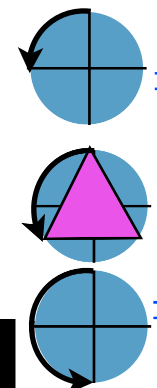
Comparing Octahedral and Asymmetric rotor states and level clusters at high J

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps* of O_h

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



Locate x, y, z axes of



±90° rotations $\mathbf{R}_x,\mathbf{R}_y,\mathbf{R}_z,\tilde{\mathbf{R}}_x,\tilde{\mathbf{R}}_y,\tilde{\mathbf{R}}_z$

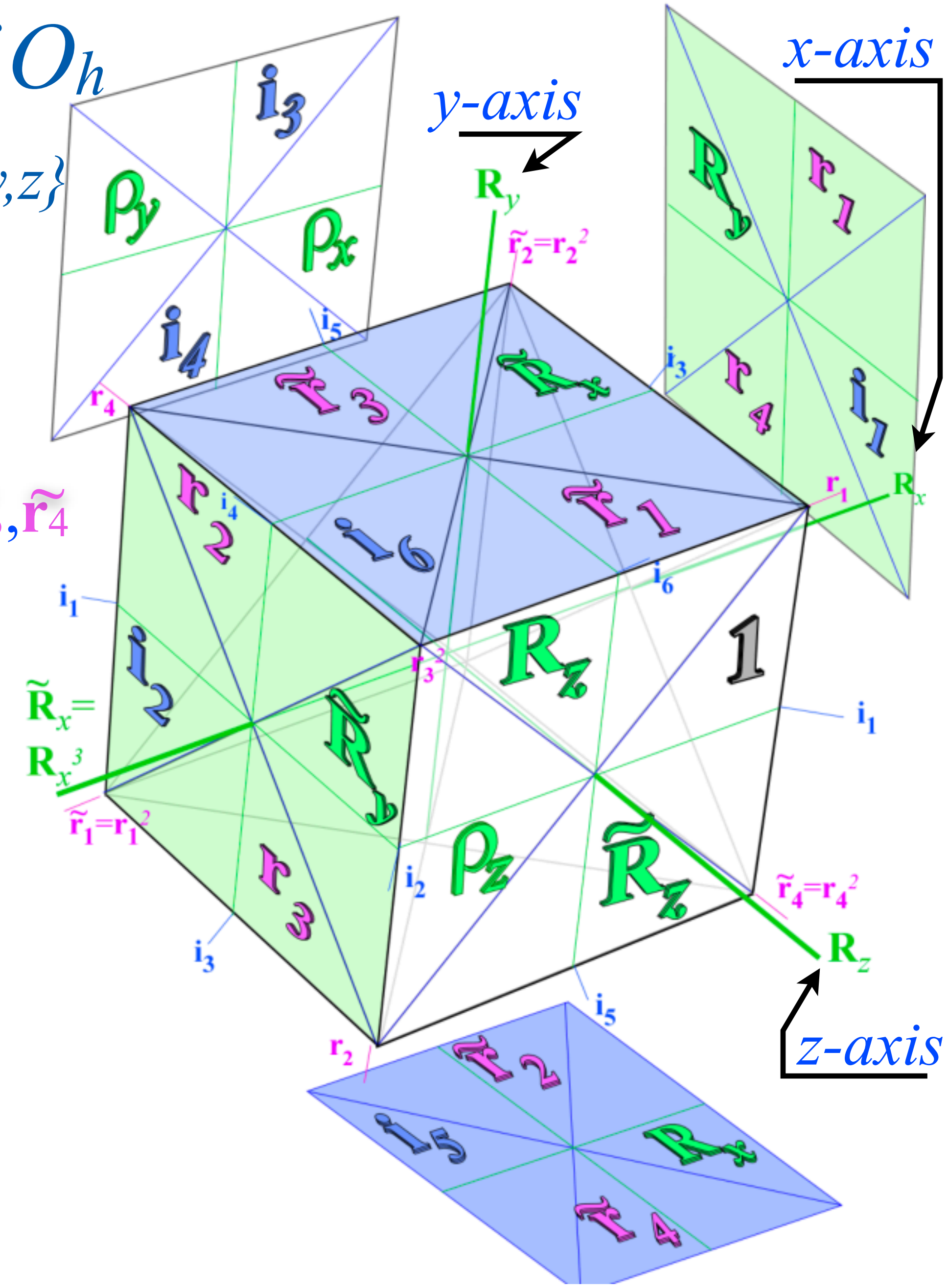
±120° rotations $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\tilde{\mathbf{r}}_1,\tilde{\mathbf{r}}_2,\tilde{\mathbf{r}}_3,\tilde{\mathbf{r}}_4$

±180° rotations $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$ $\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3,\mathbf{i}_4,\mathbf{i}_5,\mathbf{i}_6$

$$X^1_1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X^1_0(\alpha,\beta) = r\cos\beta = z$$

$$X^1_{-1}(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$



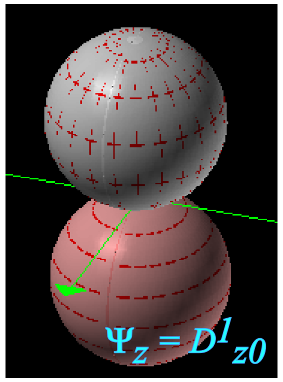
T_1 derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$

	x	y	z
$\mathbf{r}_1\mathbf{x}$ =	·	y	·
$\mathbf{r}_1\mathbf{y}$ =	·	·	z
$\mathbf{r}_1\mathbf{z}$ =	x	·	·

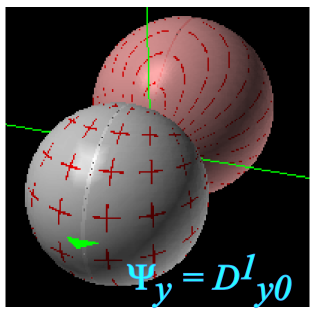
*(irrep=irreducible representations)

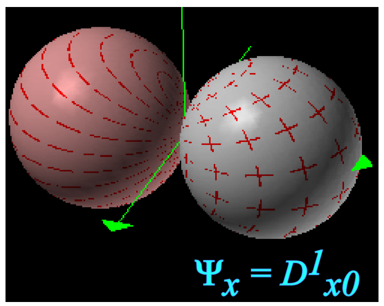
Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$

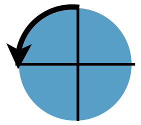


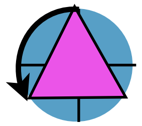
j = 1
Standing
p-Waves

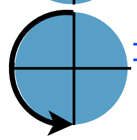




Locate x, y, z axes of

 *±90° rotations* $\mathbf{R}_x,\mathbf{R}_y,\mathbf{R}_z,\tilde{\mathbf{R}}_x,\tilde{\mathbf{R}}_y,\tilde{\mathbf{R}}_z$

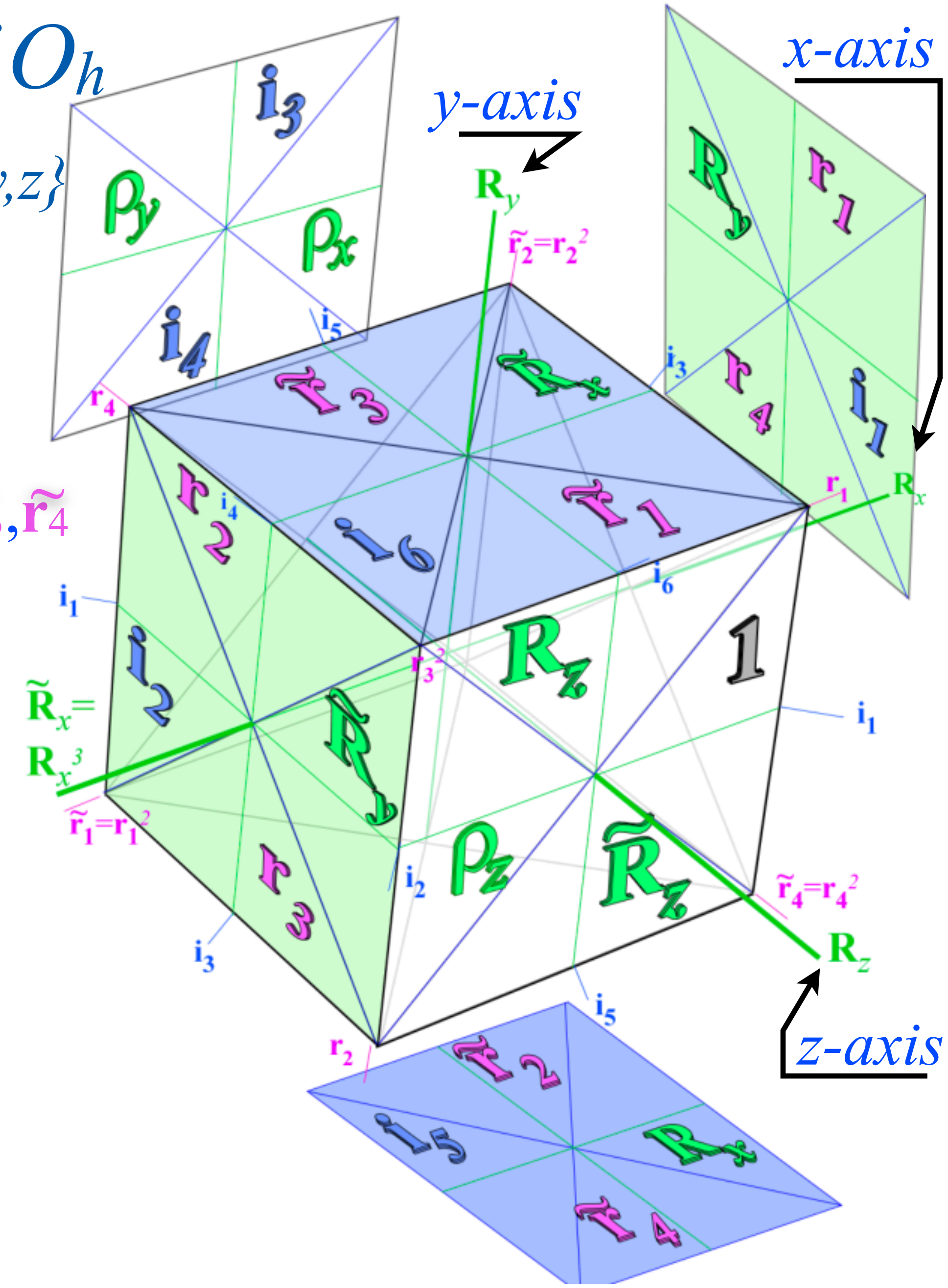
 *±120° rotations* $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\tilde{\mathbf{r}}_1,\tilde{\mathbf{r}}_2,\tilde{\mathbf{r}}_3,\tilde{\mathbf{r}}_4$

 *±180° rotations* $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$ $\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3,\mathbf{i}_4,\mathbf{i}_5,\mathbf{i}_6$

$$X^1_1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X^1_0(\alpha,\beta) = r\cos\beta = z$$

$$X^1_{-1}(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$



T_1 derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$

	x	**y**	**z**
$\mathbf{r}_1\mathbf{x} =$	·	**y**	·
$\mathbf{r}_1\mathbf{y} =$	·	·	**z**
$\mathbf{r}_1\mathbf{z} =$	**x**	·	·

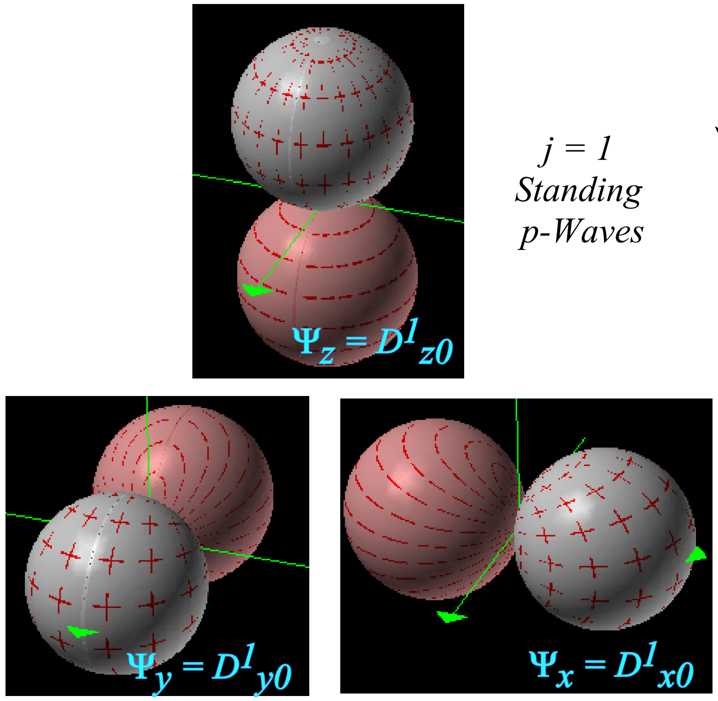
irrep notation is transpose

$$D^{T_1}(\mathbf{r}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix}$$

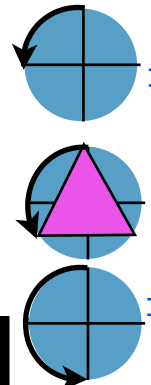
**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^E, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



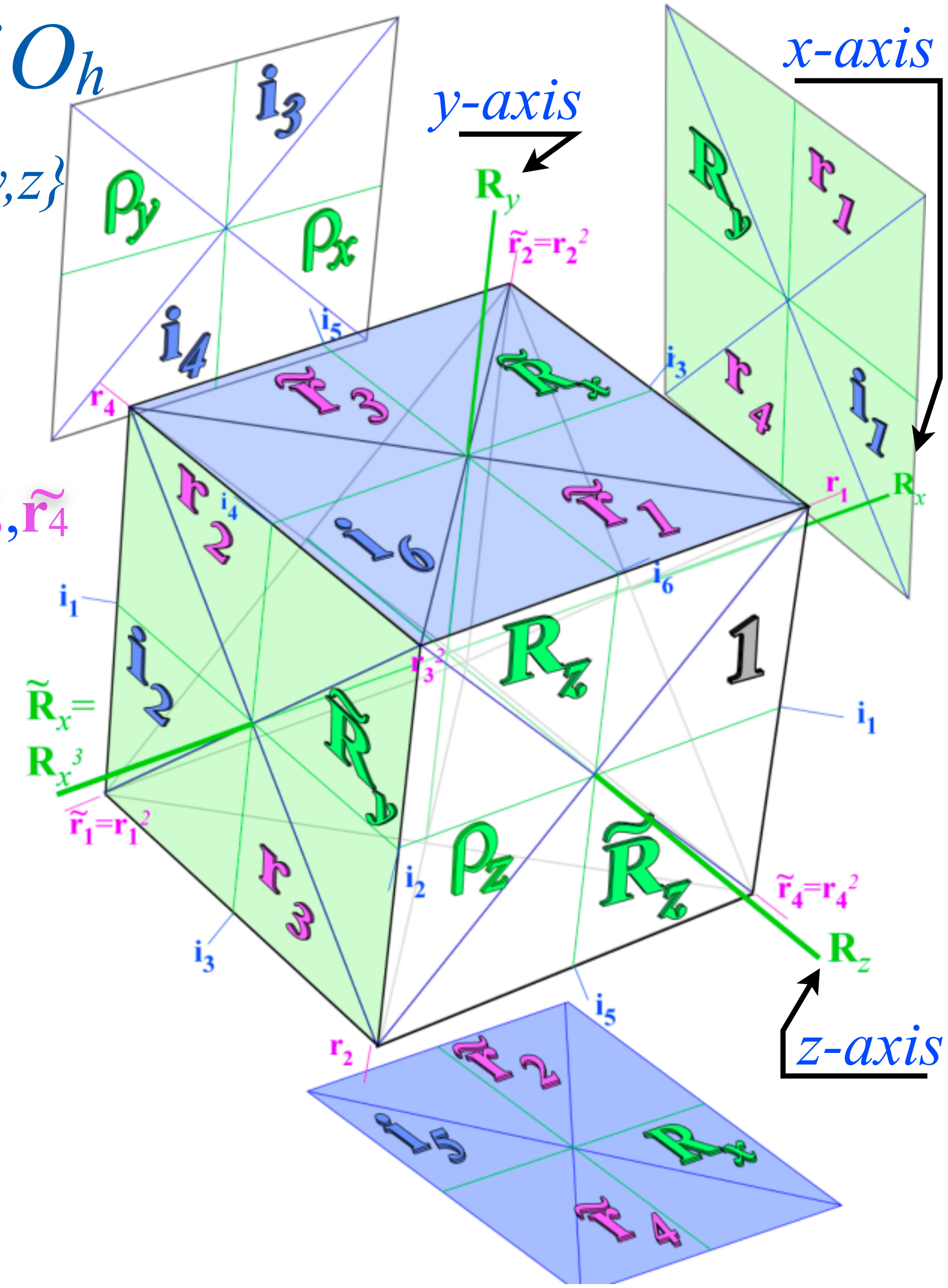
Locate x, y, z axes of



$\pm 90°$ *rotations* $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

$\pm 120°$ *rotations* $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \tilde{\mathbf{r}}_4$

$\pm 180°$ *rotations* $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$
$\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$



$$X_1^1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X_0^1(\alpha,\beta) = \quad r\cos\beta = z$$

$$X_{-1}^1(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$

T_1 derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$

	x	**y**	**z**
$\mathbf{r}_1\mathbf{x} =$	·	**y**	·
$\mathbf{r}_1\mathbf{y} =$	·	·	**z**
$\mathbf{r}_1\mathbf{z} =$	**x**	·	·

irrep notation is transpose.

$$D^{T_1}(\mathbf{r}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix}$$

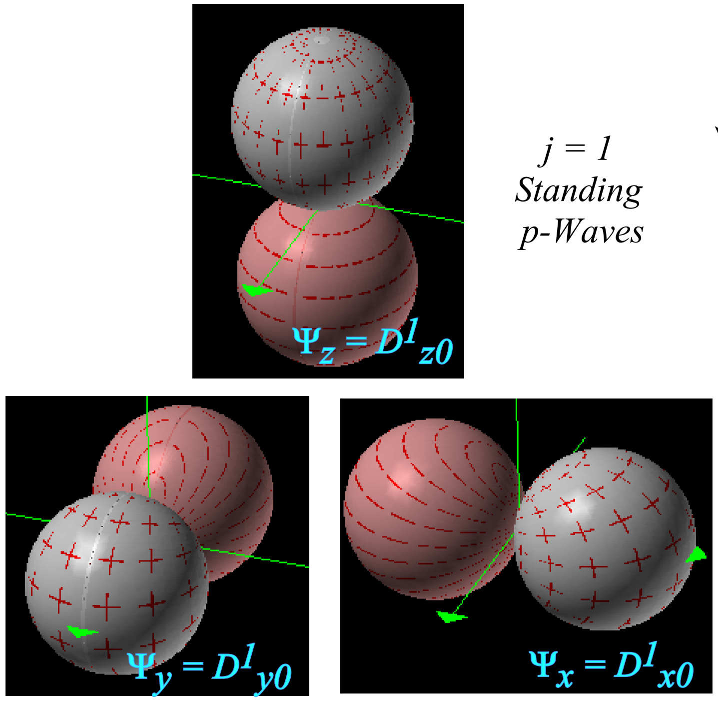
Here product $\mathbf{r}_1\mathbf{x} = \mathbf{y}$ *means unit* $_{yx}$ *element* $\mathbf{y}\mathbf{r}_1\mathbf{x} = 1$

(Perhaps, better to make array with $\mathbf{r}_1\mathbf{x}$ *at top of its column.)*

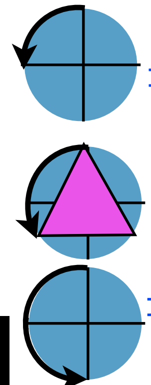
**(irrep=irreducible representations)*

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



Locate x, y, z axes of



±90° rotations $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

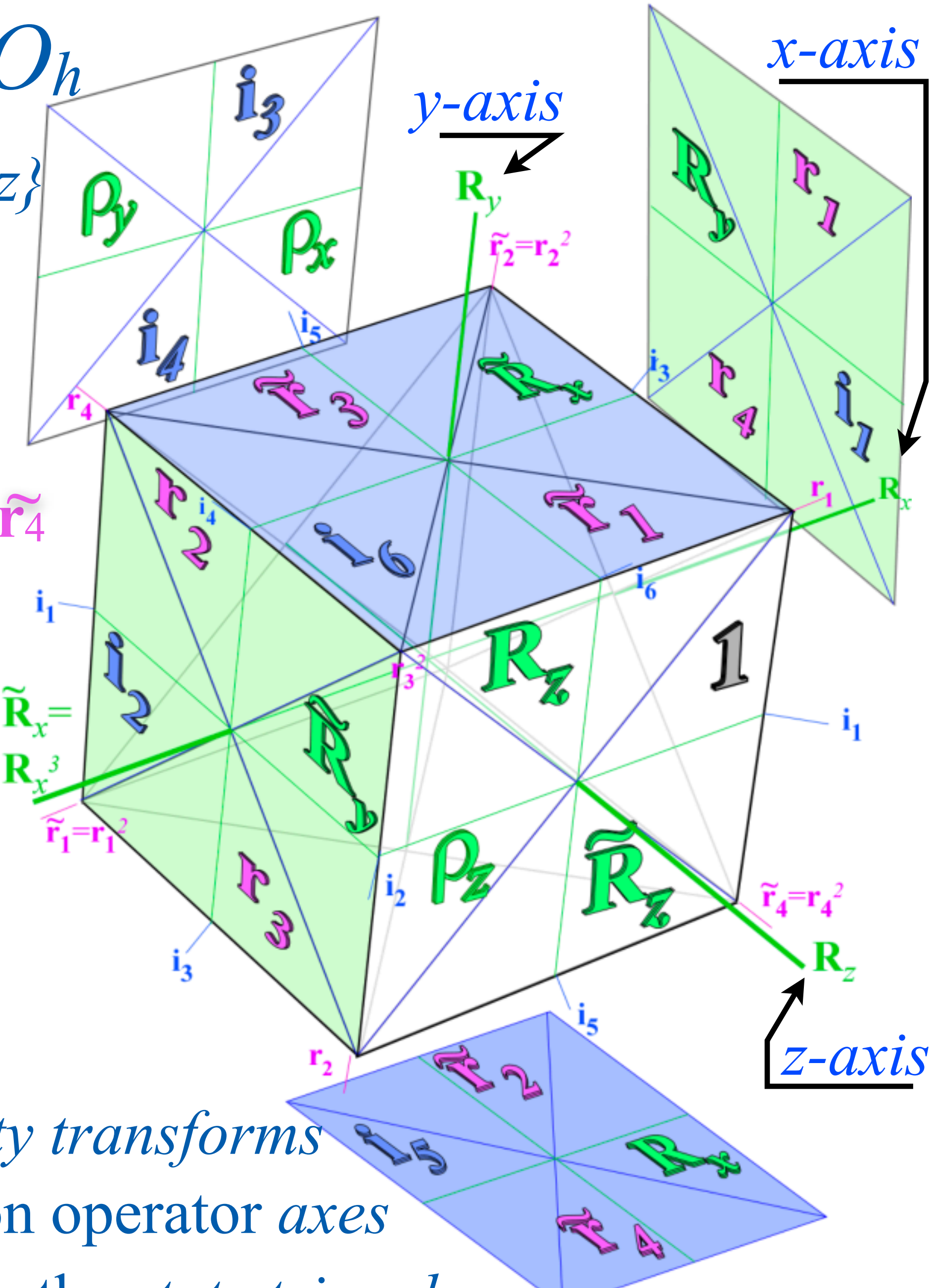
±120° rotations $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \tilde{\mathbf{r}}_4$

±180° rotations $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z$, $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$

$$X^1_1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X^1_0(\alpha,\beta) = r\cos\beta = z$$

$$X^1_{-1}(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$



T_1 derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$

The vector transforms are *operator similarity transforms*

	x	**y**	**z**
$\mathbf{r}_1\mathbf{x} =$	·	**y**	·
$\mathbf{r}_1\mathbf{y} =$	·	·	**z**
$\mathbf{r}_1\mathbf{z} =$	**x**	·	·

$\mathbf{r}_1\mathbf{R}_x\tilde{\mathbf{r}}_1 = \cdot \quad \mathbf{R}_y$ ...that work on operator *axes* and *not* on the *state triangles*.

$\mathbf{r}_1\mathbf{R}_y\tilde{\mathbf{r}}_1 = \cdot \quad \cdot \quad \mathbf{R}_z$

$\mathbf{r}_1\mathbf{R}_z\tilde{\mathbf{r}}_1 = \mathbf{R}_x \quad \cdot \quad \cdot$

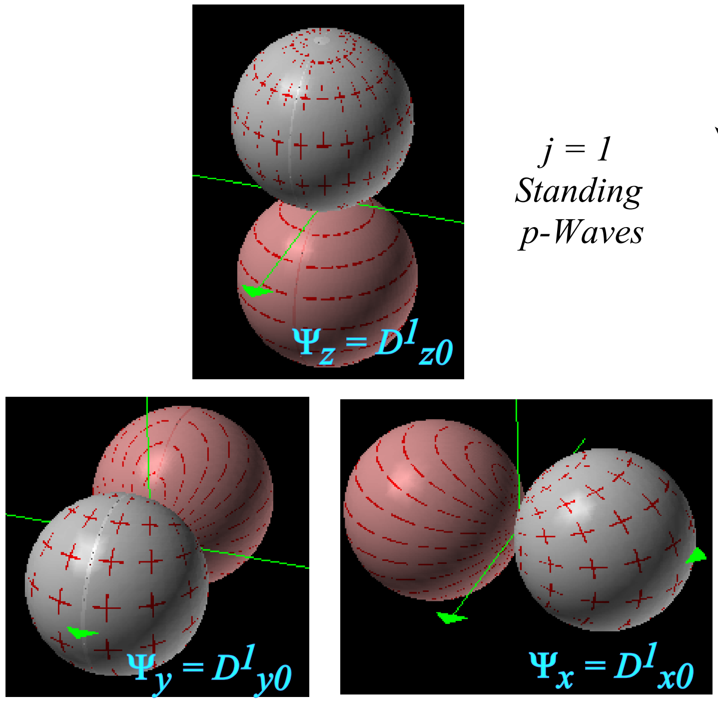
irrep notation is transpose

$$D^{T_1}(\mathbf{r}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix}$$

*(*irrep=irreducible representations*)

Matrix D^{T_1}, D^{T_2}, D^E, D^{A_2}, and D^{A_1}, irreps* of O_h

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



Locate x, y, z axes of

±90° rotations $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

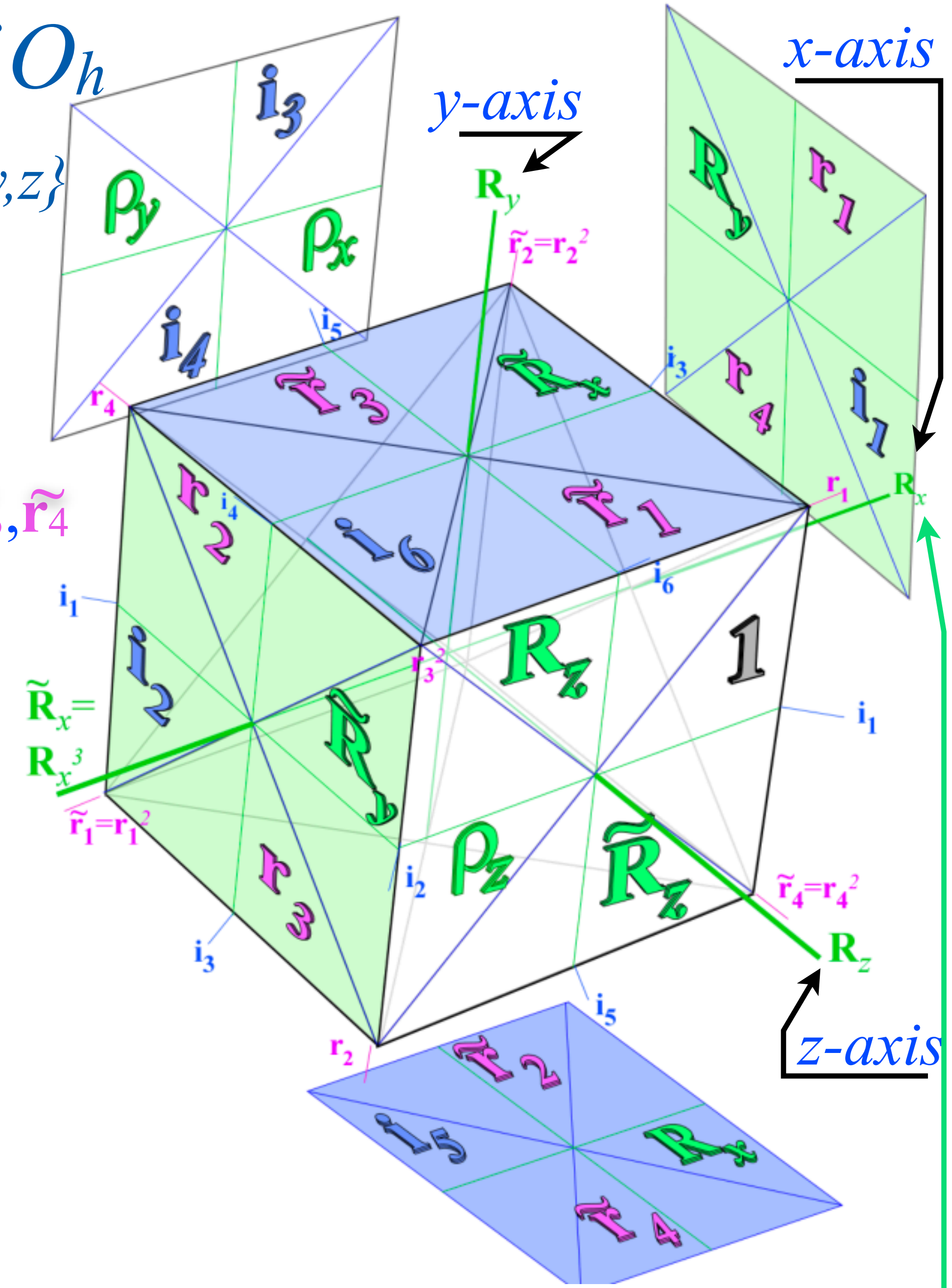
±120° rotations $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \tilde{\mathbf{r}}_4$

±180° rotations $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$ $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$

$$X_1^1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X_0^1(\alpha,\beta) = \qquad r\cos\beta = z$$

$$X_{-1}^1(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$



T_1 derived visually using unit vectors $\{\mathbf{x,y,z}\}$

	x	y	z
$\mathbf{r}_1\mathbf{x} =$	·	y	·
$\mathbf{r}_1\mathbf{y} =$	·	·	z
$\mathbf{r}_1\mathbf{z} =$	x	·	·

	x	y	z
$\mathbf{R}_x\mathbf{x} =$	x	·	·
$\mathbf{R}_x\mathbf{y} =$	·	·	z
$\mathbf{R}_x\mathbf{z} =$	·	-y	·

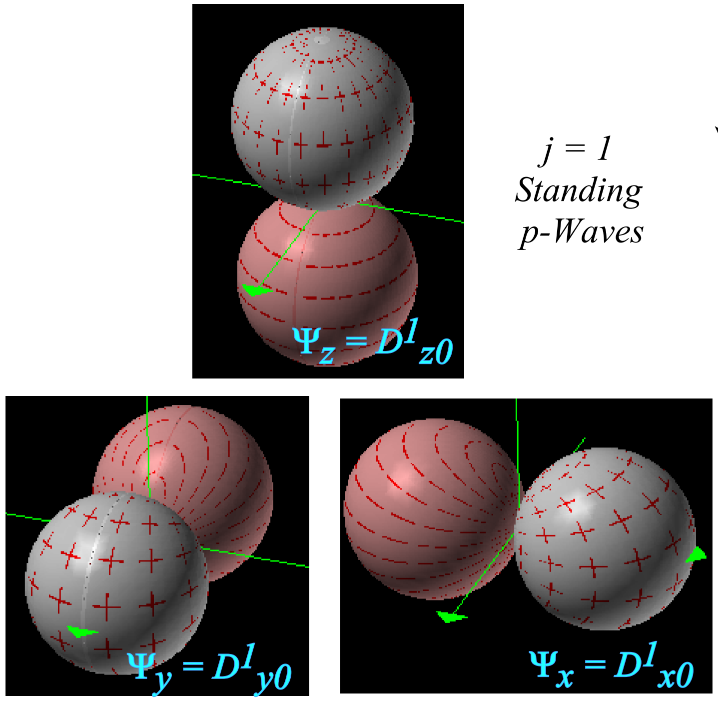
irrep notation is transpose

$$D^{T_1}(\mathbf{r}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix} \quad D^{T_1}(\mathbf{R}_x) = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & -1 \\ \cdot & 1 & \cdot \end{pmatrix}$$

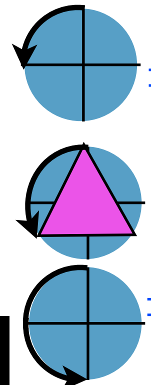
*(irrep=irreducible representations)

Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$



Locate x, y, z axes of



±90° rotations $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

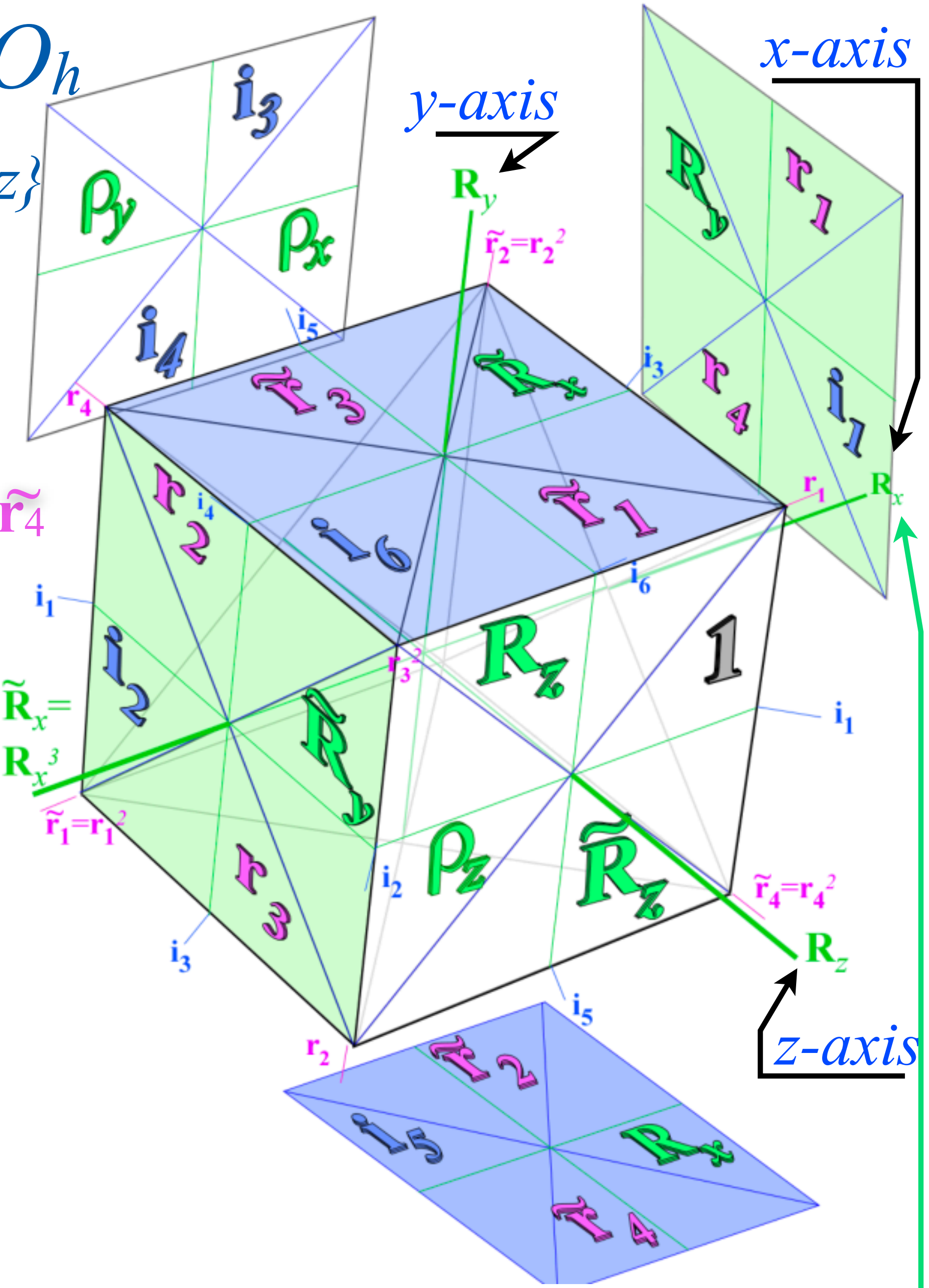
±120° rotations $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \tilde{\mathbf{r}}_4$

±180° rotations $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$ $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$

$$X_1^1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X_0^1(\alpha,\beta) = \qquad r\cos\beta = z$$

$$X_{-1}^1(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} \;=\frac{x+iy}{\sqrt{2}}$$



T_1 derived visually using unit vectors $\{\mathbf{x,y,z}\}$

$$\mathbf{r}_1\mathbf{x} = \begin{pmatrix} \cdot & \mathbf{y} & \cdot \end{pmatrix},\quad \mathbf{r}_1\mathbf{y} = \begin{pmatrix} \cdot & \cdot & \mathbf{z} \end{pmatrix},\quad \mathbf{r}_1\mathbf{z} = \begin{pmatrix} \mathbf{x} & \cdot & \cdot \end{pmatrix}$$

	x	y	z
$\mathbf{r}_1\mathbf{x}$ =	·	**y**	·
$\mathbf{r}_1\mathbf{y}$ =	·	·	**z**
$\mathbf{r}_1\mathbf{z}$ =	**x**	·	·

	x	y	z
$\mathbf{R}_x\mathbf{x}$ =	**x**	·	·
$\mathbf{R}_x\mathbf{y}$ =	·	·	**z**
$\mathbf{R}_x\mathbf{z}$ =	·	**-y**	·

	x	y	z
$\boldsymbol{\rho}_x\mathbf{x}$ =	**x**	·	·
$\boldsymbol{\rho}_x\mathbf{y}$ =	·	**-y**	·
$\boldsymbol{\rho}_x\mathbf{z}$ =	·	·	**-z**

$\boldsymbol{\rho}_x = (\mathbf{R}_x)^2$

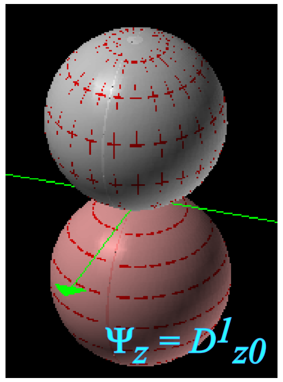
irrep notation is transpose

$$D^{T_1}(\mathbf{r}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix} \quad D^{T_1}(\mathbf{R}_x) = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & -1 \\ \cdot & 1 & \cdot \end{pmatrix} \quad D^{T_1}(\boldsymbol{\rho}_x) = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & -1 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

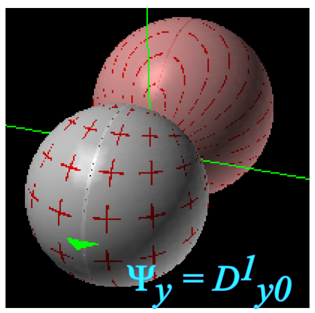
**(irrep=irreducible representations)*

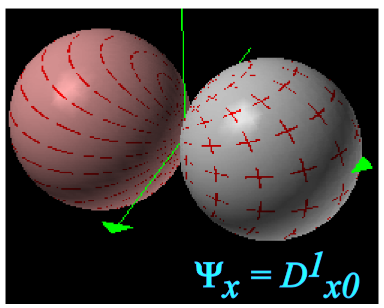
Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps* of O_h

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$

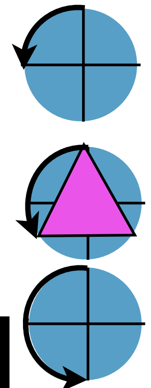


j = 1
Standing
p-Waves





Locate x, y, z axes of



±90° rotations $\mathbf{R}_x,\mathbf{R}_y,\mathbf{R}_z,\tilde{\mathbf{R}}_x,\tilde{\mathbf{R}}_y,\tilde{\mathbf{R}}_z$

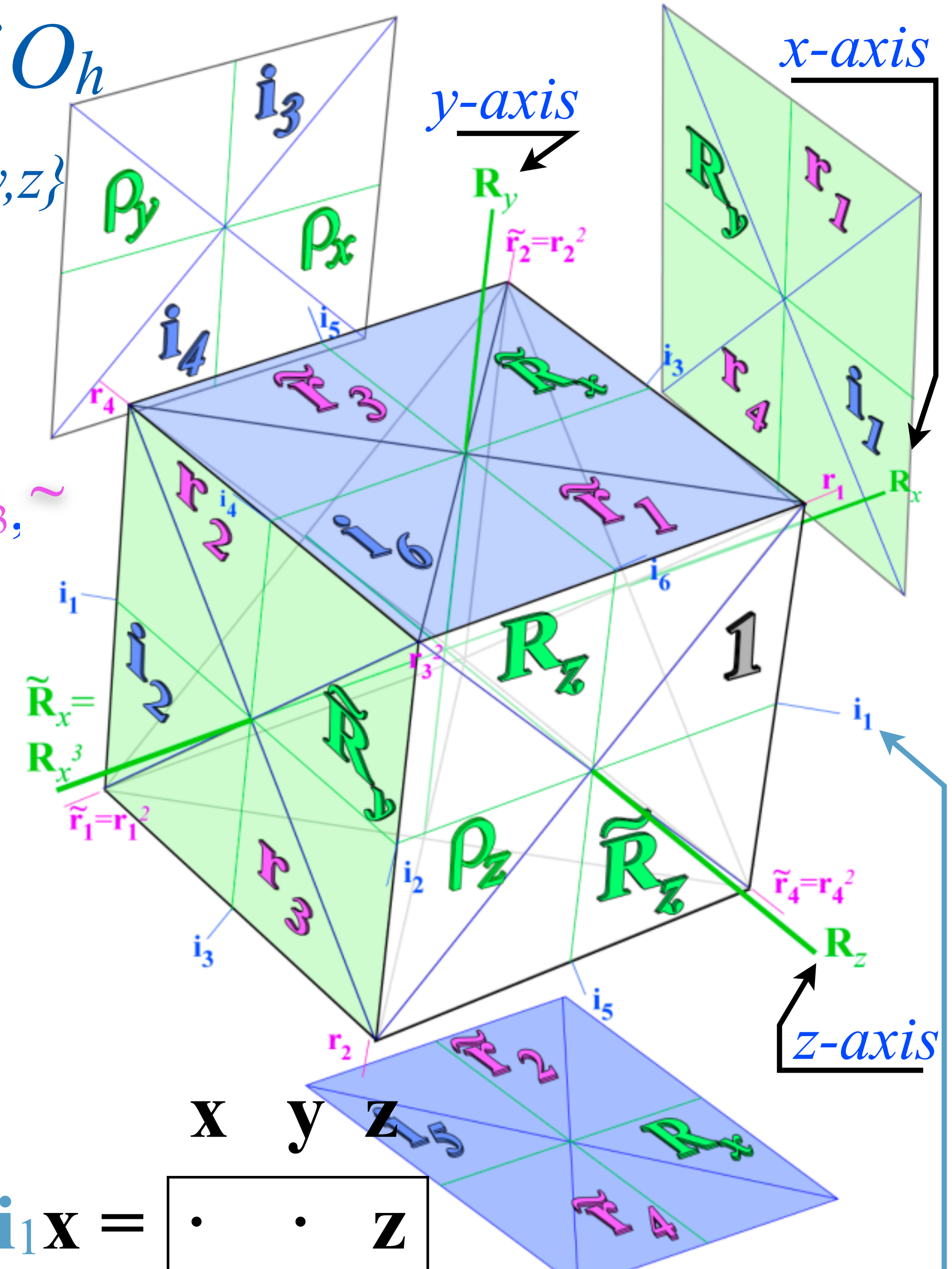
±120° rotations $\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\tilde{\mathbf{r}}_1,\tilde{\mathbf{r}}_2,\tilde{\mathbf{r}}_3,\tilde{}$

±180° rotations $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$ $\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3,\mathbf{i}_4,\mathbf{i}_5,\mathbf{i}_6$

$$X^1_1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X^1_0(\alpha,\beta) = \quad r\cos\beta = z$$

$$X^1_{-1}(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$



T_1 derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$

$$\mathbf{r}_1\mathbf{x} = \begin{pmatrix}\cdot & \mathbf{y} & \cdot\end{pmatrix},\quad \mathbf{r}_1\mathbf{y} = \begin{pmatrix}\cdot & \cdot & \mathbf{z}\end{pmatrix},\quad \mathbf{r}_1\mathbf{z} = \begin{pmatrix}\mathbf{x} & \cdot & \cdot\end{pmatrix}$$

	x	y	z
$\mathbf{r}_1\mathbf{x}=$	·	y	·
$\mathbf{r}_1\mathbf{y}=$	·	·	z
$\mathbf{r}_1\mathbf{z}=$	x	·	·

	x	y	z
$\mathbf{R}_x\mathbf{x}=$	x	·	·
$\mathbf{R}_x\mathbf{y}=$	·	·	z
$\mathbf{R}_x\mathbf{z}=$	·	-y	·

	x	y	z
$\boldsymbol{\rho}_x\mathbf{x}=$	x	·	·
$\boldsymbol{\rho}_x\mathbf{y}=$	·	-y	·
$\boldsymbol{\rho}_x\mathbf{z}=$	·	·	-z

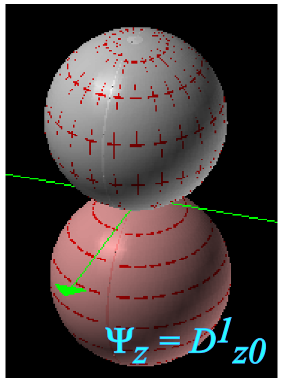
	x	y	z
$\mathbf{i}_1\mathbf{x}=$	·	·	z
$\mathbf{i}_1\mathbf{y}=$	·	-y	·
$\mathbf{i}_1\mathbf{z}=$	x	·	·

irrep notation is transpose

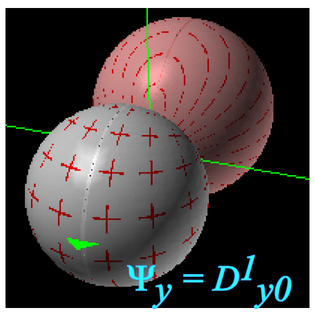
$$D^{T_1}(\mathbf{r}_1)=\begin{pmatrix}\cdot & \cdot & 1\\ 1 & \cdot & \cdot\\ \cdot & 1 & \cdot\end{pmatrix} \quad D^{T_1}(\mathbf{R}_x)=\begin{pmatrix}1 & \cdot & \cdot\\ \cdot & \cdot & -1\\ \cdot & 1 & \cdot\end{pmatrix} \quad D^{T_1}(\boldsymbol{\rho}_x)=\begin{pmatrix}1 & \cdot & \cdot\\ \cdot & -1 & \cdot\\ \cdot & \cdot & -1\end{pmatrix} \quad D^{T_1}(\mathbf{i}_1)=\begin{pmatrix}\cdot & \cdot & 1\\ \cdot & -1 & \cdot\\ 1 & \cdot & \cdot\end{pmatrix}$$

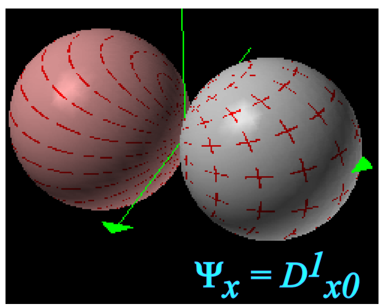
Matrix D^{T_1}, D^{T_2}, D^{E}, D^{A_2}, and D^{A_1}, irreps of O_h*

D^{T_1} derived from standing p-wave $D^{\ell=1}{}_{\{x,y,z\}}$

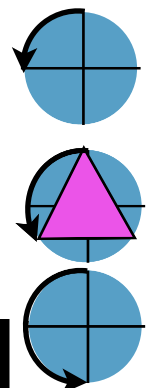


j = 1 Standing p-Waves





Locate x, y, z axes of



$\pm 90°$ rotations $\mathbf{R}_x, \mathbf{R}_y, \mathbf{R}_z, \tilde{\mathbf{R}}_x, \tilde{\mathbf{R}}_y, \tilde{\mathbf{R}}_z$

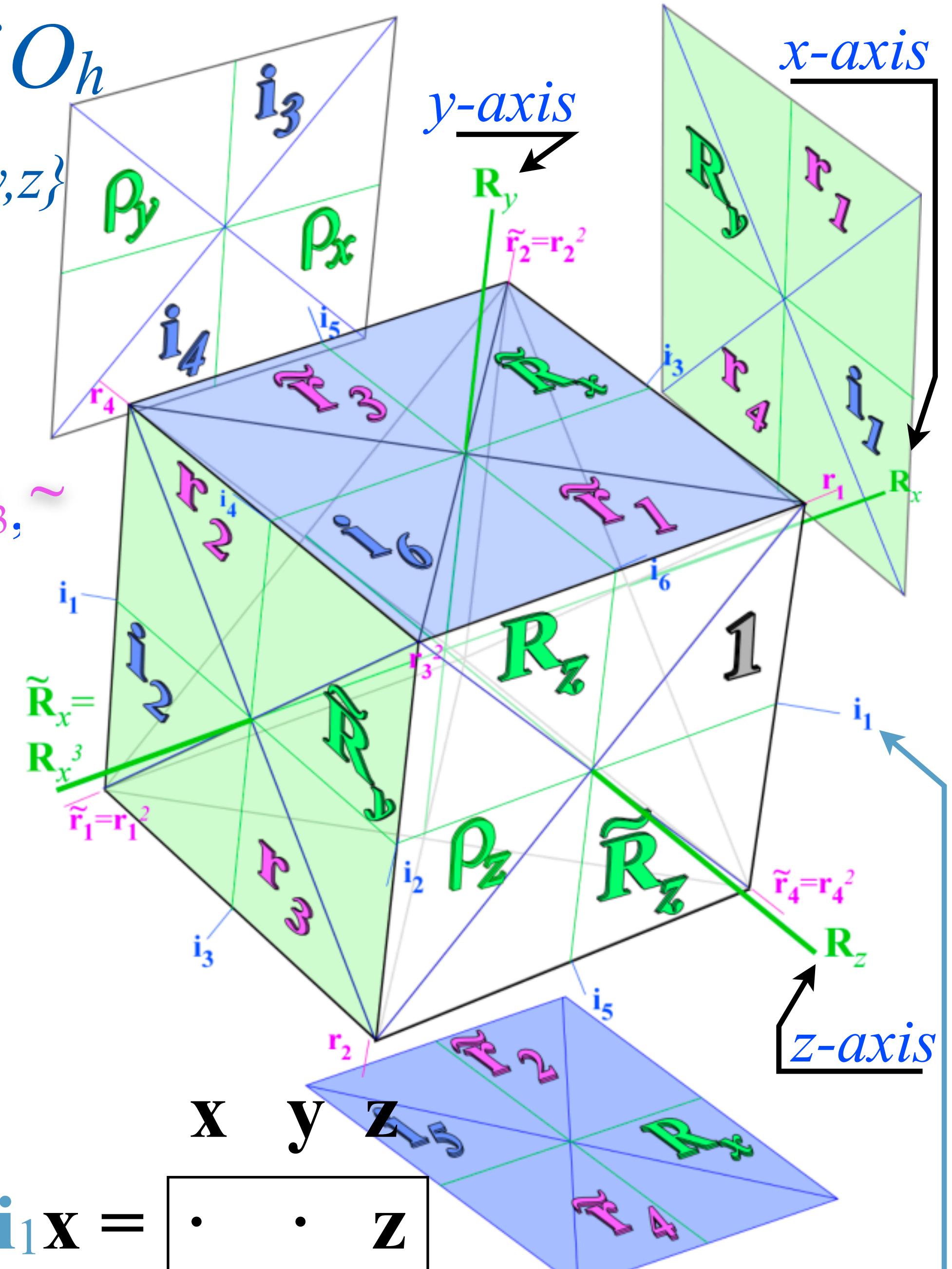
$\pm 120°$ rotations $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \tilde{\mathbf{r}}_3, \sim$

$\pm 180°$ rotations $\boldsymbol{\rho}_x, \boldsymbol{\rho}_y, \boldsymbol{\rho}_z,$ $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3, \mathbf{i}_4, \mathbf{i}_5, \mathbf{i}_6$

$$X^1_1(\alpha,\beta) = -re^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} = -\frac{x-iy}{\sqrt{2}}$$

$$X^1_0(\alpha,\beta) = r\cos\beta = z$$

$$X^1_{-1}(\alpha,\beta) = re^{+i\alpha}\frac{\sin\beta}{\sqrt{2}} = \frac{x+iy}{\sqrt{2}}$$



T_1 derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$

$$\begin{array}{c|ccc|} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \mathbf{r}_1\mathbf{x} = & \cdot & \mathbf{y} & \cdot \\ \mathbf{r}_1\mathbf{y} = & \cdot & \cdot & \mathbf{z} \\ \mathbf{r}_1\mathbf{z} = & \mathbf{x} & \cdot & \cdot \end{array} \quad \begin{array}{c|ccc|} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \mathbf{R}_x\mathbf{x} = & \mathbf{x} & \cdot & \cdot \\ \mathbf{R}_x\mathbf{y} = & \cdot & \cdot & \mathbf{z} \\ \mathbf{R}_x\mathbf{z} = & \cdot & -\mathbf{y} & \cdot \end{array} \quad \begin{array}{c|ccc|} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \boldsymbol{\rho}_x\mathbf{x} = & \mathbf{x} & \cdot & \cdot \\ \boldsymbol{\rho}_x\mathbf{y} = & \cdot & -\mathbf{y} & \cdot \\ \boldsymbol{\rho}_x\mathbf{z} = & \cdot & \cdot & -\mathbf{z} \end{array} \quad \begin{array}{c|ccc|} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \mathbf{i}_1\mathbf{x} = & \cdot & \cdot & \mathbf{z} \\ \mathbf{i}_1\mathbf{y} = & \cdot & -\mathbf{y} & \cdot \\ \mathbf{i}_1\mathbf{z} = & \mathbf{x} & \cdot & \cdot \end{array}$$

irrep notation is transpose

$$D^{T_1}(\mathbf{r}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix} \quad D^{T_1}(\mathbf{R}_x) = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & -1 \\ \cdot & 1 & \cdot \end{pmatrix} \quad D^{T_1}(\boldsymbol{\rho}_x) = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & -1 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix} \quad D^{T_1}(\mathbf{i}_1) = \begin{pmatrix} \cdot & \cdot & 1 \\ \cdot & -1 & \cdot \\ 1 & \cdot & \cdot \end{pmatrix}$$

$$\chi^{T_1}{}_{\mathbf{r}_1} = Tr D^{T_1}(\mathbf{r}_1) = 0 \qquad \chi^{T_1}{}_{\mathbf{R}_x} = +1 \qquad \chi^{T_1}{}_{\boldsymbol{\rho}_x} = -1 \qquad \chi^{T_1}{}_{\mathbf{i}_1} = -1$$

2.19.18 class 11.0: *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 O of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

➡ *D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$.* *D^{E} irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O

$R(3)\supset O$ character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group$\supset$Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

First are the j=1 dipole or "vector" functions of R(3)

TABLE F.1.1 R(3) Multiple Functions and SU(3) Harmonic Monomials

$$\mathrm{I}_1^{(1)} = -\frac{1}{\sqrt{2}}(x+iy) \qquad x = \frac{1}{\sqrt{2}}(\mathrm{I}_{-1}^{(1)} - \mathrm{I}_1^{(1)})$$

$$\mathrm{I}_{-1}^{(1)} = \frac{1}{\sqrt{2}}(x-iy) \qquad iy = -\frac{1}{\sqrt{2}}(\mathrm{I}_{-1}^{(1)} + \mathrm{I}_1^{(1)})$$

$$\mathrm{I}_0^{(1)} = z \qquad z = \mathrm{I}_0^{(1)}$$

$$\mathrm{II}_2^{(2)} = \sqrt{\frac{3}{8}}(x+iy)^2 \qquad x^2 = \frac{1}{6}(\mathrm{II}_2^{(2)} + \mathrm{II}_{-2}^{(2)}) - \frac{1}{3}\mathrm{II}_0^{(2)} + \frac{1}{3}r^2$$

$$\mathrm{II}_1^{(2)} = -\sqrt{\frac{3}{2}}z(x+iy) \qquad y^2 = -\frac{1}{6}(\mathrm{II}_2^{(2)} + \mathrm{II}_{-2}^{(2)}) - \frac{1}{3}\mathrm{II}_0^{(2)} + \frac{1}{3}r^2$$

$$\mathrm{II}_0^{(2)} = \frac{1}{2}(3z^2 - r^2) \qquad z^2 = -\frac{2}{3}\mathrm{II}_0^{(2)} + \frac{1}{3}r^2$$

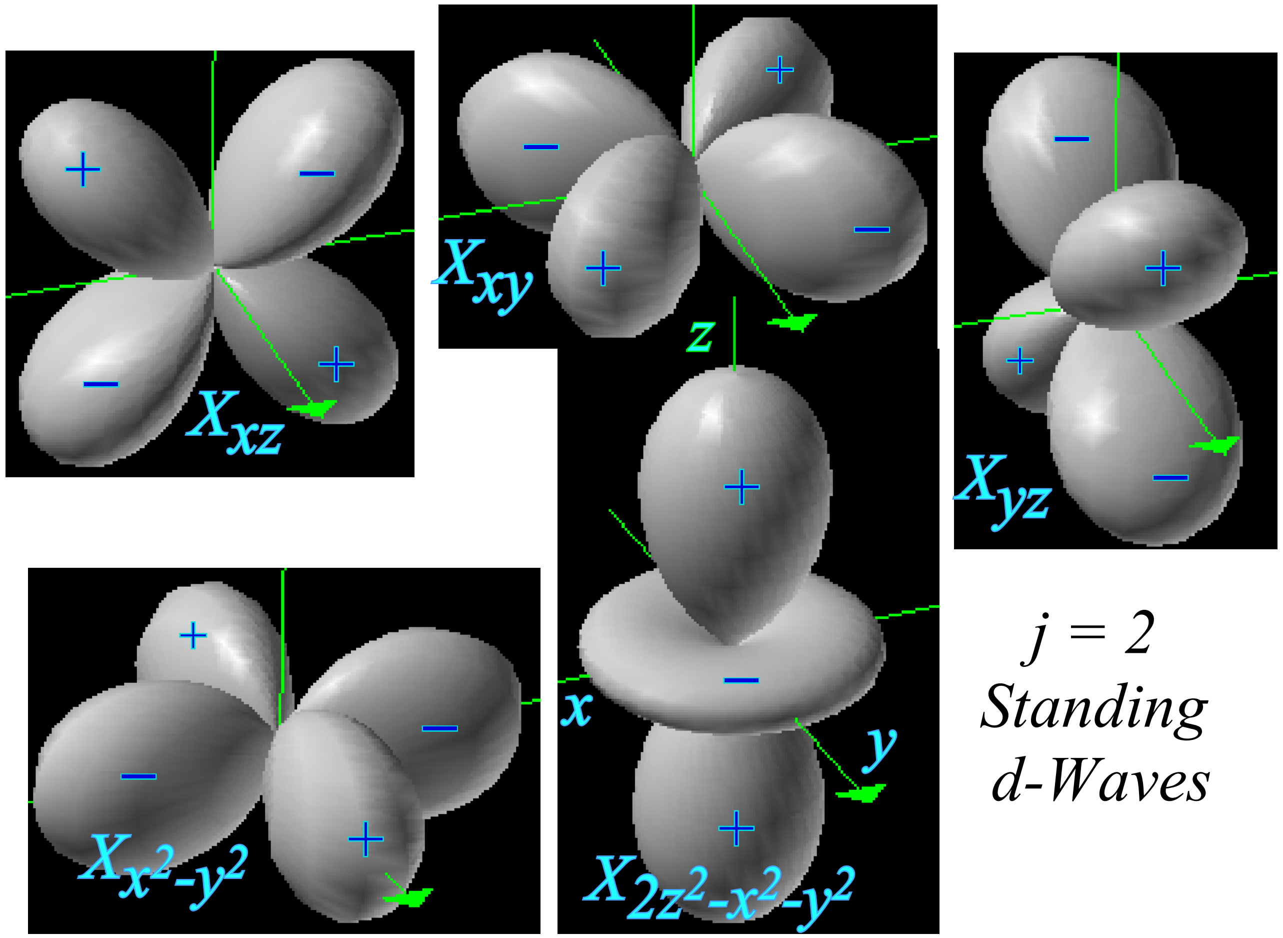
$$\mathrm{II}_{-1}^{(2)} = \sqrt{\frac{3}{2}}z(x-iy) \qquad xy = \frac{i}{\sqrt{6}}(\mathrm{II}_2^{(2)} - \mathrm{II}_{-2}^{(2)})$$

$$\mathrm{II}_{-2}^{(2)} = \sqrt{\frac{3}{8}}(x-iy)^2 \qquad xz = \frac{1}{\sqrt{6}}(\mathrm{II}_1^{(2)} - \mathrm{II}_{-1}^{(2)})$$

$$yz = \frac{i}{\sqrt{6}}(\mathrm{II}_1^{(2)} + \mathrm{II}_{-1}^{(2)})$$

Here we use the j=2 quadrupole or "tensor" functions of R(3)

D^{T_2}, D^E irreps* derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$



j = 2
Standing
d-Waves

j =2 Moving d-Waves (all real)

D^{T_2} irrep basis

$$\tfrac{1}{2i}\left(X^2_{-1}(\alpha,\beta)+X^2_{1}(\alpha,\beta)\right) = yz$$
$$\tfrac{1}{2}\left(X^2_{-1}(\alpha,\beta)-X^2_{1}(\alpha,\beta)\right) = xz$$
$$\tfrac{1}{4i}\left(X^2_{2}(\alpha,\beta)-X^2_{-2}(\alpha,\beta)\right) = xy$$

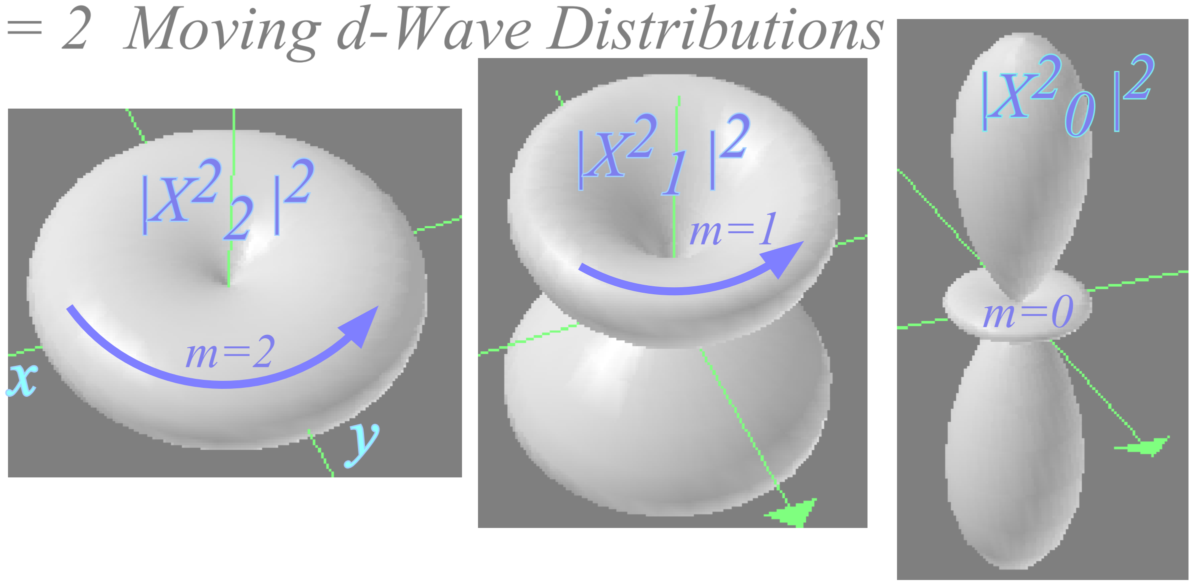
D^E irrep basis

$$\tfrac{1}{\sqrt{2}}\left(X^2_{2}(\alpha,\beta)+X^2_{-2}(\alpha,\beta)\right)=\left(x^2-y^2\right)\tfrac{1}{\sqrt{2}}$$
$$\tfrac{1}{\sqrt{6}}X^2_{0}(\alpha,\beta) =\left(2z^2-x^2-y^2\right)\tfrac{1}{\sqrt{6}}$$

j =2 Moving d-Waves (mostly complex)

$$X^2_{2}(\alpha,\beta)= r^2e^{i2\alpha}\sin^2\beta =(x+iy)^2 =x^2-y^2+2ixy$$
$$X^2_{1}(\alpha,\beta)=-r^2e^{i\alpha}\sin\beta\cos\beta =-(x+iy)z=-xz-iyz$$
$$X^2_{0}(\alpha,\beta)= r^2(3\cos^2\beta-1) = 3z^2-r^2 =2z^2-x^2-y^2$$
$$X^2_{-1}(\alpha,\beta)=r^2e^{-i\alpha}\sin\beta\cos\beta = (x-iy)z = xz-iyz$$
$$X^2_{-2}(\alpha,\beta)= r^2e^{-i2\alpha}\sin^2\beta =(x-iy)^2 =x^2-y^2-2ixy$$

j = 2 Moving d-Wave Distributions



*(irrep=irreducible representations)

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank $[k=4]$ multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x,y,z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^{E} irrep tensor basis*

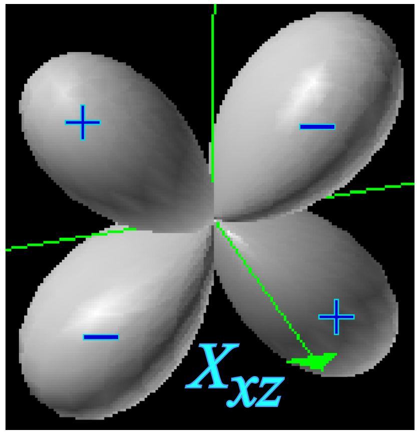
Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O

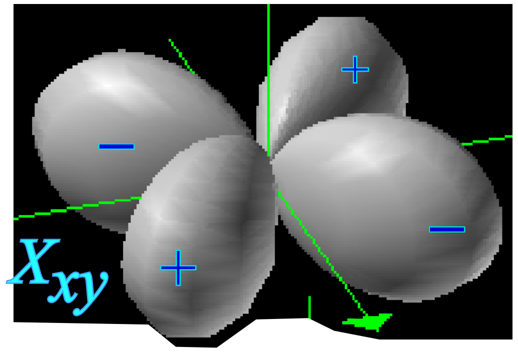
$R(3)\supset O$ character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

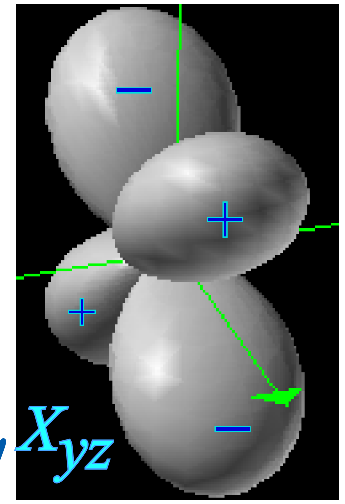
Applications of Group$\supset$Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

D^{T_2} derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$

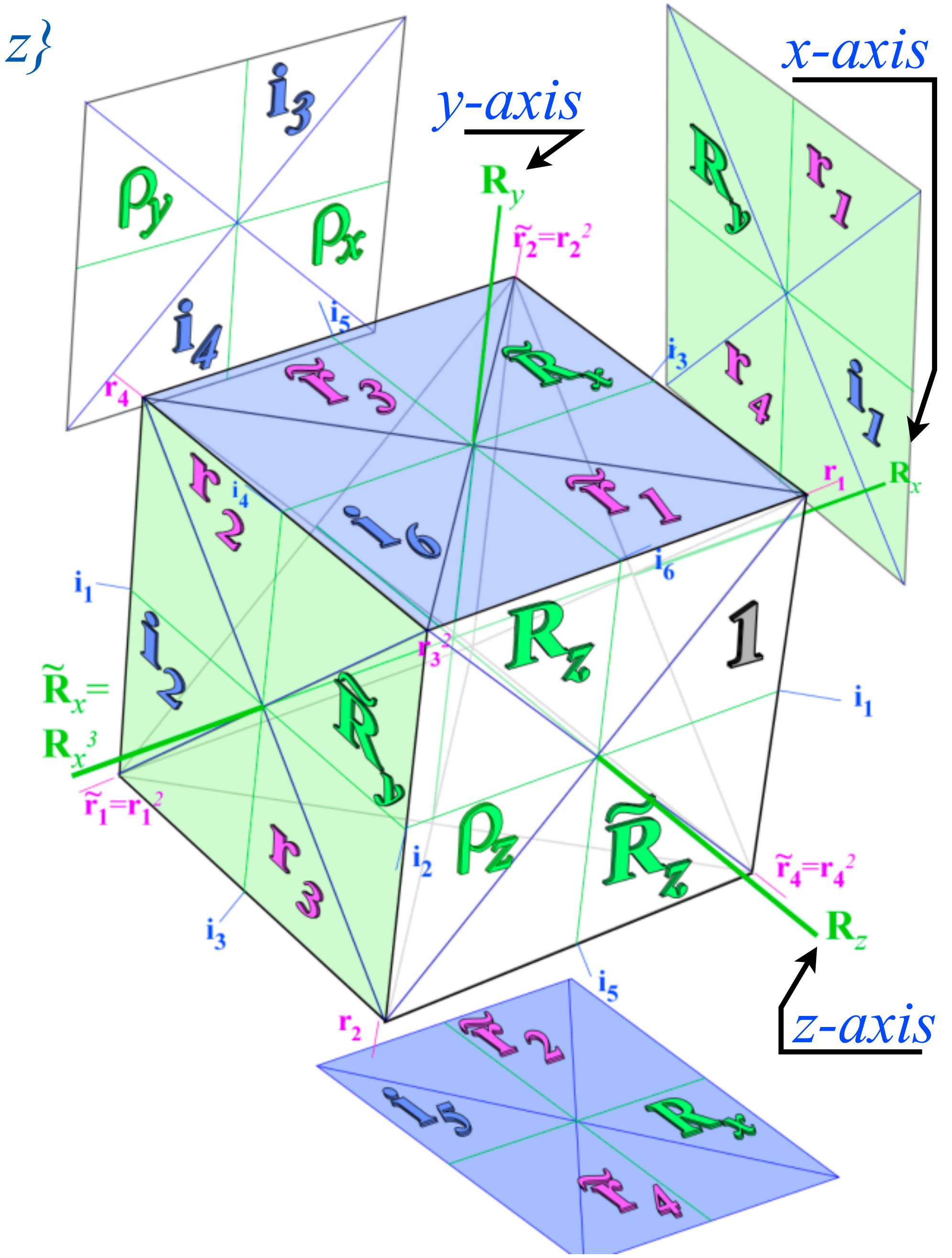






using unit tensors

{xy,xz,yz}



Vector-tran gives tensor-tran!

	x	y	z
$\mathbf{r}_1\mathbf{x} =$	·	y	·
$\mathbf{r}_1\mathbf{y} =$	·	·	z
$\mathbf{r}_1\mathbf{z} =$	x	·	·

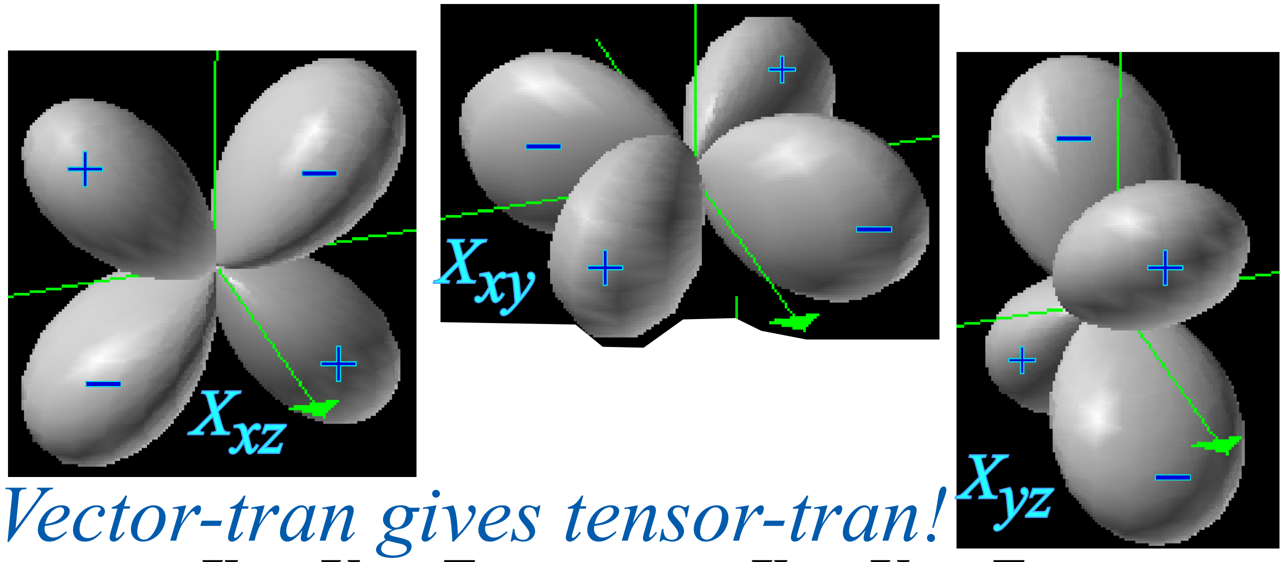
	xy	xz	yz
$\mathbf{r}_1\mathbf{xy} =$	·	·	yz
$\mathbf{r}_1\mathbf{xz} =$	xy	·	·
$\mathbf{r}_1\mathbf{yz} =$	·	xz	·

irrep notation is transpose

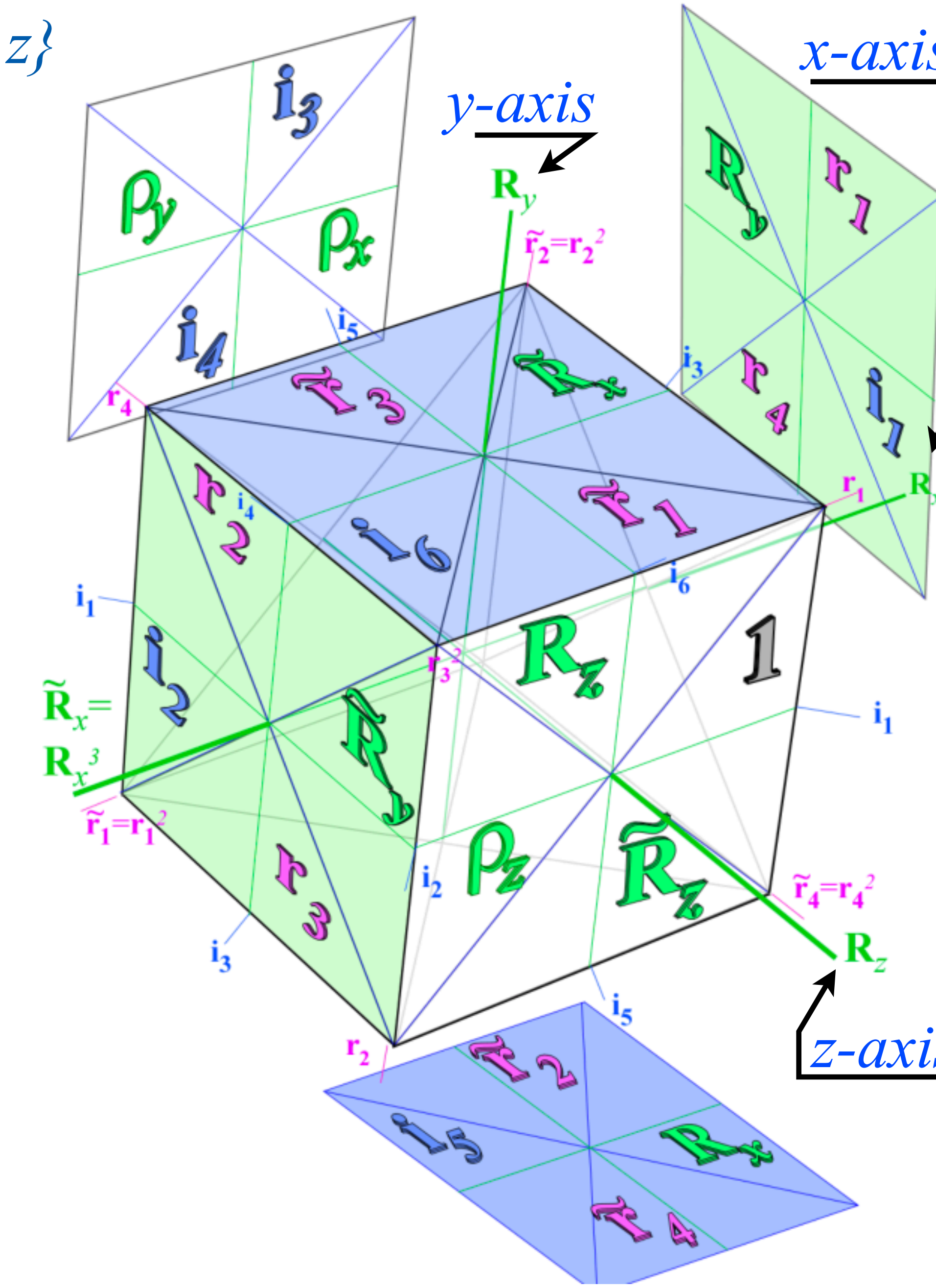
$$D^{T_2}(\mathbf{r}_1)=\begin{pmatrix} \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \end{pmatrix}$$

$$\chi^{T_2}{}_{\mathbf{r}_1}=\mathit{Trace}D^{T_1}(\mathbf{r}_1)=0$$

D^{T_2} derived from standing d-wave $D^{\ell=2}_{\{x,y,z\}}$



using unit tensors {**xy,xz,yz**}



Vector-tran gives tensor-tran!

	x	y	z
$\mathbf{r}_1$x =	·	y	·
$\mathbf{r}_1$y =	·	·	z
$\mathbf{r}_1$z =	x	·	·

	x	y	z
$\mathbf{R}_x$x =	x	·	·
$\mathbf{R}_x$y =	·	·	z
$\mathbf{R}_x$z =	·	-y	·

	xy	xz	yz
$\mathbf{r}_1$xy=	·	·	yz
$\mathbf{r}_1$xz=	xy	·	·
$\mathbf{r}_1$yz=	·	xz	·

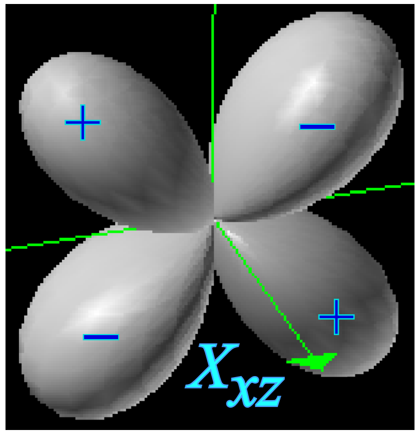
	xy	xz	yz
$\mathbf{R}_x$xy=	·	xz	·
$\mathbf{R}_x$xz=	-xy	·	·
$\mathbf{R}_x$yz=	·	·	yz

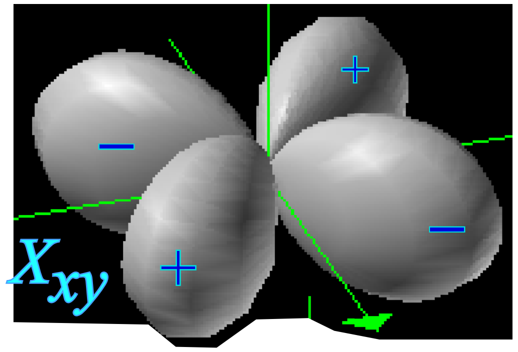
irrep notation is transpose

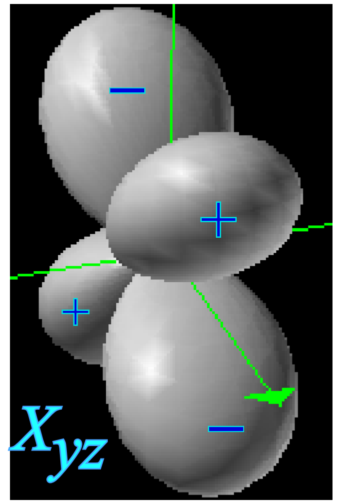
$$D^{T_2}(\mathbf{r}_1)=\begin{pmatrix} \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \end{pmatrix} \quad D^{T_2}(\mathbf{R}_x)=\begin{pmatrix} \cdot & -1 & \cdot \\ 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \end{pmatrix}$$

$$\chi^{T_2}_{\mathbf{r}_1}=Trace D^{T_1}(\mathbf{r}_1)=0 \qquad \chi^{T_2}_{\mathbf{R}_x}=+1$$

D^{T_2} derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$







using unit tensors

{xy,xz,yz}

Vector-tran gives tensor-tran!

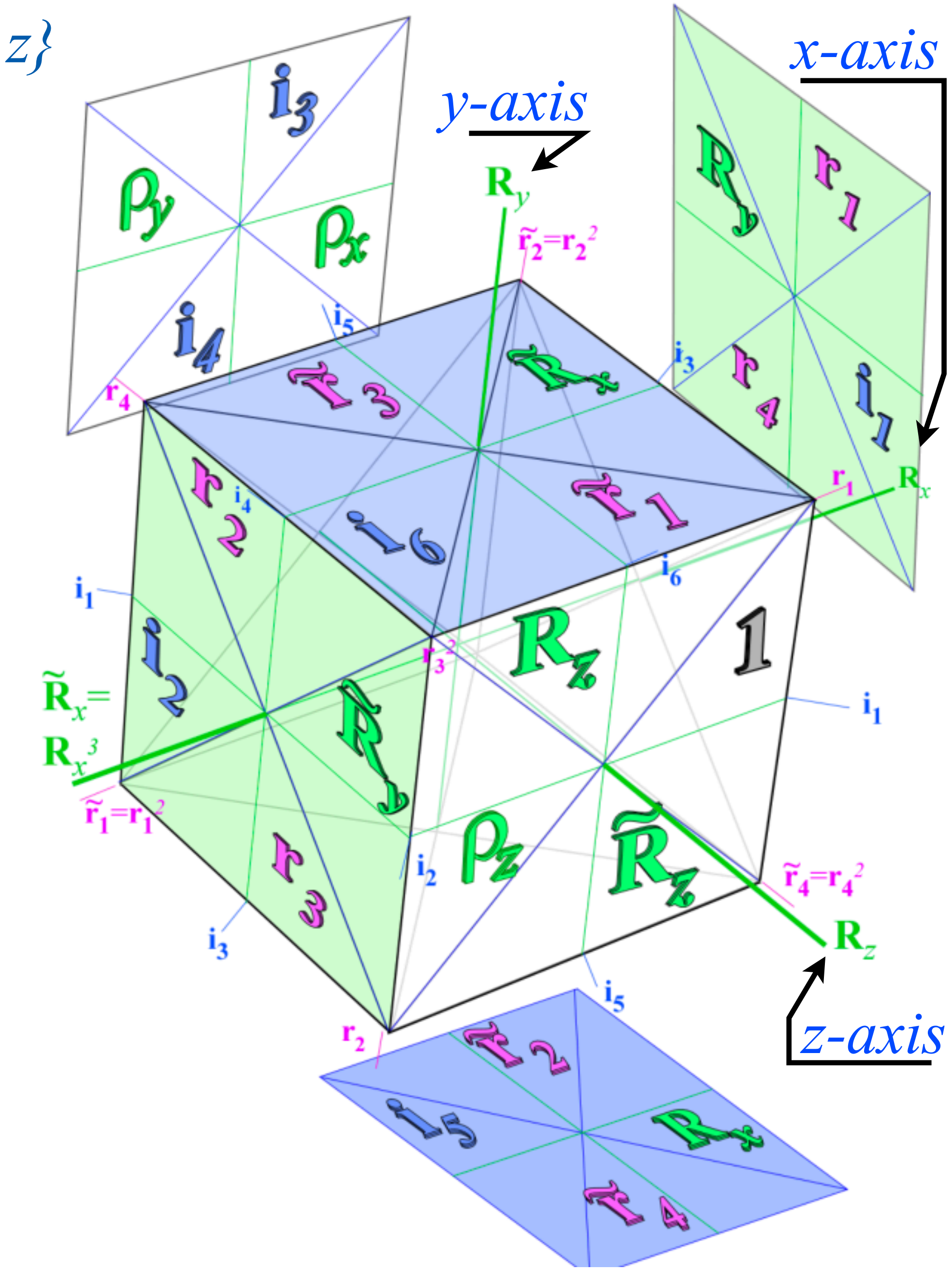
$$\begin{array}{c} \\ \mathbf{r}_1 x = \\ \mathbf{r}_1 y = \\ \mathbf{r}_1 z = \end{array}\begin{array}{ccc} x & y & z \\ \hline \cdot & y & \cdot \\ \cdot & \cdot & z \\ x & \cdot & \cdot \end{array}\qquad \begin{array}{c} \\ \mathbf{R}_x x = \\ \mathbf{R}_x y = \\ \mathbf{R}_x z = \end{array}\begin{array}{ccc} x & y & z \\ \hline x & \cdot & \cdot \\ \cdot & \cdot & z \\ \cdot & -y & \cdot \end{array}\qquad \begin{array}{c} \\ \rho_x x = \\ \rho_x y = \\ \rho_x z = \end{array}\begin{array}{ccc} x & y & z \\ \hline x & \cdot & \cdot \\ \cdot & -y & \cdot \\ \cdot & \cdot & -z \end{array}$$

$$\begin{array}{c} \\ \mathbf{r}_1 xy= \\ \mathbf{r}_1 xz= \\ \mathbf{r}_1 yz= \end{array}\begin{array}{ccc} xy & xz & yz \\ \hline \cdot & \cdot & yz \\ xy & \cdot & \cdot \\ \cdot & xz & \cdot \end{array}\qquad \begin{array}{c} \\ \mathbf{R}_x xy= \\ \mathbf{R}_x xz= \\ \mathbf{R}_x yz= \end{array}\begin{array}{ccc} xy & xz & yz \\ \hline \cdot & xz & \cdot \\ -xy & \cdot & \cdot \\ \cdot & \cdot & yz \end{array}\qquad \begin{array}{c} \\ \rho_x xy= \\ \rho_x xz= \\ \rho_x yz= \end{array}\begin{array}{ccc} xy & xz & yz \\ \hline -xy & \cdot & \cdot \\ \cdot & -xz & \cdot \\ \cdot & \cdot & yz \end{array}$$

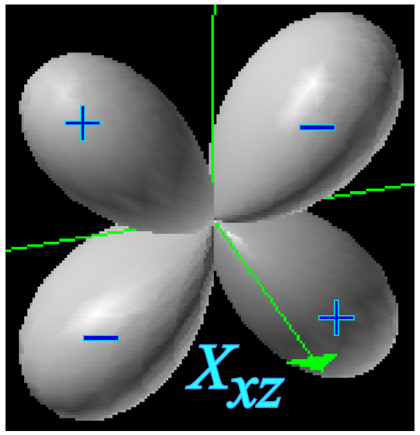
irrep notation is transpose

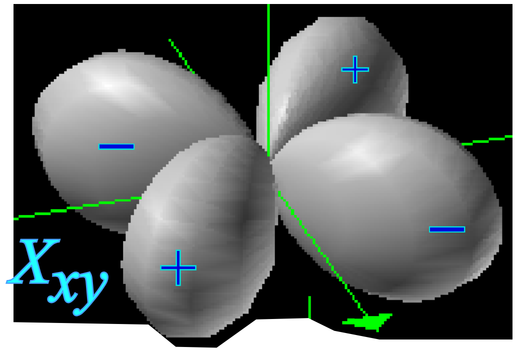
$$D^{T_2}(\mathbf{r}_1)=\begin{pmatrix} \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \end{pmatrix} \quad D^{T_2}(\mathbf{R}_x)=\begin{pmatrix} \cdot & -1 & \cdot \\ 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \end{pmatrix} \quad D^{T_2}(\rho_x)=\begin{pmatrix} -1 & \cdot & \cdot \\ \cdot & -1 & \cdot \\ \cdot & \cdot & 1 \end{pmatrix}$$

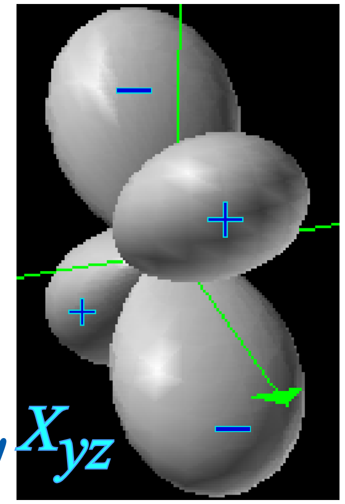
$$\chi^{T_2}{}_{\mathbf{r}_1}=\mathrm{Trace}D^{T_1}(\mathbf{r}_1)=0 \qquad \chi^{T_2}{}_{\mathbf{R}_x}=+1 \qquad \chi^{T_2}{}_{\rho_x}=-1$$



D^{T_2} derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$







using unit tensors {xy,xz,yz}

Vector-tran gives tensor-tran!

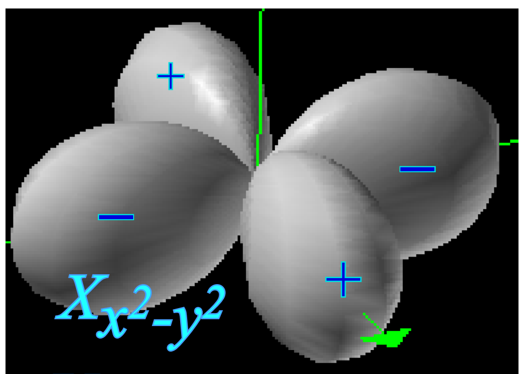
$$\begin{matrix} & x & y & z \\ \mathbf{r}_1 x = & \cdot & y & \cdot \\ \mathbf{r}_1 y = & \cdot & \cdot & z \\ \mathbf{r}_1 z = & x & \cdot & \cdot \end{matrix} \quad \begin{matrix} & x & y & z \\ \mathbf{R}_x x = & x & \cdot & \cdot \\ \mathbf{R}_x y = & \cdot & \cdot & z \\ \mathbf{R}_x z = & \cdot & -y & \cdot \end{matrix} \quad \begin{matrix} & x & y & z \\ \rho_x x = & x & \cdot & \cdot \\ \rho_x y = & \cdot & -y & \cdot \\ \rho_x z = & \cdot & \cdot & -z \end{matrix} \quad \begin{matrix} & x & y & z \\ \mathbf{i}_1 x = & \cdot & \cdot & z \\ \mathbf{i}_1 y = & \cdot & -y & \cdot \\ \mathbf{i}_1 z = & x & \cdot & \cdot \end{matrix}$$

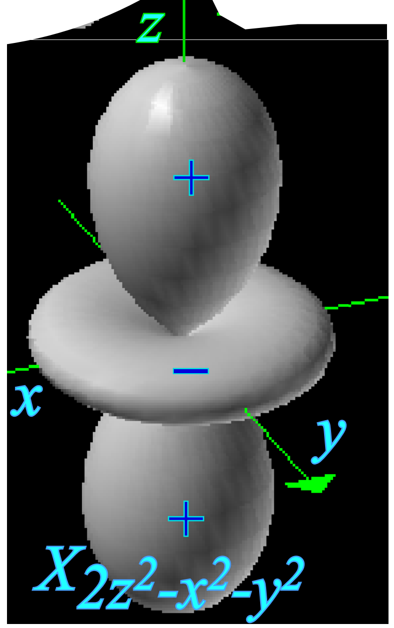
$$\begin{matrix} & xy & xz & yz \\ \mathbf{r}_1 xy = & \cdot & \cdot & yz \\ \mathbf{r}_1 xz = & xy & \cdot & \cdot \\ \mathbf{r}_1 yz = & \cdot & xz & \cdot \end{matrix} \quad \begin{matrix} & xy & xz & yz \\ \mathbf{R}_x xy = & \cdot & xz & \cdot \\ \mathbf{R}_x xz = & -xy & \cdot & \cdot \\ \mathbf{R}_x yz = & \cdot & \cdot & yz \end{matrix} \quad \begin{matrix} & xy & xz & yz \\ \rho_x xy = & -xy & \cdot & \cdot \\ \rho_x xz = & \cdot & -xz & \cdot \\ \rho_x yz = & \cdot & \cdot & yz \end{matrix} \quad \begin{matrix} & xy & xz & yz \\ \mathbf{i}_1 xy = & \cdot & \cdot & -zy \\ \mathbf{i}_1 xz = & \cdot & zx & \cdot \\ \mathbf{i}_1 yz = & -xy & \cdot & \cdot \end{matrix}$$

irrep notation is transpose

$$D^{T_2}(\mathbf{r}_1) = \begin{pmatrix} \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \end{pmatrix} \quad D^{T_2}(\mathbf{R}_x) = \begin{pmatrix} \cdot & -1 & \cdot \\ 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \end{pmatrix} \quad D^{T_2}(\rho_x) = \begin{pmatrix} -1 & \cdot & \cdot \\ \cdot & -1 & \cdot \\ \cdot & \cdot & 1 \end{pmatrix} \quad D^{T_2}(\mathbf{i}_1) = \begin{pmatrix} \cdot & \cdot & -1 \\ \cdot & 1 & \cdot \\ -1 & \cdot & \cdot \end{pmatrix}$$

$$\chi^{T_2}{}_{\mathbf{r}_1} = Trace D^{T_1}(\mathbf{r}_1) = 0 \qquad \chi^{T_2}{}_{\mathbf{R}_x} = +1 \qquad \chi^{T_2}{}_{\rho_x} = -1 \qquad \chi^{T_2}{}_{\mathbf{i}_1} = +1$$





D^E *irrep basis*

$$\tfrac{1}{\sqrt{2}}\left(X_2^2(\alpha,\beta)+X_{-2}^2(\alpha,\beta)\right)=\left(\;x^2-y^2\right)\tfrac{1}{\sqrt{2}}$$

$$\tfrac{1}{\sqrt{6}}X_0^2(\alpha,\beta)\;=\left(-x^2-y^2+2z^2\right)\tfrac{1}{\sqrt{6}}$$

j = 2
Standing d-Waves

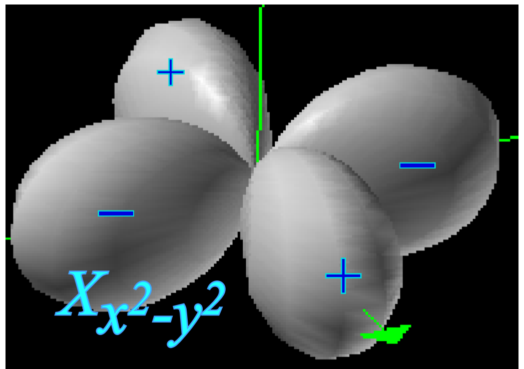
Vector-tran gives tensor-tran!

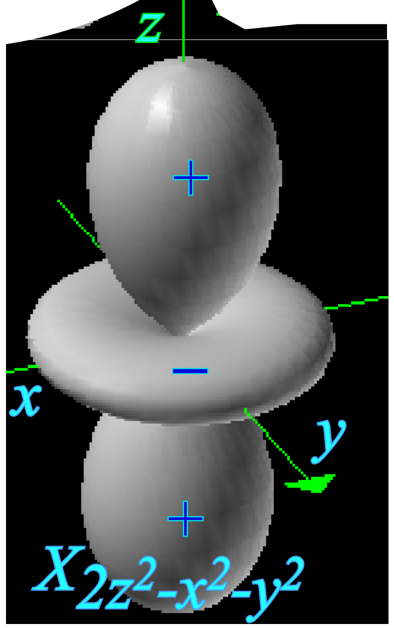
$$\begin{array}{rccc} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \mathbf{r}_1\mathbf{x} = & \cdot & \mathbf{y} & \cdot \\ \mathbf{r}_1\mathbf{y} = & \cdot & \cdot & \mathbf{z} \\ \mathbf{r}_1\mathbf{z} = & \mathbf{x} & \cdot & \cdot \end{array}$$

	$(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$	$(\text{xx-yy})\frac{1}{\sqrt{2}}$
$\mathbf{r}_1(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$	$(+2\text{xx-yy-zz})\frac{1}{\sqrt{6}}$ $(-2+1-2)\frac{1}{6}=\frac{-3}{6}=\frac{-1}{2}$	$(+2\text{xx-yy-zz})\frac{1}{\sqrt{6}}$ $(2+1+0)\frac{1}{2\sqrt{3}}=\frac{\sqrt{3}}{2}$
$\mathbf{r}_1(\text{xx-yy})\frac{1}{\sqrt{2}}$	$(0+\text{yy-zz})\frac{1}{\sqrt{2}}$ $(0-1-2)\frac{1}{2\sqrt{3}}=\frac{-\sqrt{3}}{2}$	$(0+\text{yy-zz})\frac{1}{\sqrt{2}}$ $(0-1+0)\frac{1}{2}=\frac{-1}{2}$

$$D^E(\mathbf{r}_1)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$

$$\chi^E_{\mathbf{r}_1}=Trace D^E(\mathbf{r}_1)=-1$$





D^E *irrep basis*

$$\tfrac{1}{\sqrt{2}}\left(X^2_2(\alpha,\beta)+X^2_{-2}(\alpha,\beta)\right)=\left(x^2-y^2\right)\tfrac{1}{\sqrt{2}}$$

$$\tfrac{1}{\sqrt{6}}X^2_0(\alpha,\beta)=\left(-x^2-y^2+2z^2\right)\tfrac{1}{\sqrt{6}}$$

j = 2
Standing
d-Waves

Vector-tran gives tensor-tran!

$$\begin{array}{c|ccc|} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \hline \mathbf{r}_1\mathbf{x} = & \cdot & \mathbf{y} & \cdot \\ \mathbf{r}_1\mathbf{y} = & \cdot & \cdot & \mathbf{z} \\ \mathbf{r}_1\mathbf{z} = & \mathbf{x} & \cdot & \cdot \\ \hline \end{array}$$

$$\begin{array}{c|ccc|} & \mathbf{x} & \mathbf{y} & \mathbf{z} \\ \hline \mathbf{R}_x\mathbf{x} = & \mathbf{x} & \cdot & \cdot \\ \mathbf{R}_x\mathbf{y} = & \cdot & \cdot & \mathbf{z} \\ \mathbf{R}_x\mathbf{z} = & \cdot & \mathbf{-y} & \cdot \\ \hline \end{array}$$

	(-xx-yy+2zz)$\frac{1}{\sqrt{6}}$	(xx-yy)$\frac{1}{\sqrt{2}}$
$\mathbf{r}_1$(-xx-yy+2zz)$\frac{1}{\sqrt{6}}$	(+2xx-yy-zz)$\frac{1}{\sqrt{6}}$ $(-2+1-2)\frac{1}{6}=\frac{-3}{6}=\frac{-1}{2}$	(+2xx-yy-zz)$\frac{1}{\sqrt{6}}$ $(2+1+0)\frac{1}{2\sqrt{3}}=\frac{\sqrt{3}}{2}$
$\mathbf{r}_1$(xx-yy)$\frac{1}{\sqrt{2}}$	(0+yy-zz)$\frac{1}{\sqrt{2}}$ $(0-1-2)\frac{1}{2\sqrt{3}}=\frac{-\sqrt{3}}{2}$	(0+yy-zz)$\frac{1}{\sqrt{2}}$ $(0-1+0)\frac{1}{2}=\frac{-1}{2}$

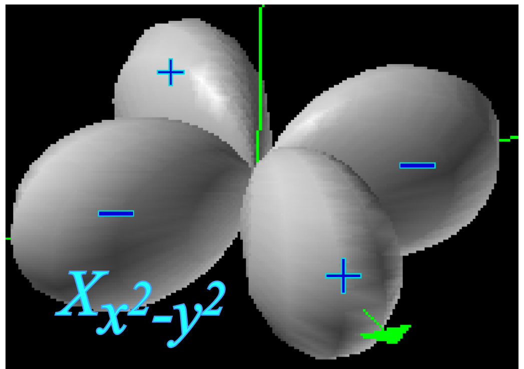
	(-xx-yy+2zz)$\frac{1}{\sqrt{6}}$	(xx-yy)$\frac{1}{\sqrt{2}}$
$\mathbf{R}_x$(-xx-yy+2zz)$\frac{1}{\sqrt{6}}$	(-xx+2yy-zz)$\frac{1}{\sqrt{6}}$ $(+1-2-2)\frac{1}{6}=\frac{-3}{6}=\frac{-1}{2}$	(-xx+2yy-zz)$\frac{1}{\sqrt{6}}$ $(-1-2+0)\frac{1}{2\sqrt{3}}=\frac{-\sqrt{3}}{2}$
$\mathbf{R}_x$(xx-yy)$\frac{1}{\sqrt{2}}$	(xx+0−zz)$\frac{1}{\sqrt{2}}$ $(-1+0-2)\frac{1}{2\sqrt{3}}=\frac{-\sqrt{3}}{2}$	(xx+0−zz)$\frac{1}{\sqrt{2}}$ $(1-0+0)\frac{1}{2}=\frac{1}{2}$

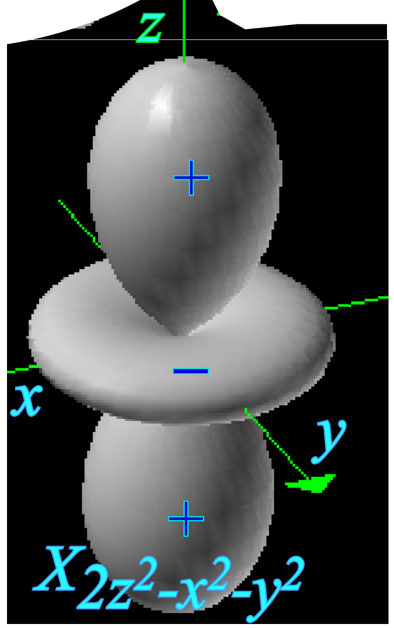
$$D^E(\mathbf{r}_1)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$

$$\chi^E_{\mathbf{r}_1}=TraceD^E(\mathbf{r}_1)=-1$$

$$D^E(\mathbf{R}_x)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

$$\chi^E_{\mathbf{R}_x}=TraceD^E(\mathbf{R}_x)=0$$





D^E irrep basis

$$\frac{1}{\sqrt{2}}\left(X^2_2(\alpha,\beta)+X^2_{-2}(\alpha,\beta)\right)=\left(x^2-y^2\right)\frac{1}{\sqrt{2}}$$

$$\frac{1}{\sqrt{6}}X^2_0(\alpha,\beta)=\left(-x^2-y^2+2z^2\right)\frac{1}{\sqrt{6}}$$

j = 2
Standing
d-Waves

Vector-tran gives tensor-tran!

	x	y	z
ρ_x **x** =	**x**	·	·
ρ_x **y** =	·	**-y**	·
ρ_x **z** =	·	·	**-z**

	x	y	z
i_1 **x** =	·	·	**z**
i_1 **y** =	·	**-y**	·
i_1 **z** =	**x**	·	·

	$(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$	$(\text{xx-yy})\frac{1}{\sqrt{2}}$
$\rho_x(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$	$(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$ $(-1-1+2)\frac{1}{6}=\frac{6}{6}=1$	$(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$ $(-1+1+0)\frac{0}{2\sqrt{3}}=0$
$\rho_x(\text{xx-yy})\frac{1}{\sqrt{2}}$	$(\text{xx-yy}+0)\frac{1}{\sqrt{2}}$ $(-1+1+0)\frac{0}{2\sqrt{3}}=0$	$(\text{xx-yy}+0)\frac{1}{\sqrt{2}}$ $(1+1+0)\frac{1}{2}=\frac{2}{2}=1$

	$(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$	$(\text{xx-yy})\frac{1}{\sqrt{2}}$
$i_1(\text{-xx-yy+2zz})\frac{1}{\sqrt{6}}$	$(\text{+2xx-yy-zz})\frac{1}{\sqrt{6}}$ $(-2+1-2)\frac{1}{6}=\frac{-3}{6}=\frac{-1}{2}$	$(\text{+2xx-yy-zz})\frac{1}{\sqrt{6}}$ $(+2+1+0)\frac{3}{2\sqrt{3}}=\frac{+\sqrt{3}}{2}$
$i_1(\text{xx-yy})\frac{1}{\sqrt{2}}$	$(0-\text{yy}+\text{zz})\frac{1}{\sqrt{2}}$ $(0+1+2)\frac{1}{2\sqrt{3}}=\frac{+\sqrt{3}}{2}$	$(0-\text{yy}+\text{zz})\frac{1}{\sqrt{2}}$ $(0+1+0)\frac{1}{2}=\frac{1}{2}$

$$D^E(\rho_x)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$\chi^E_{\rho_x}=\mathit{Trace}D^E(\rho_x)=-1$$

$$D^E(i_1)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

$$\chi^E_{i_1}=\mathit{Trace}D^E(i_1)=0$$

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ *tensor* $\mathbf{H}$*-expansions*

What tensors go in tetrahedral *(T_d)* or octahedral *(O_h)* free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ *and* $\mathbf{T}_q^{[2,2]}$ *tensor* $\mathbf{H}$*-expansions*

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^{E} irrep tensor basis*

➡ *Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O*

R(3)⊃O character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

Summary of irrep characters χ^{T_1}, χ^{T_2}, χ^{E}, χ^{A_2}, and χ^{A_1} of O

$$D^E(\mathbf{r}_1)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}\quad D^E(\boldsymbol{\rho}\mathrm{x})=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\quad D^E(\mathbf{R}_\mathrm{x})=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}\quad D^E(\mathbf{i}_1)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

$$\chi^E_{\mathbf{r}_1}=Trace D^E(\mathbf{r}_1)=-1\quad \chi^E_{\boldsymbol{\rho}\mathrm{x}}=Tr D^E(\boldsymbol{\rho}\mathrm{x})=2\quad \chi^E_{\mathbf{R}_\mathrm{x}}=Trace D^E(\mathbf{R}_\mathrm{x})=0\quad \chi^E_{\mathbf{i}_1}=Trace D^E(\mathbf{i}_1)=0$$

$$D^{T_1}(\mathbf{r}_1)=\begin{pmatrix}\cdot & \cdot & 1\\ 1 & \cdot & \cdot\\ \cdot & 1 & \cdot\end{pmatrix}\quad D^{T_1}(\boldsymbol{\rho}_\mathrm{x})=\begin{pmatrix}1 & \cdot & \cdot\\ \cdot & -1 & \cdot\\ \cdot & \cdot & -1\end{pmatrix}\quad D^{T_1}(\mathbf{R}_\mathrm{x})=\begin{pmatrix}1 & \cdot & \cdot\\ \cdot & \cdot & -1\\ \cdot & 1 & \cdot\end{pmatrix}\quad D^{T_1}(\mathbf{i}_1)=\begin{pmatrix}\cdot & \cdot & 1\\ \cdot & -1 & \cdot\\ 1 & \cdot & \cdot\end{pmatrix}$$

$$\chi^{T_1}{}_{\mathbf{r}_1}=Tr D^{T_1}(\mathbf{r}_1)=0\quad \chi^{T_1}{}_{\boldsymbol{\rho}_\mathrm{x}}=-1\quad \chi^{T_1}{}_{\mathbf{R}\mathrm{x}}=+1\quad \chi^{T_1}{}_{\mathbf{i}_1}=-1$$

$$D^{T_2}(\mathbf{r}_1)=\begin{pmatrix}\cdot & 1 & \cdot\\ \cdot & \cdot & 1\\ 1 & \cdot & \cdot\end{pmatrix}\quad D^{T_2}(\boldsymbol{\rho}_\mathrm{x})=\begin{pmatrix}-1 & \cdot & \cdot\\ \cdot & -1 & \cdot\\ \cdot & \cdot & 1\end{pmatrix}\quad D^{T_2}(\mathbf{R}_\mathrm{x})=\begin{pmatrix}\cdot & -1 & \cdot\\ 1 & \cdot & \cdot\\ \cdot & \cdot & 1\end{pmatrix}\quad D^{T_2}(\mathbf{i}_1)=\begin{pmatrix}\cdot & \cdot & -1\\ \cdot & 1 & \cdot\\ -1 & \cdot & \cdot\end{pmatrix}$$

$$\chi^{T_2}{}_{\mathbf{r}_1}=Tr D^{T_1}(\mathbf{r}_1)=0\quad \chi^{T_2}{}_{\boldsymbol{\rho}_\mathrm{x}}=-1\quad \chi^{T_2}{}_{\mathbf{R}\mathrm{x}}=+1\quad \chi^{T_2}{}_{\mathbf{i}_1}=+1$$

$O: \chi^{\mu}_{\mathbf{g}}$	$\mathbf{g}=\mathbf{1}$	$\mathbf{r}_{1-4}$ $\tilde{\mathbf{r}}_{1-4}$	$\boldsymbol{\rho}_{xyz}$	$\mathbf{R}_{xyz}$ $\tilde{\mathbf{R}}_{xyz}$	$\mathbf{i}_{1-6}$
$\mu=A_1$	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

A_2 singlet based on rank-3 tensor

xyz

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^E, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x,y,z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^E irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^E, χ^{A2}, and χ^{A1} of O

$R(3)\supset O$ character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations* s

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

R(3)⊃O character analysis (Principles of Symmetry Dynamics & Spectroscopy)

(Ch.5 p.384)

	Trace $\mathscr{D}^l(\omega 00)$					Single Electron Orbital Spectroscopic Labeling
	$\omega = 0°$	$\Theta = \frac{2\pi}{3}$ $\omega = 120°$	$\Theta = \pi$ $\omega = 180°$	$\Theta = \frac{2\pi}{4}$ $\omega = 90°$	$\Theta = \pi$ $\omega = 180°$	
$l = 0$	1	1	1	1	1	s_g
1	3	0	−1	1	−1	P_u
2	5	−1	1	−1	1	d_g
3	7	1	−1	−1	−1	f_u
4	9	0	1	1	1	g_g
5	11	−1	−1	1	−1	h_u
6	13	1	1	−1	1	i_g
7	15	0	−1	−1	−1	k_u
8	17	−1	1	1	1	l_g
9	19	1	−1	1	−1	m_u
10	21	0	1	−1	1	n_g
11	23	−1	−1	−1	−1	o_u
12	25	1	1	1	1	q_g
13	27	0	−1	1	−1	r_u
14	29	−1	1	−1	1	t_g
15	31	1	−1	−1	−1	u_u
16	33	0	1	1	1	
17	35	−1	−1	1	−1	
18	37	1	1	−1	1	
19	39	0	−1	−1	−1	
20	41	−1	1	1	1	

(5.6.5a)

Frequency of O Irreps

	f^{A_1}	f^{A_2}	f^{E}	f^{T_1}	f^{T_2}	
$l = 0$	1	·	·	·	·	A_{1g}
1	·	·	·	1	·	T_{1u}
2	·	·	1	·	1	$E_g + T_{2g}$
3	·	1	·	1	1	$A_{2u} + T_{1u} + T_{2u}$
4	1	·	1	1	1	$A_{1g} + E_g + T_{1g} + T_{2g}$
5	·	·	1	2	1	
6	1	1	1	1	2	
7	·	1	1	2	2	
8	1	·	2	2	2	
9	1	1	1	3	2	
10	1	1	2	2	3	
11	·	1	2	3	3	
12	2	1	2	3	3	
13	1	1	2	4	3	
14	1	1	3	3	4	
15	1	2	2	4	4	
16	2	1	3	4	4	
17	1	1	3	5	4	
18	2	2	3	4	5	
19	1	2	3	5	5	
20	2	1	4	5	5	

(5.6.5b)

O	**1**	**r**	$\mathbf{R}^2$	$\mathbf{R}^3$	$\mathbf{i}_k$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

R(3) characters $\chi^{\ell}(\Theta) = \dfrac{\sin(\ell + \frac{1}{2})\Theta}{\sin\frac{\Theta}{2}}$

O characters

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^{E}, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ *or* $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ *or* $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x,y,z}\}$ of *p-wave* $D^{\ell=1}_{\{x,y,z\}}$

D^{T2} irreps derived from standing d-wave $D^{\ell=2}_{\{x,y,z\}}$. *D^{E} irrep tensor basis*

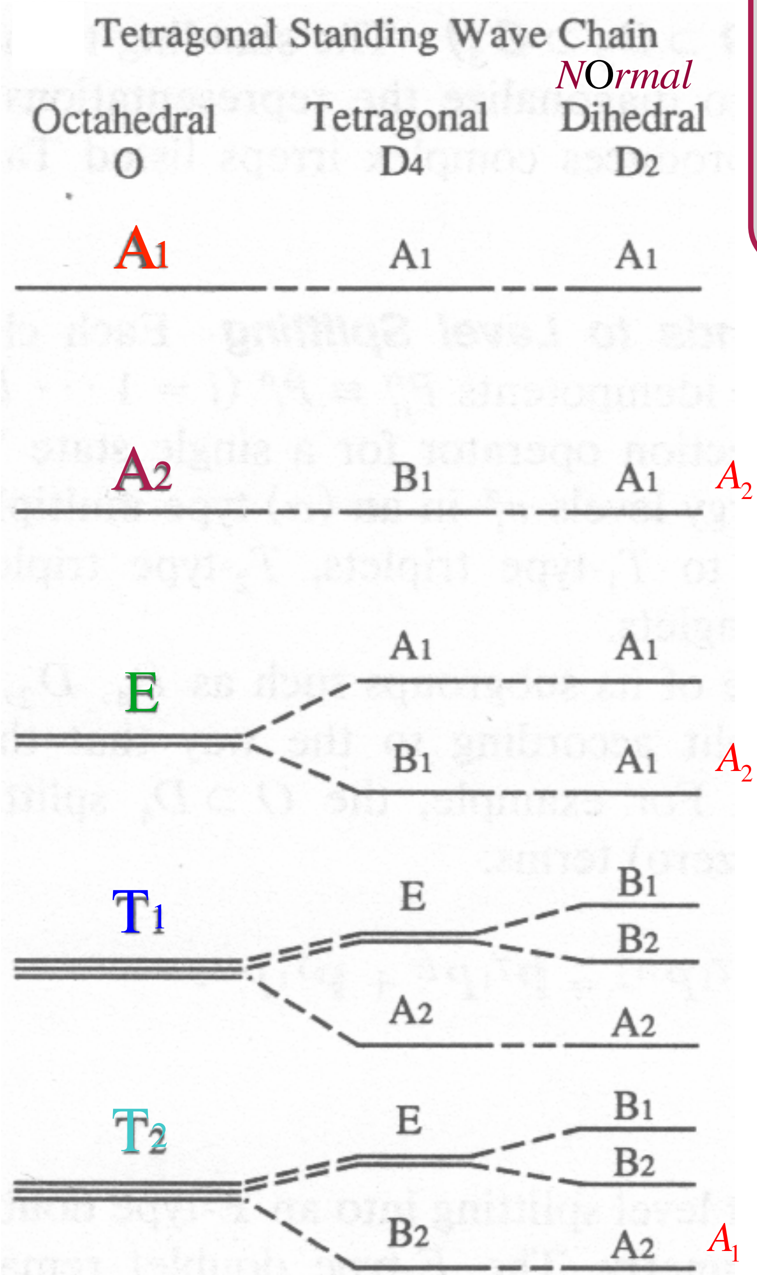
Summary of irrep characters χ^{T1}, χ^{T2}, χ^{E}, χ^{A2}, and χ^{A1} of O

R(3)⊃O character analysis. → *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group⊃Sub-group correlation

Comparing Octahedral and Asymmetric rotor states and level clusters at high J

O⊃D_4⊃D_2 correlation



D_4	$\mathbf{1}$	ρ_z	$\mathbf{R}_z$	$\rho_{x,y}$	$\mathbf{i}_{3,4}$
A_1	1	1	1	1	1
B_1	1	1	-1	1	-1
A_2	1	1	1	-1	-1
B_2	1	1	-1	-1	1
E	2	-2	0	0	0

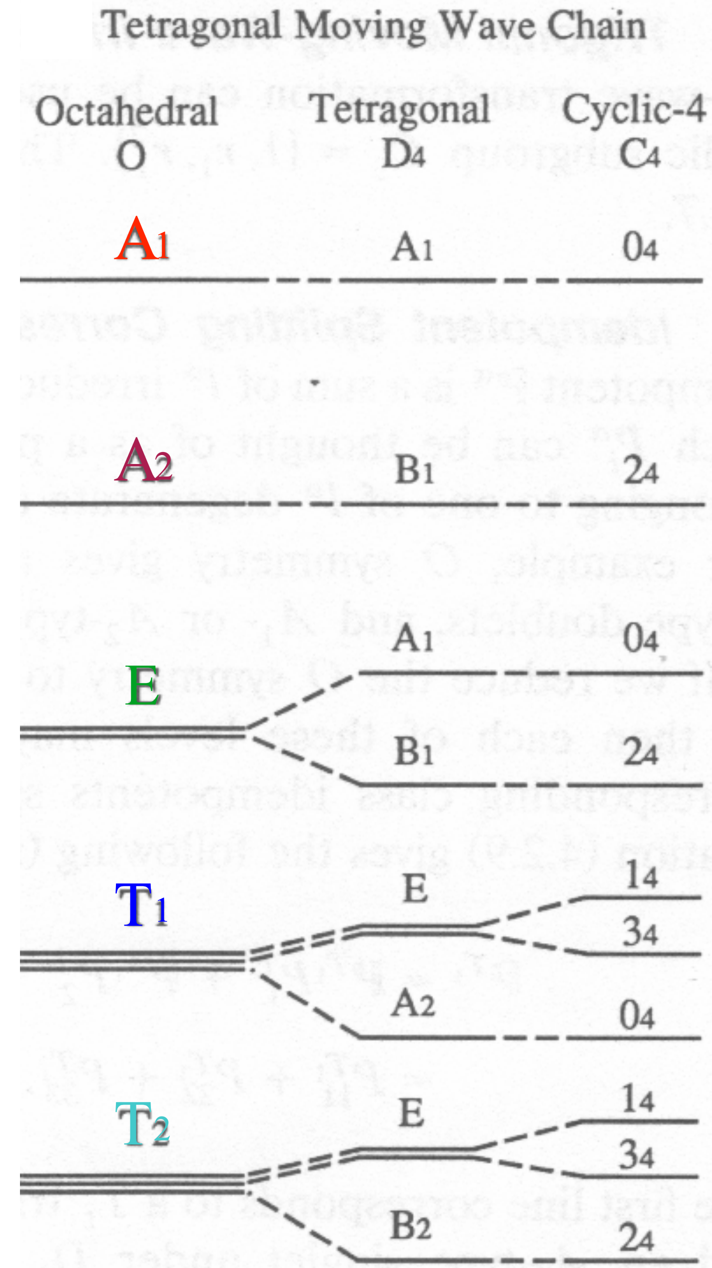
NOrmal $D_2 = \{1, \mathbf{R}_3^2, \mathbf{R}_1^2, \mathbf{R}_2^2\}$

$D_4 \downarrow D_2$	A_1	B_1	A_2	B_2
A_1	1	·	·	·
B_1	1	·	·	·
A_2	·	·	1	·
B_2	·	·	1	·
E	·	1	·	1

UnOrmal $D_2 = \{1, \mathbf{R}_3^2, \mathbf{i}_3, \mathbf{i}_4\}$

$D_4 \downarrow D_2$	A_1	B_1	A_2	B_2
A_1	1	·	·	·
B_1	·	·	1	·
A_2	·	·	1	·
B_2	1	·	·	·
E	·	1	·	1

O⊃D_4⊃C_4 correlation



D_2^{Nm}	$\{\mathbf{1},$	$\mathbf{R}_z^2,$	$\mathbf{R}_x^2,$	$\mathbf{R}_y^2\}$
D_2^{Un}	$\{\mathbf{1},$	$\mathbf{R}_z^2,$	$\mathbf{i}_3,$	$\mathbf{i}_4\}$
A_1	1	1	1	1
B_1	1	-1	1	-1
A_2	1	1	-1	-1
B_2	1	-1	-1	1

$-1_4 =$

$D_4 \downarrow C_4$	0_4	1_4	2_4	3_4
A_1	1	·	·	·
B_1	·	·	1	·
A_2	1	·	·	·
B_2	·	·	1	·
E	·	1	·	1

$\mathbf{r}, \tilde{\mathbf{r}}_i$ ρ_{xyz} $\mathbf{R}, \tilde{\mathbf{R}}_{xyz}$

O	$\mathbf{1}$	$\mathbf{r}$	$\mathbf{R}^2$	$\mathbf{R}^3$	$\mathbf{i}_k$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

NOrmal $D_2 = \{1, \mathbf{R}_3^2, \mathbf{R}_1^2, \mathbf{R}_2^2\}$

O↓D_2	A_1	B_1	A_2	B_2
A_1	1	·	·	·
A_2	1	·	·	·
E	2	·	·	·
T_1	·	1	1	1
T_2	·	1	1	1

UnOrmal $D_2 = \{1, \mathbf{R}_3^2, \mathbf{i}_3, \mathbf{i}_4\}$

O↓D_2	A_1	B_1	A_2	B_2
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	·	1	1	1
T_2	1	1	·	1

O↓D_4	A_1	B_1	A_2	B_2	E
A_1	1	·	·	·	·
A_2	·	1	·	·	·
E	1	1	·	·	·
T_1	·	·	1	·	1
T_2	·	·	·	1	1

$-1_4 =$

O↓C_4	0_4	1_4	2_4	3_4
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	1	1	·	1
T_2	·	1	1	1

2.19.18 class 11.0: *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 *O* of octahedral rotors $\mathbf{H}=B\mathbf{J}^2+\Sigma t_{kq}\mathbf{T}_q^k$

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

RES and matrix representation of multipole $\mathbf{T}_q^k$ tensor $\mathbf{H}$-expansions

What tensors go in tetrahedral (T_d) or octahedral (O_h) free-rotor Hamiltonia $\mathbf{H}$?

4^{th}-rank [$k=4$] multipole terms

O_h-symmetric function and O_h operator $\mathbf{T}^{\{4\}}$

RES and matrix irreps of O_h multipole $\mathbf{T}_q^{[4]}$ and $\mathbf{T}_q^{[2,2]}$ tensor $\mathbf{H}$-expansions

Matrix D^{T1}, D^{T2}, D^E, D^{A2}, and D^{A1}, irreducible representations (irreps) of O

Finding O_h group products. *Examples:* $\mathbf{R}_z\mathbf{1}=\mathbf{R}_z$ or $\mathbf{R}_z\mathbf{i}_6=\mathbf{r}_3$ or $\mathbf{i}_6\mathbf{R}_z=\mathbf{r}_1$

D^{T1} irreps derived visually using unit vectors $\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ of *p-wave* $D^{\ell=1}{}_{\{x,y,z\}}$

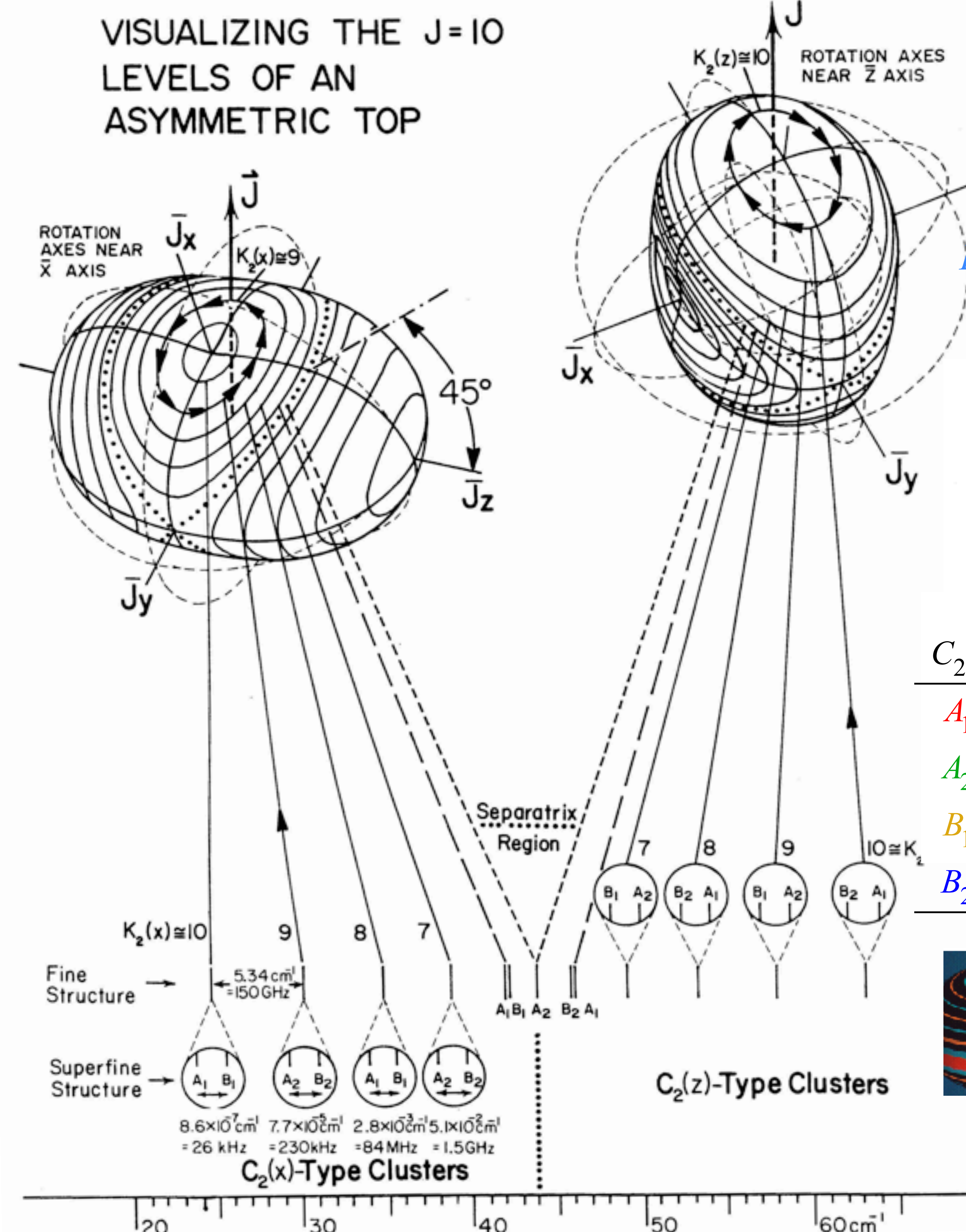
D^{T2} irreps derived from standing d-wave $D^{\ell=2}{}_{\{x,y,z\}}$. *D^E irrep tensor basis*

Summary of irrep characters χ^{T1}, χ^{T2}, χ^E, χ^{A2}, and χ^{A1} of O

R(3)⊃O character analysis. *$O\supset D_4\supset D_2$ and $O\supset D_4\supset C_4$ level correlations s*

Applications of Group⊃Sub-group correlation

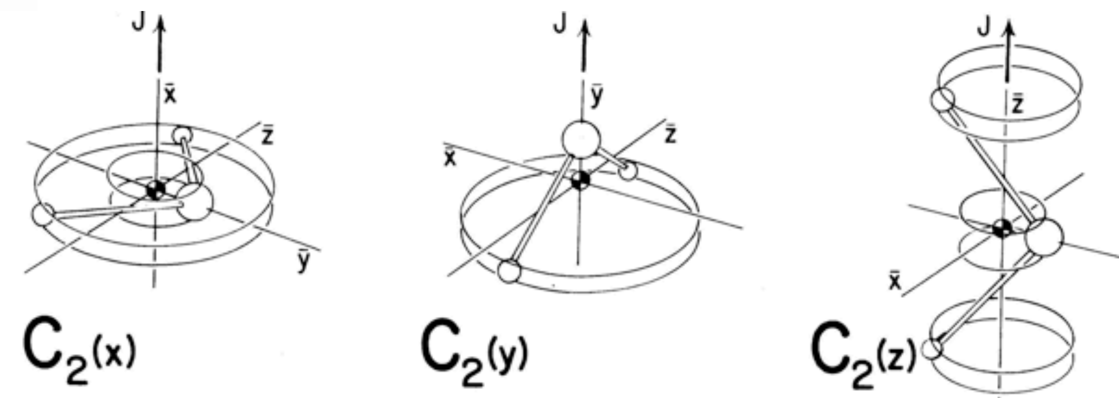
Comparing Octahedral and Asymmetric rotor states and level clusters at high J



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

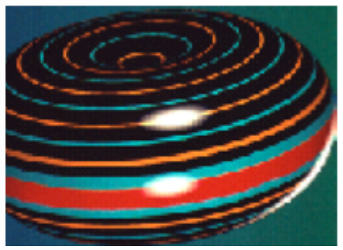
$D_2 \supset C_2(x)$ *$D_2 \supset C_2(y)$*   *$D_2 \supset C_2(z)$*



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	·

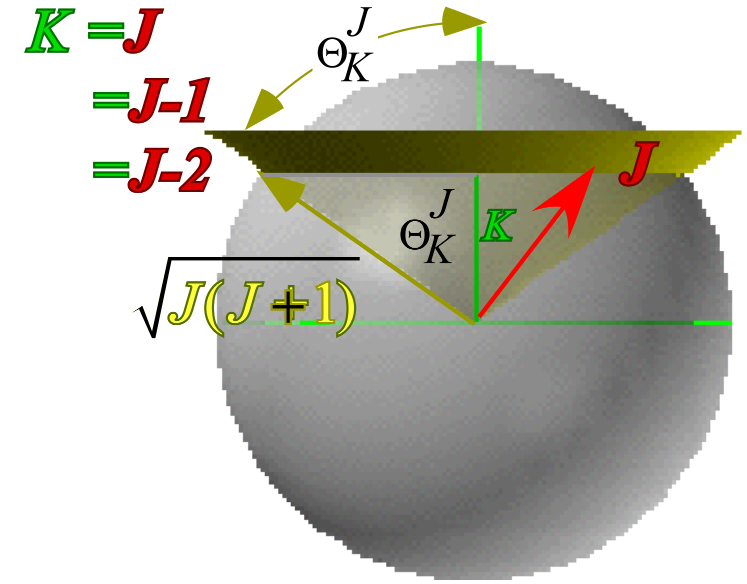


after QTforCA Unit 8. Ch. 25 Fig. 25.4.2

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.*

Finding Hamiltonian Eigensolutions by Geometry using Uncertainty Cone Angles

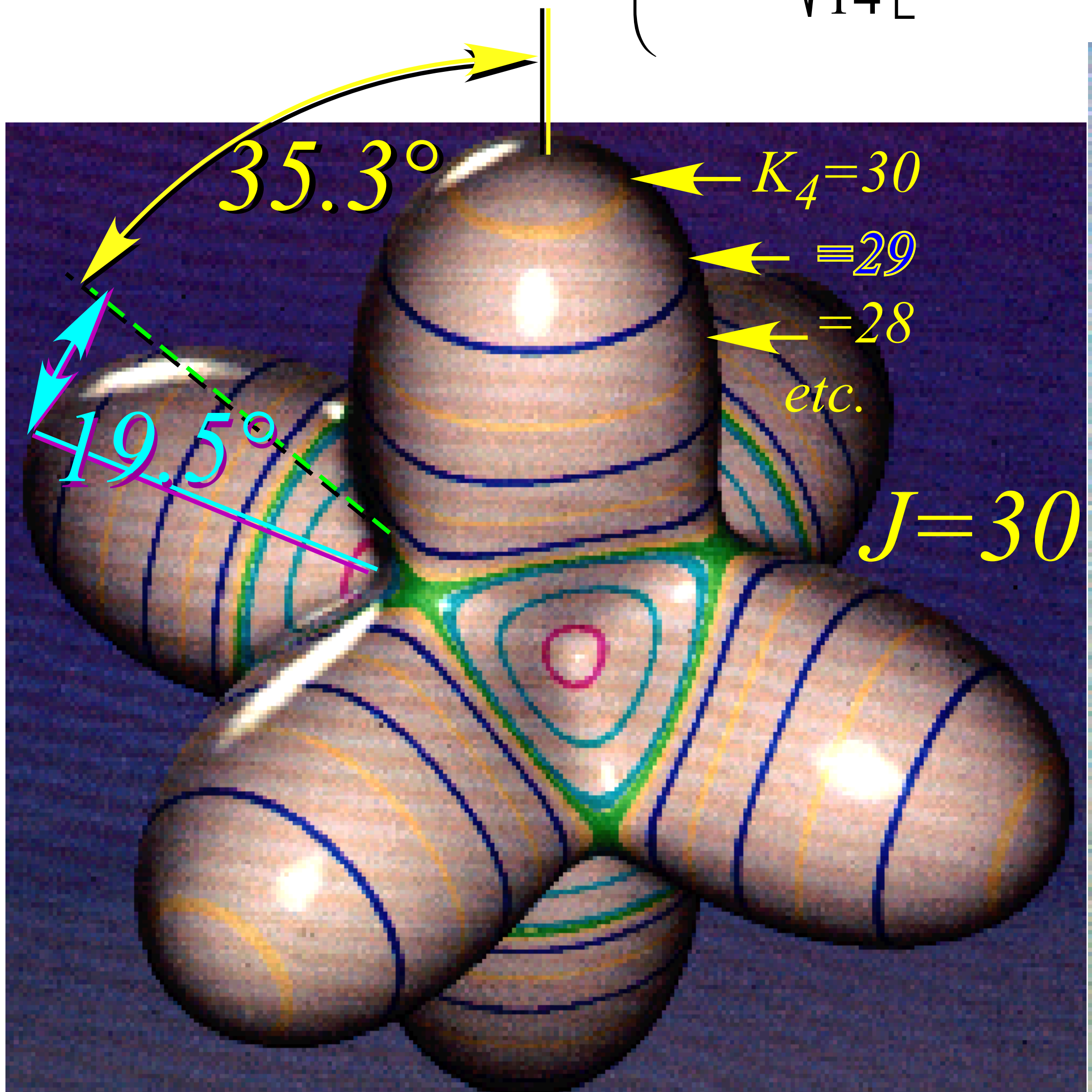
$$\cos\Theta_K^J = \frac{K}{\sqrt{J(J+1)}}$$

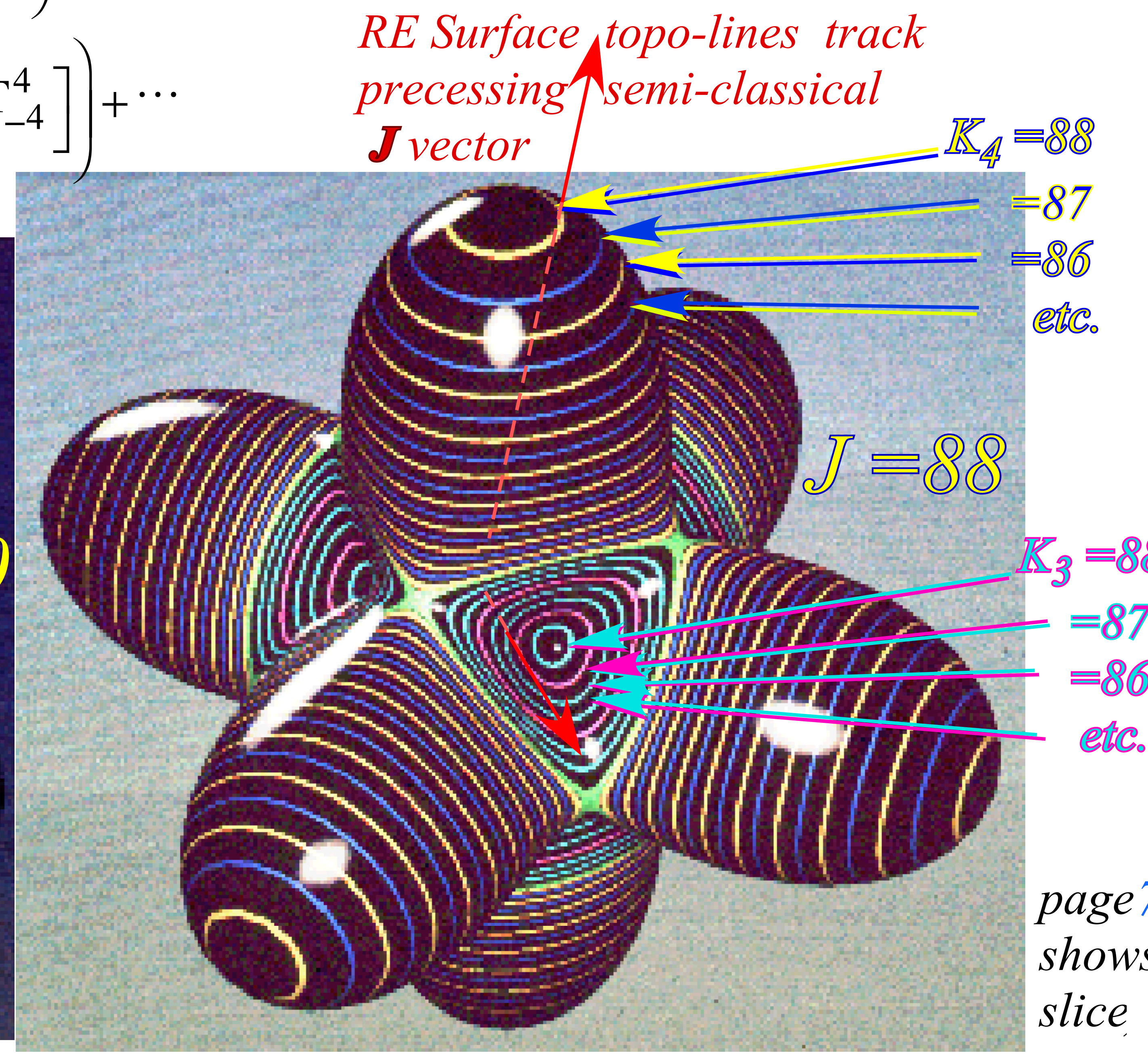


O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

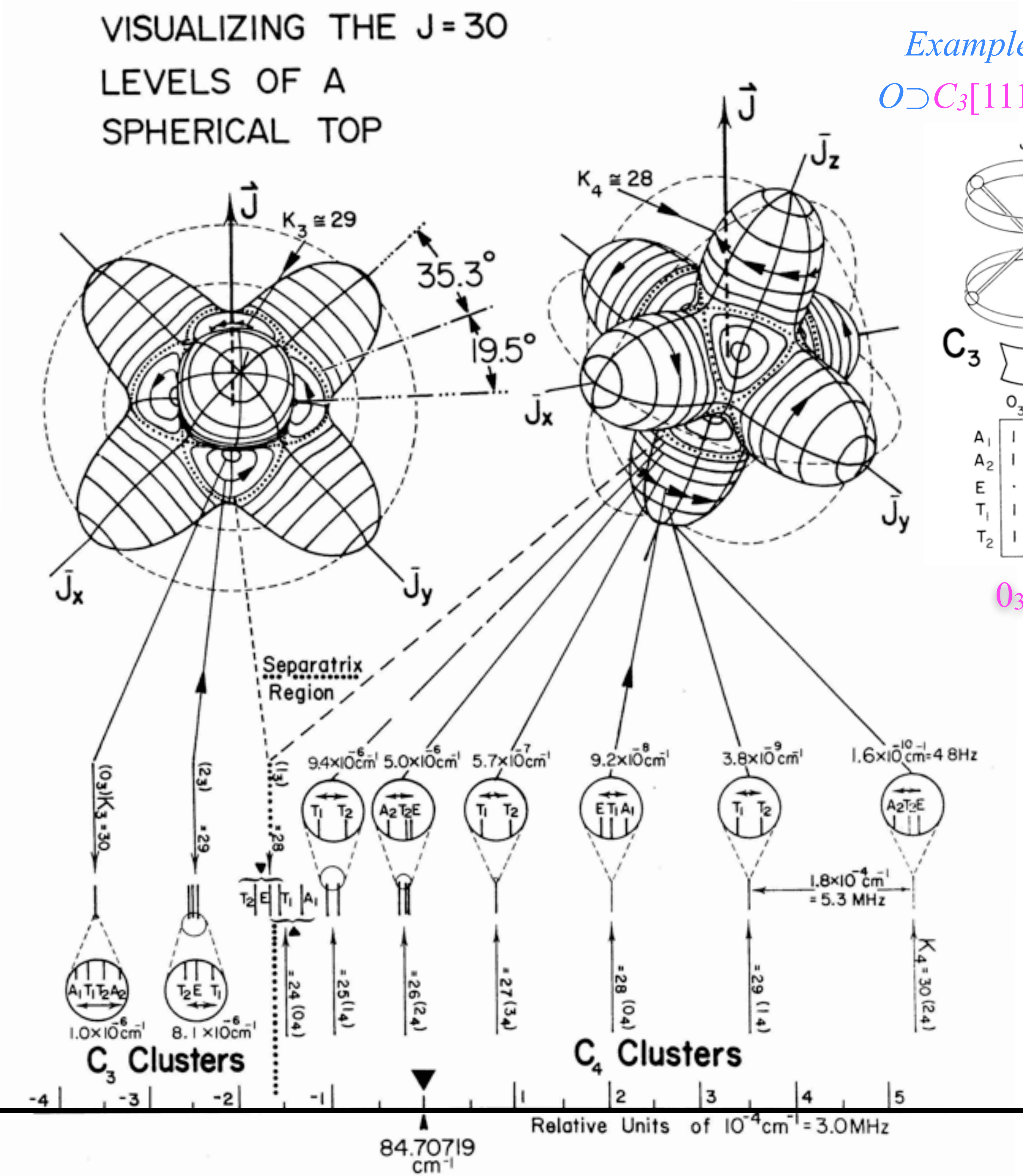
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



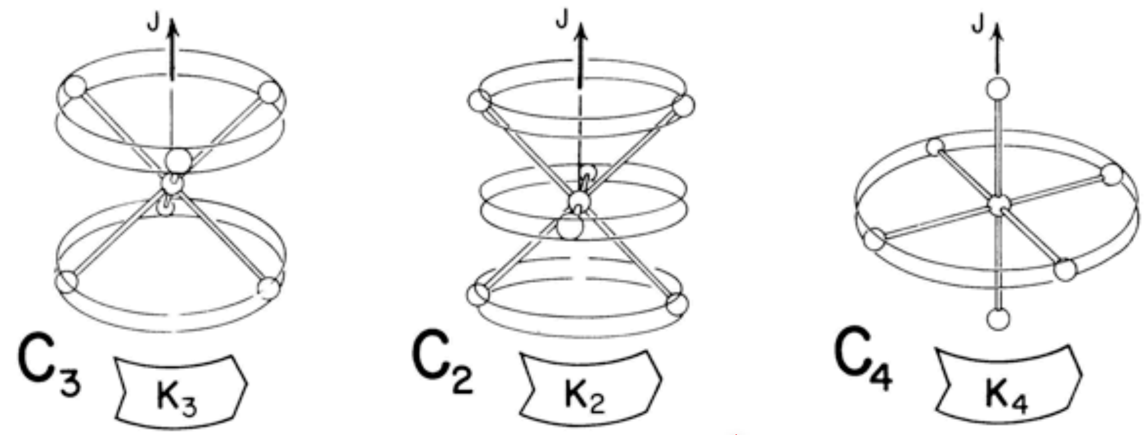


page 75 shows slice



Examples of Group⊃Sub-group correlation

$O \supset C_3[111]$ $O \supset C_2[110]$ $O \supset C_4[001]$



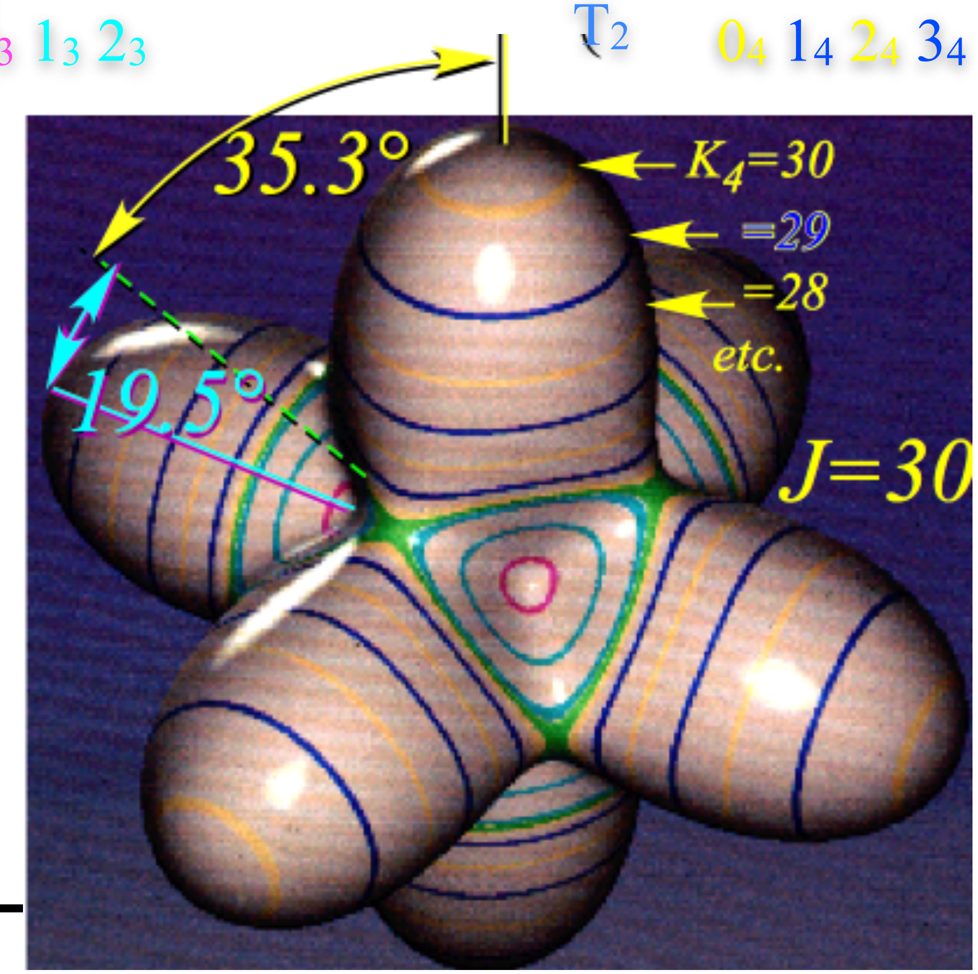
	0_3	1_3	2_3
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

	0_2	1_2
A_1	1	·
A_2	·	1
E	1	1
T_1	1	2
T_2	2	1

	0_4	1_4	2_4	3_4
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	1	1	·	1
T_2	·	1	1	1

A_1 A_2 E T_1 T_2

0_3 1_3 2_3 0_4 1_4 2_4 3_4



O⊃D_4⊃C_4 correlation

This refers: QTforCA Unit 8. Ch. 25 Fig. 25.4.9

Fig. 25.4.9 *Infrared spectra showing fine structure clusters. Tetrafluorosilane (SiF_4) spectrum from a ν_3 R(30) transition ____.*
[After C. W. Patterson, R. S. McDowell, N. G. Nereson, B. J. Krohn, J. S. Wells, and F. R. Peterson, J. Mol. Spectrosc. ***91****, 416 (1982).*
[Cubane (C_8H_8) spectrum from ν_{11} P(30), P(31), and P(32), transitions; cubane (C_8H_8) spectrum from ν_{12} R(36), transition.
[After A. S. Pine, A. G. Maki, A. G. Robiette, B. J. Krohn, J. K. G. Watson, and Th Urbanek, J. Am. Chem. Soc., ***106****, 891 (1984).]*

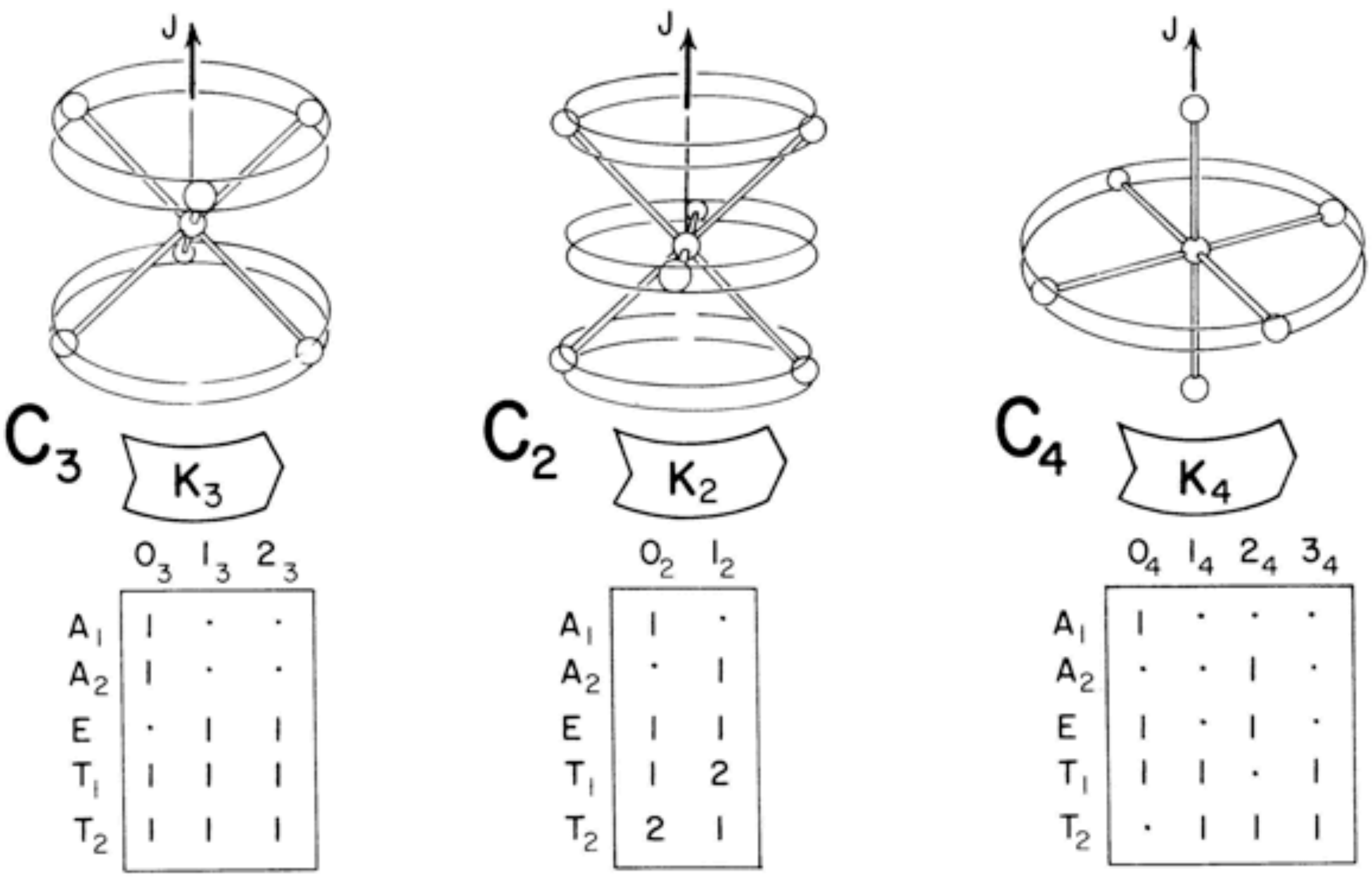
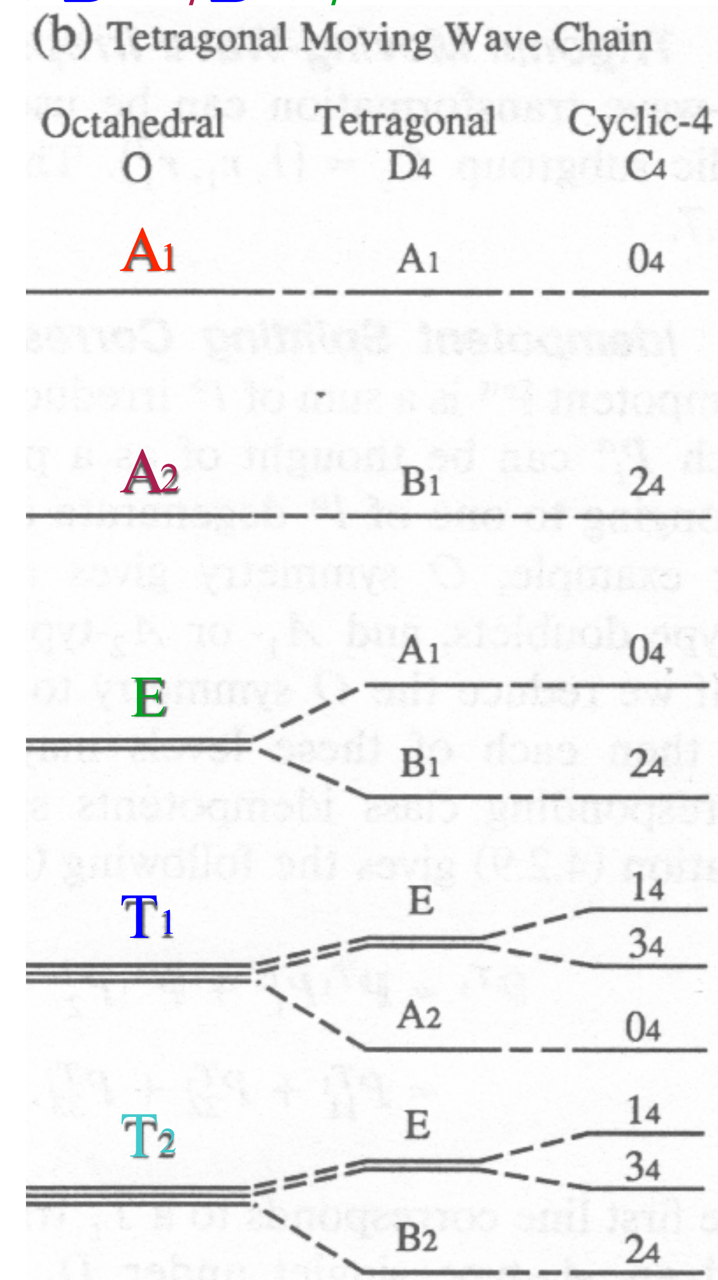


Fig. 25.4.7 *Different choices of rotation axes for octahedral rotor corresponding to local symmetry C_3, C_2, and C_4. Tables correlate global octahedral symmetry species with the local ones.*

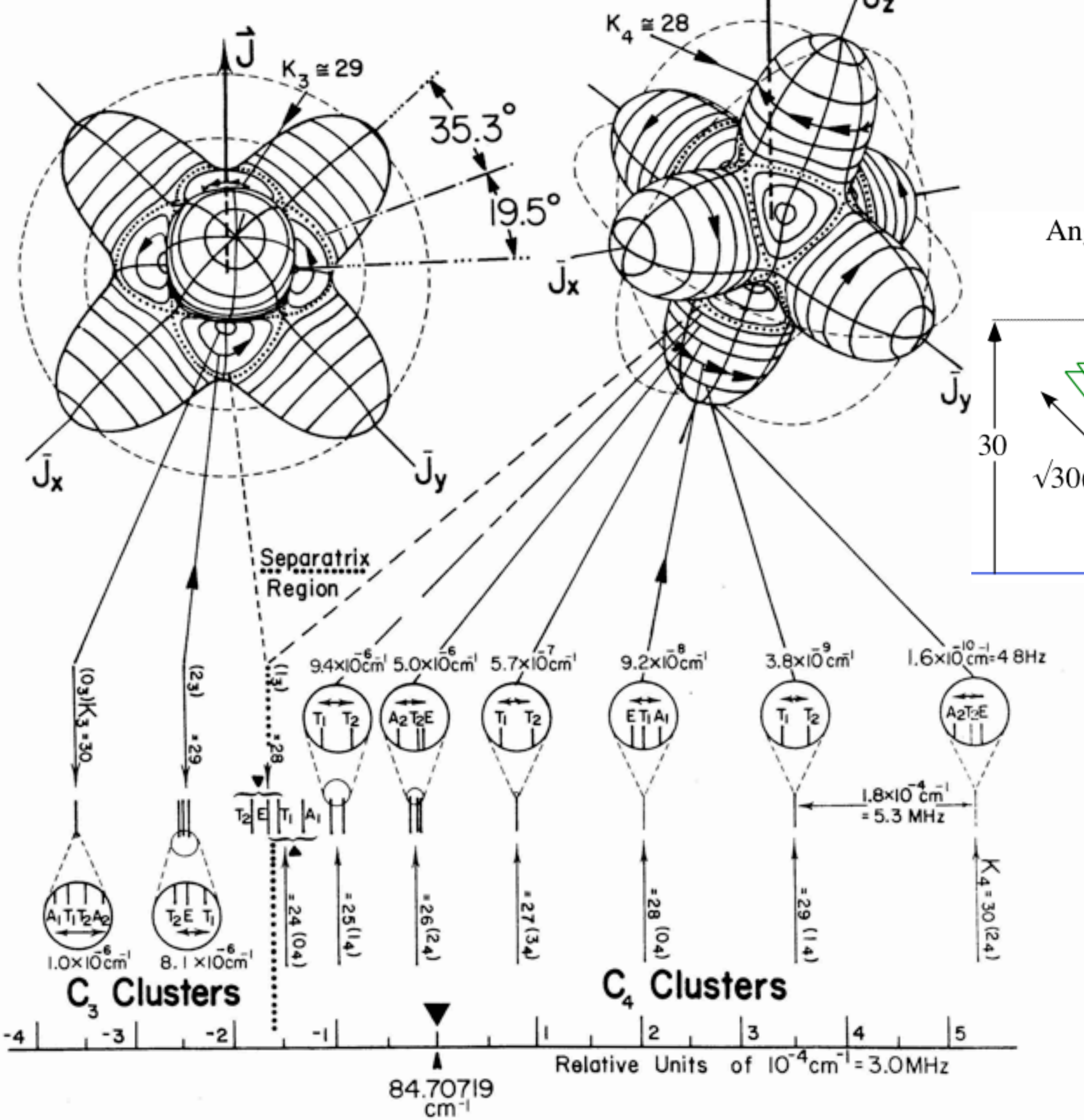
QTforCA Unit 8. Ch. 25 Fig. 25.4.7

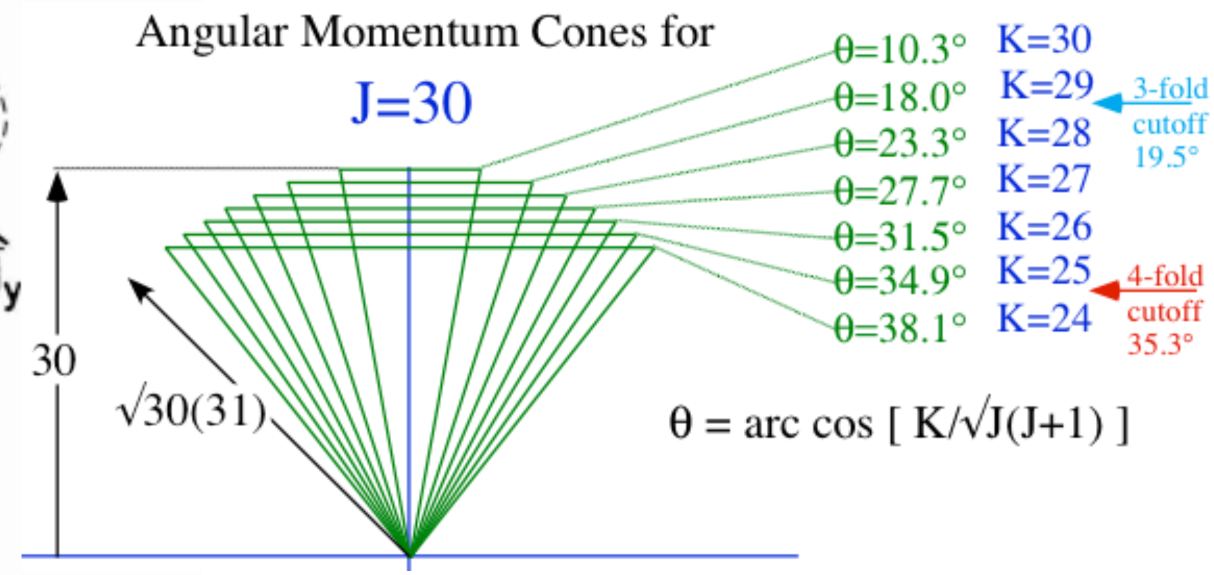


$-1_4 =$

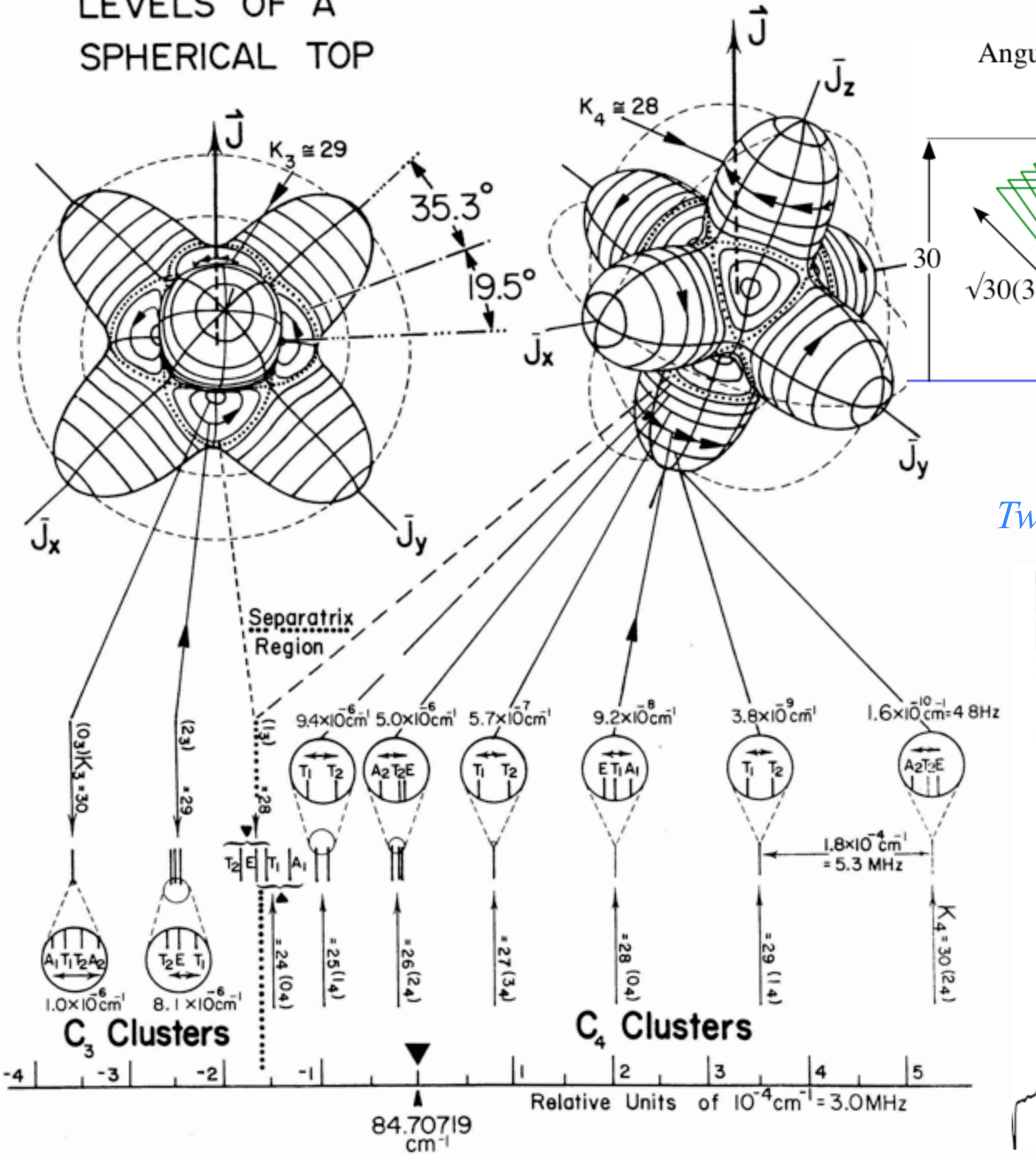
O↓C_4	0_4	1_4	2_4	3_4
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	1	1	·	1
T_2	·	1	1	1

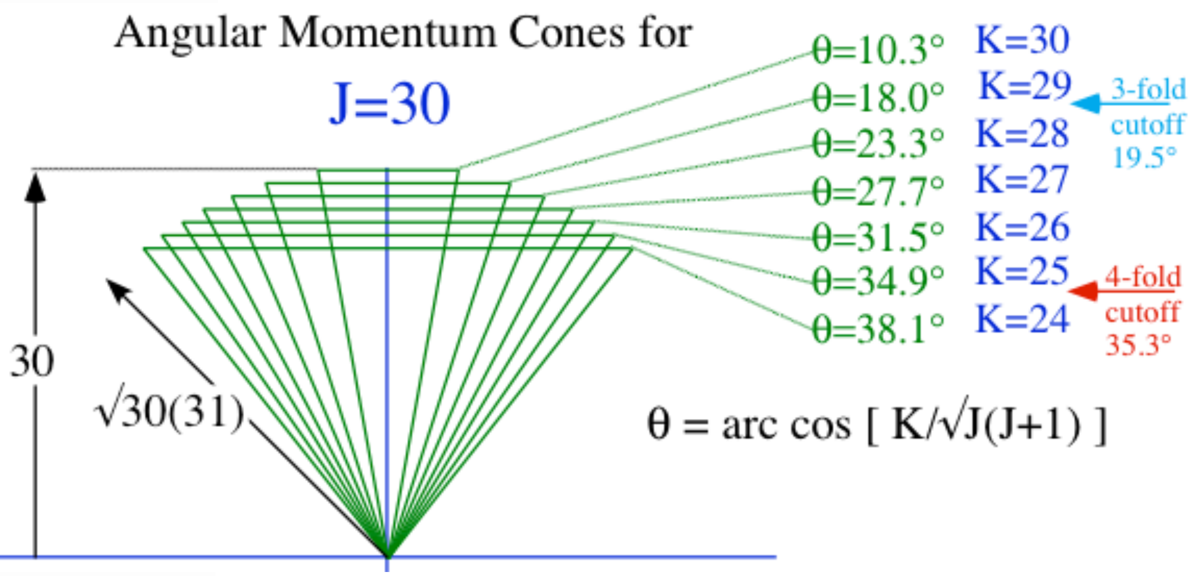
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP



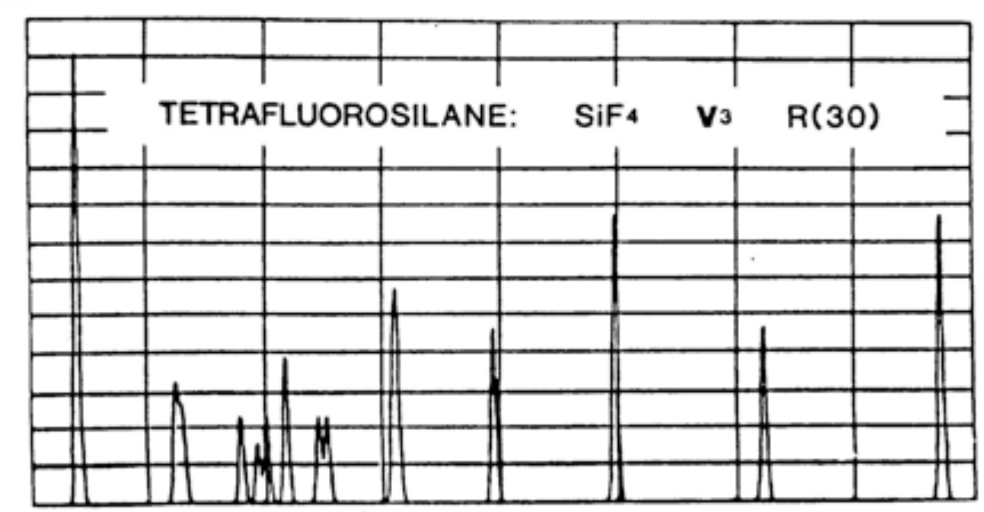


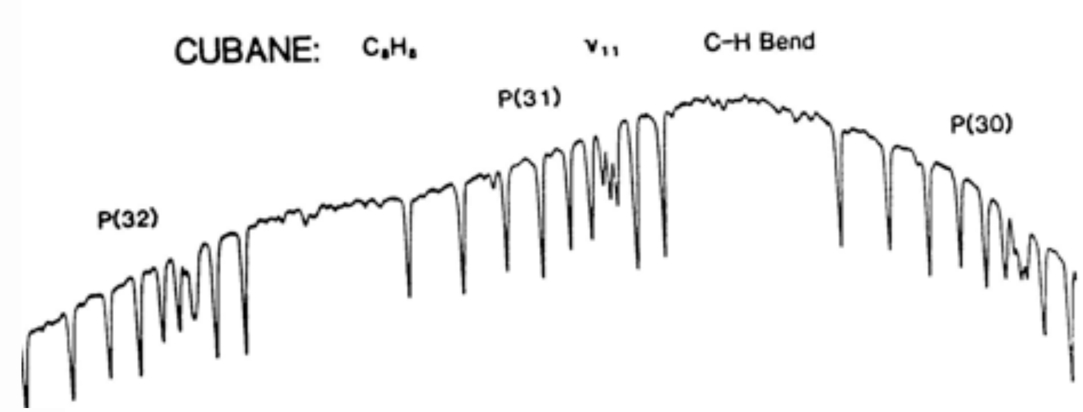
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP



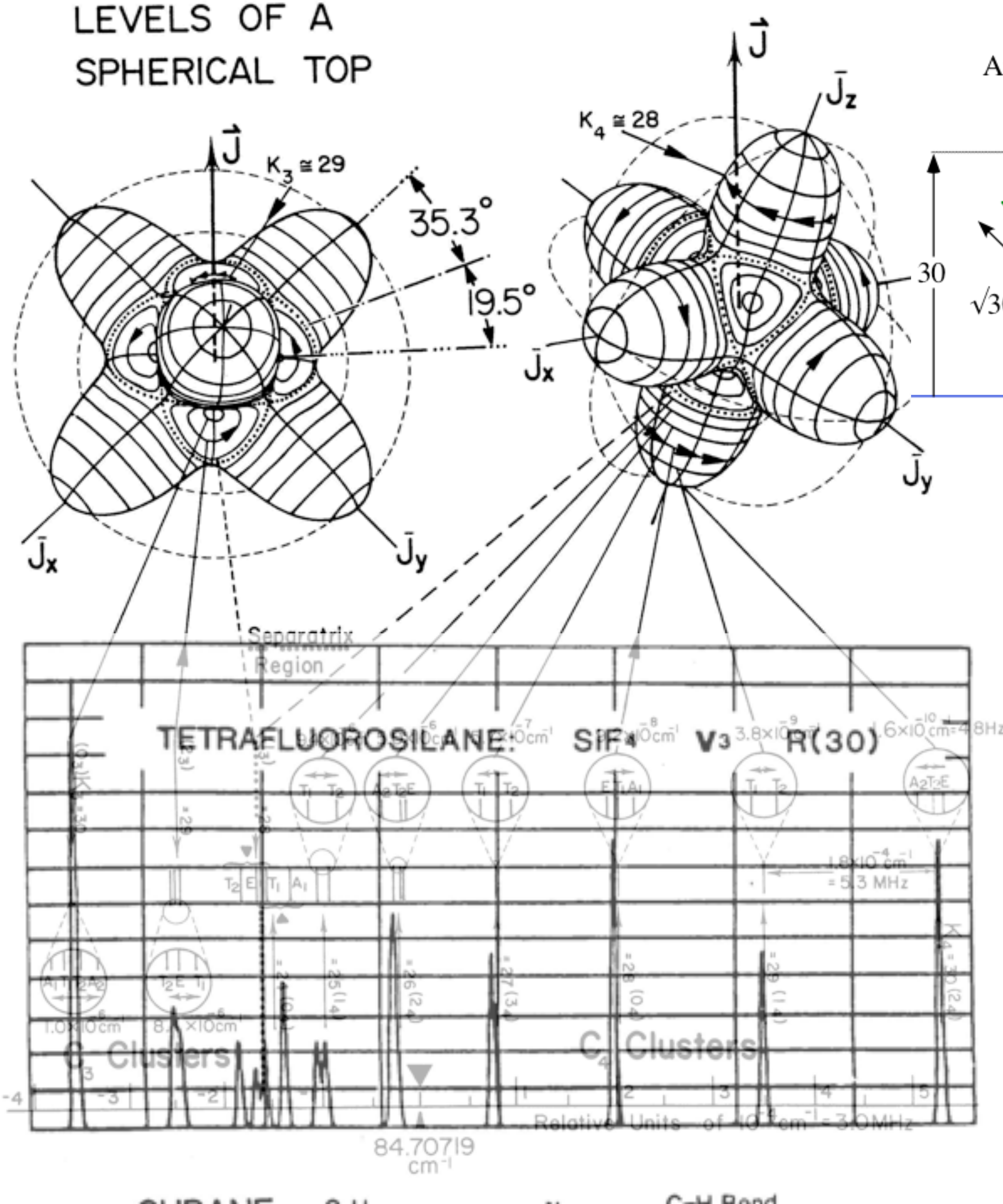


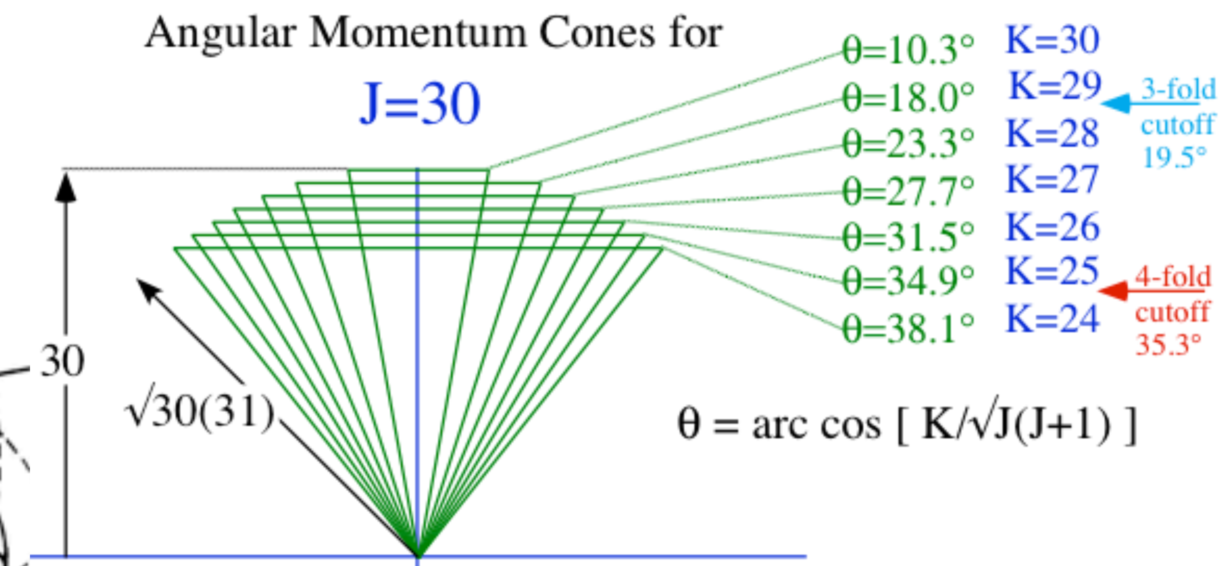
Two molecular examples: SiF_4 and C_8H_8



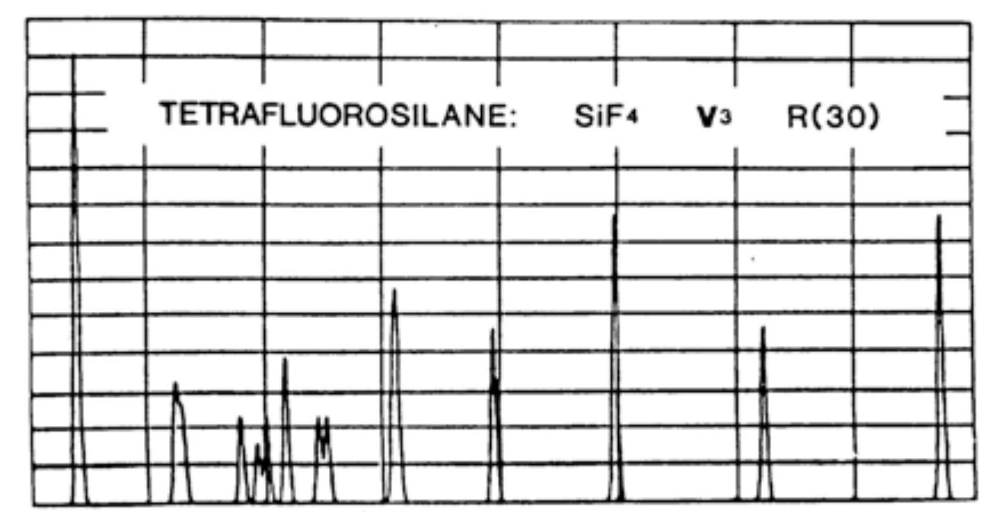


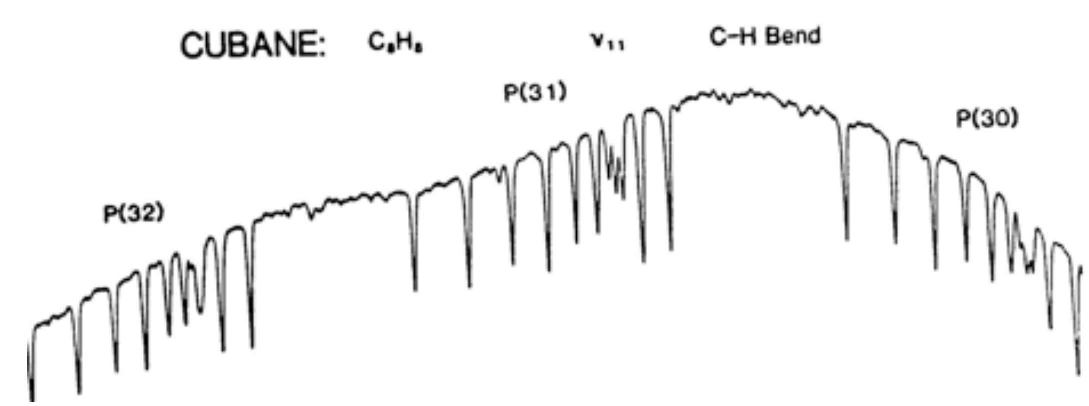
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP





Two molecular examples: SiF_4 and C_8H_8



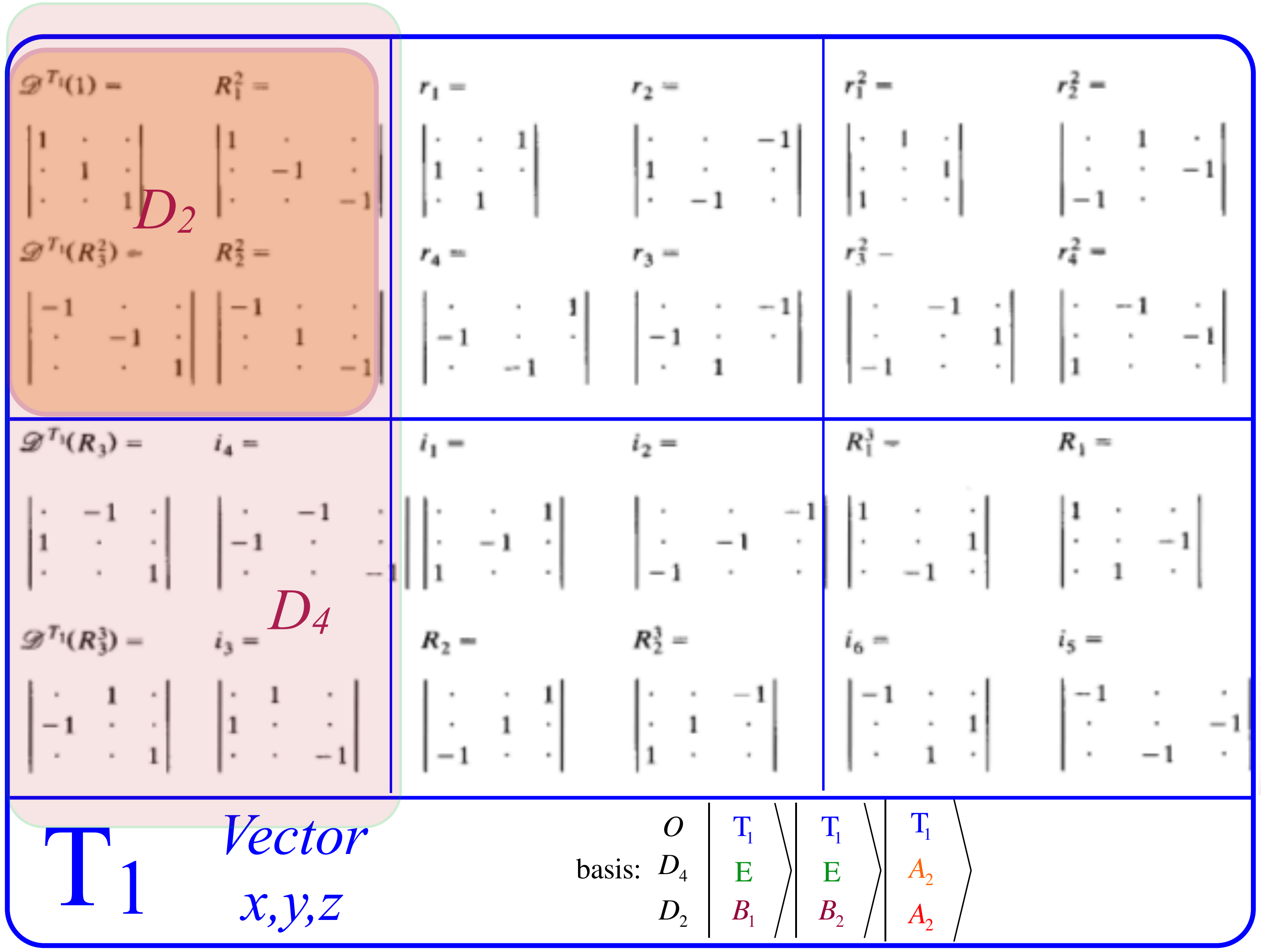


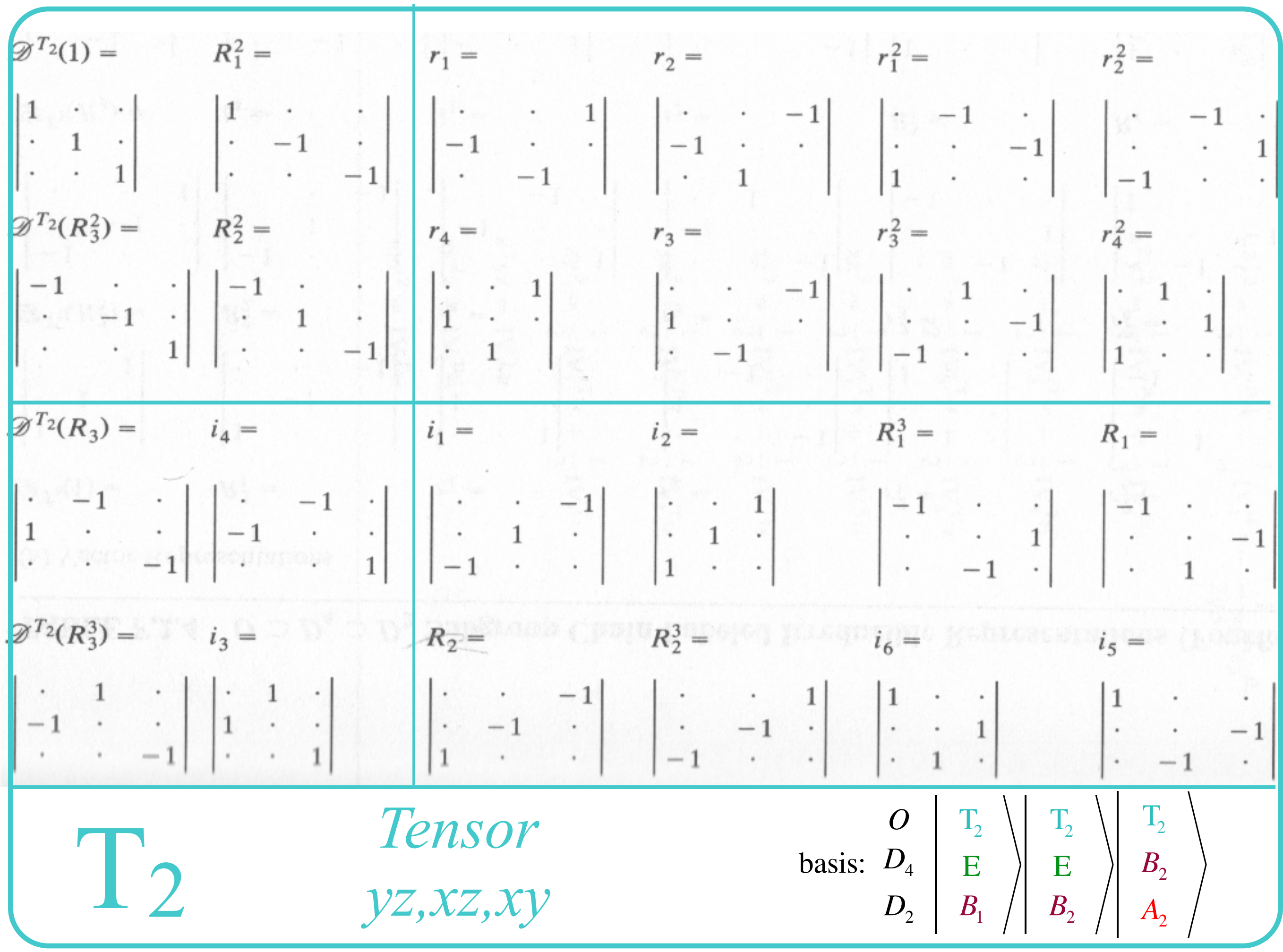
Appendix: *$O \supset D_4 \supset D_2$ irrep table very similar to our irreps on p.48*

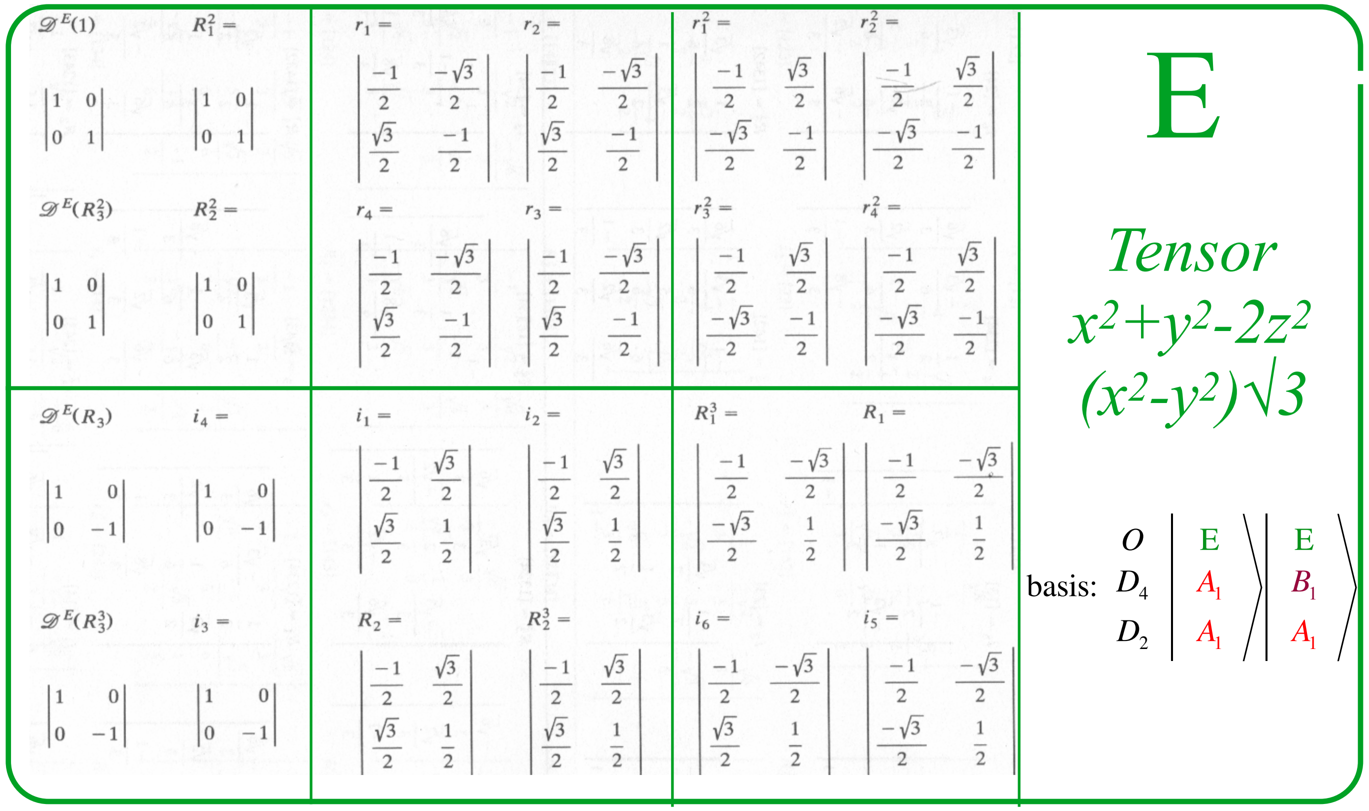
QTCALect.21p.77

See link for there types, choices, and approaches.
This is a "Bottom-up" development

Ireps for O⊃D₄⊃D₂ subgroup chain







$O: \chi^{\mu}_{\mathbf{g}}$	$\mathbf{g}=1$	$\mathbf{r}_{1-4}$ $\tilde{\mathbf{r}}_{1-4}$	ρ_{xyz}	$\mathbf{R}_{xyz}$ $\tilde{\mathbf{R}}_{xyz}$	$\mathbf{i}_{1-6}$
$\mu=A_1$	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1