Group Theory in Quantum Mechanics

Lecture 25 (4.27.17)

Based on AMOP Lectures 14-15
Atomic, Molecular, and Optical Physics

Introduction to Rotational Eigenstates and Spectra I

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 , QTCA Unit 7 Ch. 21-25)
(PSDS - Ch. 5, 7)

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions
   - "Mock-Mach" lab-vs-body-defined states $\left|{}^J_{mn}\right\rangle = \mathbf{P}_{mn}{}^J\left|(0,0,0)\right\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)\left|(0,0,0)\right\rangle$
2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices
   - General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)\left|{}^J_{mn}\right\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)\left|{}^J_{m'n}\right\rangle$
   - Angular momentum cones and high J properties ← End Lect.24
3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues
   - Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$
   - Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$
     - Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions
     - Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

Sketch of modern molecular electronic, vibrational, and rotational spectroscopy
   - Example of CO_2 rovibrational $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

→ Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians ← Go to Lect.26
   - Asymmetric Top eigensolutions for J=1-2

Partial listing of the Harter-Soft/Heyoka LearnIt Web Apps as of April 24, 2017
(Apps are being upgraded as time permits)

Production Links - ***For the students &*** ***general public***

BohrIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BohrItWeb.html"
BounceIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BounceItWeb.html"
BoxIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BoxItWeb.html"
CoulIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/CoulItWeb.html"
Cycloidulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/CycloidulumWeb.html"
LearnIt - Production; URL is "**http://www.uark.edu/ua/modphys**" or "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
Pendulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/PendulumWeb.html"
QuantIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/QuantItWeb.html"
Relativity - Pirelli Entrant: URL is "http://www.uark.edu/ua/pirelli" or "http://www.uark.edu/ua/pirelli/html/default.html"
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"

Testing Links - ***For internal use and testing by*** ***Harter & Heyoka***

BohrIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BohrItWeb.html"
BounceIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BounceItWeb.html"
BounceIt Title Page - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BounceItTitlePage.html"
BoxIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BoxItWeb.html"
CoulIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/CoulItWeb.html"
Cycloidulum - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/CycloidulumWeb.html"
Harter-Soft Web Apps - Quick Reference - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
JerkIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
ModernPhysics - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/IntroCover.html"
Pendulum - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/PendulumWeb.html"
QuantIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/QuantItWeb.html"
Trebuchet Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/TrebuchetWeb.html"

Link to the complete listing of Harter-Soft LearnIt Web Apps and resources for Physics

Three (3) applications of $R(3)$ rotation and $U(2)$ unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|{}^J_{mn}\rangle = \mathbf{P}^J_{mn}|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. $R(3)$ rotation and $U(2)$ unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|{}^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|{}^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}^k_q$ and eigenvalues

Multipole $\mathbf{T}^k_q$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Multipole $\mathbf{T}^k_q$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

Asymmetric Top eigensolutions for J=1-2

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

$$\left\langle {}^{j}_{m}\right|\mathbf{R}(\alpha\beta\gamma)\left|{}^{j}_{n}\right\rangle = D^{j}_{m,n}(\alpha\beta\gamma) = \sqrt{(j+n)!(j-n)!}\sqrt{(j+m)!(j-m)!}\,\frac{\sum_k (-1)^k \left(\cos\frac{\beta}{2}\right)^{2j+m-n-2k}\left(\sin\frac{\beta}{2}\right)^{n-m+2k} e^{-i(m\alpha+n\gamma)}}{(j+m-k)!(n-m+k)!k!(j-n-k)!}$$

Vector ($j=\ell=1$) representation

$$D^1(\alpha\beta\gamma)=\begin{pmatrix} e^{-i\alpha} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\alpha}\end{pmatrix}\begin{pmatrix} \frac{1+\cos\beta}{2} & \frac{-\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2}\end{pmatrix}\begin{pmatrix} e^{-i\gamma} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\gamma}\end{pmatrix} = \begin{pmatrix} e^{-i\alpha}\frac{1+\cos\beta}{2}e^{-i\gamma} & e^{-i\alpha}\frac{-\sin\beta}{\sqrt{2}} & e^{-i\alpha}\frac{1-\cos\beta}{2}e^{i\gamma} \\ \frac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\frac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\frac{1+\cos\beta}{2}e^{i\gamma}\end{pmatrix}$$

Notation Switch:
azimuth angle:
$\alpha\rightarrow\phi$
polar angle:
$\beta\rightarrow\theta$

Here half-angle identities were used. $\cos^2\frac{\beta}{2}=\frac{1+\cos\beta}{2}$, $\sin^2\frac{\beta}{2}=\frac{1-\cos\beta}{2}$, $\sin\frac{\beta}{2}\cos\frac{\beta}{2}=\frac{\sin\beta}{2}$,

$$Y_1^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}} = D^1_{1,0}(\phi,\theta)$$

$$Y_0^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,\cos\beta = D^1_{0,0}(\phi,\theta)$$

$$Y_{-1}^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,e^{+i\phi}\frac{\sin\theta}{\sqrt{2}} = D^1_{-1,0}(\phi,\theta)$$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

$$\left\langle {}^{j}_{m}\right|\mathbf{R}(\alpha\beta\gamma)\left|{}^{j}_{n}\right\rangle = D^{j}_{m,n}(\alpha\beta\gamma) = \sqrt{(j+n)!(j-n)!}\sqrt{(j+m)!(j-m)!}\,\frac{\sum_k (-1)^k \left(\cos\frac{\beta}{2}\right)^{2j+m-n-2k}\left(\sin\frac{\beta}{2}\right)^{n-m+2k} e^{-i(m\alpha+n\gamma)}}{(j+m-k)!(n-m+k)!k!(j-n-k)!}$$

Vector ($j=\ell=1$) representation

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$$Y_1^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}}=D^1_{1,0}(\phi,\theta)$$

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$$Y_{-1}^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,e^{+i\phi}\frac{\sin\theta}{\sqrt{2}}=D^1_{-1,0}(\phi,\theta)$$

Center ($n=0$) column with the factor $\sqrt{\frac{2\ell+1}{4\pi}}$ gives set of *spherical harmonics* Y^{ℓ}_{m}.

$$Y^{\ell}_{m}(\phi\theta)=D^{\ell*}_{m,n=0}(\phi\theta 0)\sqrt{\frac{2\ell+1}{4\pi}}$$

Dipole ($j=\ell=1$) wavefunctions

$$D^{1*}_{1,0}(\phi\theta 0)=-e^{i\phi}\frac{\sin\theta}{\sqrt{2}}=-\frac{\cos\phi\sin\theta+i\cos\phi\sin\theta}{\sqrt{2}}=-\frac{x+iy}{r\sqrt{2}}$$

$$D^{1*}_{0,0}(\phi\theta 0)=\cos\theta=\cos\theta=z/r$$

$$D^{1*}_{-1,0}(\phi\theta 0)=e^{-i\phi}\frac{\sin\theta}{\sqrt{2}}=\frac{\cos\phi\sin\theta-i\cos\phi\sin\theta}{\sqrt{2}}=\frac{x-iy}{r\sqrt{2}}$$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

$$\left\langle {j \atop m}\right|\mathbf{R}(\alpha\beta\gamma)\left|{j \atop n}\right\rangle = D^j_{m,n}(\alpha\beta\gamma) = \sqrt{(j+n)!(j-n)!}\sqrt{(j+m)!(j-m)!}\,\frac{\sum_k (-1)^k \left(\cos\frac{\beta}{2}\right)^{2j+m-n-2k}\left(\sin\frac{\beta}{2}\right)^{n-m+2k} e^{-i(m\alpha+n\gamma)}}{(j+m-k)!(n-m+k)!k!(j-n-k)!}$$

Vector ($j=\ell=1$) representation

$$D^1(\alpha\beta\gamma)=\begin{pmatrix} e^{-i\alpha} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\alpha}\end{pmatrix}\begin{pmatrix} \frac{1+\cos\beta}{2} & \frac{-\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2}\end{pmatrix}\begin{pmatrix} e^{-i\gamma} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\gamma}\end{pmatrix} = \begin{pmatrix} e^{-i\alpha}\frac{1+\cos\beta}{2}e^{-i\gamma} & e^{-i\alpha}\frac{-\sin\beta}{\sqrt{2}} & e^{-i\alpha}\frac{1-\cos\beta}{2}e^{i\gamma} \\ \frac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\frac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\frac{1+\cos\beta}{2}e^{i\gamma}\end{pmatrix}$$

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Center ($n=0$) column with the factor $\sqrt{\frac{2\ell+1}{4\pi}}$ gives set of *spherical harmonics* Y^ℓ_m.

$$Y^\ell_m(\phi\theta) = D^{\ell*}_{m,n=0}(\phi\theta 0)\sqrt{\frac{2\ell+1}{4\pi}}$$

Dipole ($j=\ell=1$) wave functions

$$D^{1*}_{1,0}(\phi\theta 0) = -e^{i\phi}\frac{\sin\theta}{\sqrt{2}} = -\frac{\cos\phi\sin\theta + i\cos\phi\sin\theta}{\sqrt{2}} = -\frac{x+iy}{r\sqrt{2}}$$

$$D^{1*}_{0,0}(\phi\theta 0) = \cos\theta = \cos\theta = z/r$$

$$D^{1*}_{-1,0}(\phi\theta 0) = e^{-i\phi}\frac{\sin\theta}{\sqrt{2}} = \frac{\cos\phi\sin\theta - i\cos\phi\sin\theta}{\sqrt{2}} = \frac{x-iy}{r\sqrt{2}}$$

3-D linear-circular polarization T-matrix:

$$\begin{pmatrix} \left\langle {1 \atop 1}\middle|{1 \atop x}\right\rangle & \left\langle {1 \atop 1}\middle|{1 \atop y}\right\rangle & \left\langle {1 \atop 1}\middle|{1 \atop z}\right\rangle \\ \left\langle {1 \atop 0}\middle|{1 \atop x}\right\rangle & \left\langle {1 \atop 0}\middle|{1 \atop y}\right\rangle & \left\langle {1 \atop 0}\middle|{1 \atop z}\right\rangle \\ \left\langle {1 \atop -1}\middle|{1 \atop x}\right\rangle & \left\langle {1 \atop -1}\middle|{1 \atop y}\right\rangle & \left\langle {1 \atop -1}\middle|{1 \atop z}\right\rangle \end{pmatrix} = \begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \end{pmatrix}$$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

$$\left\langle {j \atop m}\right|\mathbf{R}(\alpha\beta\gamma)\left|{j \atop n}\right\rangle = D^{j}_{m,n}(\alpha\beta\gamma) = \sqrt{(j+n)!(j-n)!}\sqrt{(j+m)!(j-m)!}\,\frac{\sum_k (-1)^k \left(\cos\frac{\beta}{2}\right)^{2j+m-n-2k}\left(\sin\frac{\beta}{2}\right)^{n-m+2k} e^{-i(m\alpha+n\gamma)}}{(j+m-k)!(n-m+k)!k!(j-n-k)!}$$

Vector ($j=\ell=1$) representation

$$D^1(\alpha\beta\gamma)=\begin{pmatrix} e^{-i\alpha} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\alpha}\end{pmatrix}\begin{pmatrix} \frac{1+\cos\beta}{2} & \frac{-\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2}\end{pmatrix}\begin{pmatrix} e^{-i\gamma} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\gamma}\end{pmatrix} = \begin{pmatrix} e^{-i\alpha}\frac{1+\cos\beta}{2}e^{-i\gamma} & e^{-i\alpha}\frac{-\sin\beta}{\sqrt{2}} & e^{-i\alpha}\frac{1-\cos\beta}{2}e^{i\gamma} \\ \frac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\frac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\frac{1+\cos\beta}{2}e^{i\gamma}\end{pmatrix}$$

Notation Switch:
azimuth angle: $\alpha\to\phi$
polar angle: $\beta\to\theta$

Here half-angle identities were used. $\cos^2\frac{\beta}{2}=\frac{1+\cos\beta}{2}$, $\sin^2\frac{\beta}{2}=\frac{1-\cos\beta}{2}$, $\sin\frac{\beta}{2}\cos\frac{\beta}{2}=\frac{\sin\beta}{2}$,

$$Y^{1*}_{1}(\phi,\theta)=\sqrt{\frac{3}{4\pi}}\,e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}} = D^1_{1,0}(\phi,\theta)$$

$$Y^{1*}_{0}(\phi,\theta)=\sqrt{\frac{3}{4\pi}}\,\cos\beta = D^1_{0,0}(\phi,\theta)$$

$$Y^{1*}_{-1}(\phi,\theta)=\sqrt{\frac{3}{4\pi}}\,e^{+i\phi}\frac{\sin\theta}{\sqrt{2}} = D^1_{-1,0}(\phi,\theta)$$

Center ($n=0$) column with the factor $\sqrt{\frac{2\ell+1}{4\pi}}$ gives set of *spherical harmonics* Y^{ℓ}_{m}.

$$Y^{\ell}_{m}(\phi\theta) = D^{\ell*}_{m,n=0}(\phi\theta 0)\sqrt{\frac{2\ell+1}{4\pi}}$$

Dipole ($j=\ell=1$) wave functions

$$D^{1*}_{1,0}(\phi\theta 0) = -e^{i\phi}\frac{\sin\theta}{\sqrt{2}} = -\frac{\cos\phi\sin\theta + i\cos\phi\sin\theta}{\sqrt{2}} = -\frac{x+iy}{r\sqrt{2}}$$

$$D^{1*}_{0,0}(\phi\theta 0) = \cos\theta = \cos\theta = z/r$$

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3-D linear-circular polarization T-matrix:

$$\begin{pmatrix} \left\langle {1 \atop 1}\middle|{1 \atop x}\right\rangle & \left\langle {1 \atop 1}\middle|{1 \atop y}\right\rangle & \left\langle {1 \atop 1}\middle|{1 \atop z}\right\rangle \\ \left\langle {1 \atop 0}\middle|{1 \atop x}\right\rangle & \left\langle {1 \atop 0}\middle|{1 \atop y}\right\rangle & \left\langle {1 \atop 0}\middle|{1 \atop z}\right\rangle \\ \left\langle {1 \atop -1}\middle|{1 \atop x}\right\rangle & \left\langle {1 \atop -1}\middle|{1 \atop y}\right\rangle & \left\langle {1 \atop -1}\middle|{1 \atop z}\right\rangle \end{pmatrix} = \begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \end{pmatrix}$$

Applying T-matrix:

$$\begin{pmatrix} \frac{-1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix}\cdot\begin{pmatrix} \frac{1+\cos\beta}{2} & \frac{-\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2}\end{pmatrix}\cdot\begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \end{pmatrix} = \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \sin\beta \end{pmatrix}$$

$$\begin{pmatrix} \frac{-1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix}\cdot\begin{pmatrix} e^{-i\alpha} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\alpha}\end{pmatrix}\cdot\begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} D^1_{x,x}(\alpha\beta\gamma) & D^1_{x,y} & D^1_{x,z} \\ D^1_{y,x} & D^1_{y,y} & D^1_{y,z} \\ D^1_{z,x} & D^1_{z,y} & D^1_{z,z} \end{pmatrix} =$$

$$\begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & \cos\alpha\sin\beta \\ \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\alpha\sin\beta \\ -\cos\gamma\sin\beta & \sin\gamma\sin\beta & \cos\beta \end{pmatrix}$$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

Vector ($j=\ell=1$) representation

$$D^1(\alpha\beta\gamma)=\begin{pmatrix} e^{-i\alpha} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\alpha}\end{pmatrix}\begin{pmatrix} \frac{1+\cos\beta}{2} & \frac{-\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2}\end{pmatrix}\begin{pmatrix} e^{-i\gamma} & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & e^{i\gamma}\end{pmatrix}=\begin{pmatrix} e^{-i\alpha}\frac{1+\cos\beta}{2}e^{-i\gamma} & e^{-i\alpha}\frac{-\sin\beta}{\sqrt{2}} & e^{-i\alpha}\frac{1-\cos\beta}{2}e^{i\gamma} \\ \frac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & \frac{-\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\frac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\frac{1+\cos\beta}{2}e^{i\gamma}\end{pmatrix}$$

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Here half-angle identities were used. $\cos^2\frac{\beta}{2}=\frac{1+\cos\beta}{2}$, $\sin^2\frac{\beta}{2}=\frac{1-\cos\beta}{2}$, $\sin\frac{\beta}{2}\cos\frac{\beta}{2}=\frac{\sin\beta}{2}$,

$$Y_1^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}}=D^1_{1,0}(\phi,\theta)$$

$$Y_0^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\cos\beta=D^1_{0,0}(\phi,\theta)$$

$$Y_{-1}^{1*}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\,e^{+i\phi}\frac{\sin\theta}{\sqrt{2}}=D^1_{-1,0}(\phi,\theta)$$

Center ($n=0$) column with the factor $\sqrt{\frac{2\ell+1}{4\pi}}$ gives set of *spherical harmonics* Y^ℓ_m.

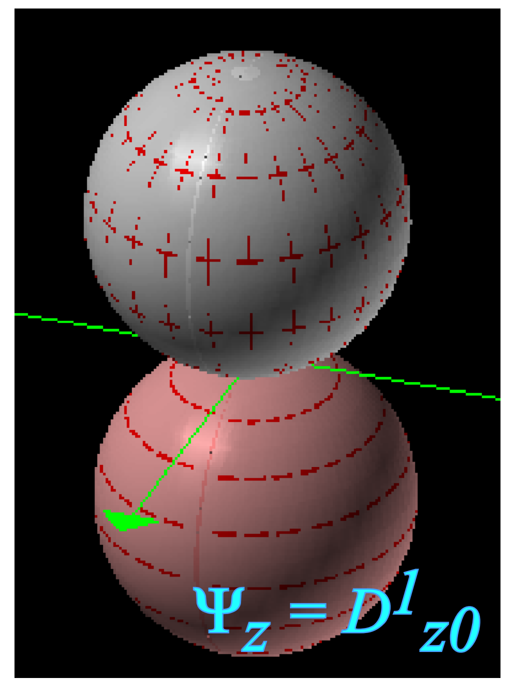
$$Y^\ell_m(\phi\theta)=D^{\ell*}_{m,n=0}(\phi\theta 0)\sqrt{\frac{2\ell+1}{4\pi}}$$

Dipole ($j=\ell=1$) wave functions

$$D^{1*}_{1,0}(\phi\theta 0)=-e^{i\phi}\frac{\sin\theta}{\sqrt{2}}=-\frac{\cos\phi\sin\theta+i\cos\phi\sin\theta}{\sqrt{2}}=-\frac{x+iy}{r\sqrt{2}}$$

$$D^{1*}_{0,0}(\phi\theta 0)=\cos\theta=\cos\theta=z/r$$

$$D^{1*}_{-1,0}(\phi\theta 0)=e^{-i\phi}\frac{\sin\theta}{\sqrt{2}}=\frac{\cos\phi\sin\theta-i\cos\phi\sin\theta}{\sqrt{2}}=\frac{x-iy}{r\sqrt{2}}$$

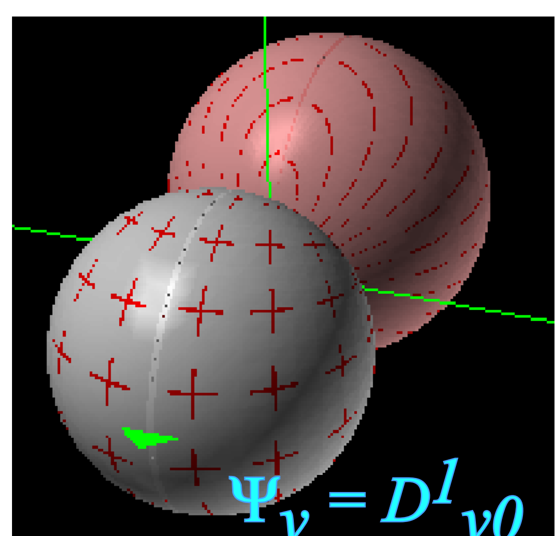


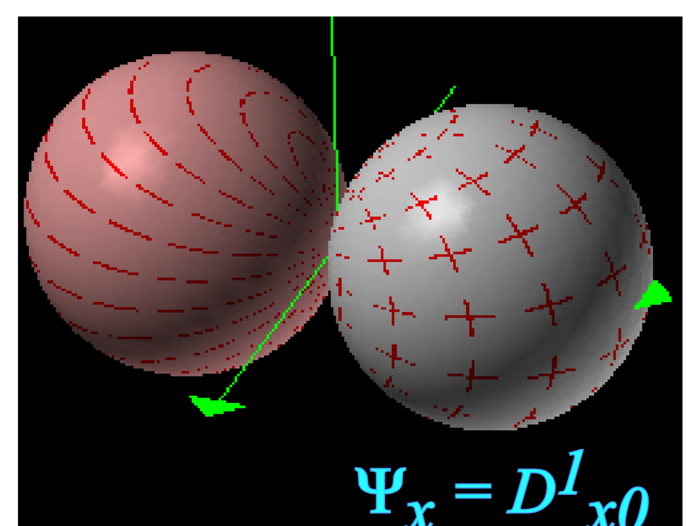
j = 1
Standing
p-Waves

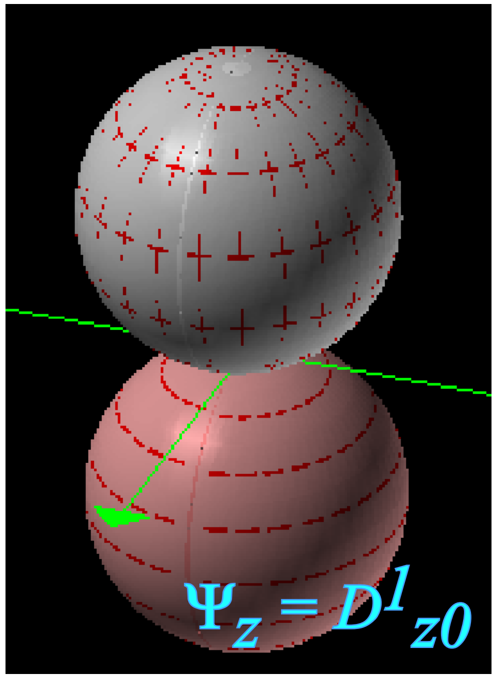
$$\Psi^1_x(\phi,\theta)=D^1_{x,z}(\phi,\theta,0)=\cos\phi\sin\theta$$

$$\Psi^1_y(\phi,\theta)=D^1_{y,z}(\phi,\theta,0)=\sin\phi\sin\theta$$

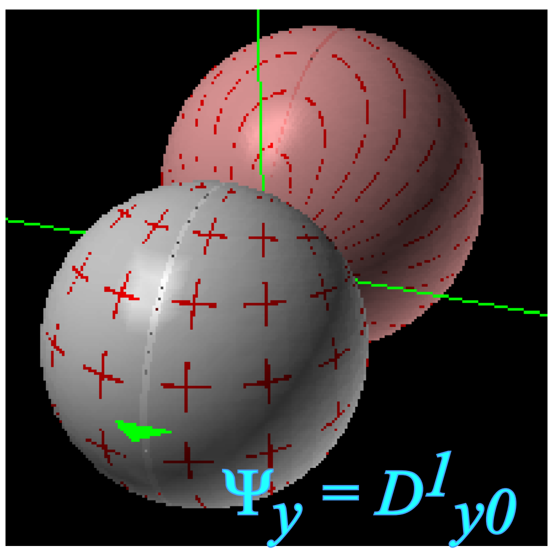
$$\Psi^1_z(\phi,\theta)=D^1_{z,z}(\phi,\theta,0)=\cos\theta$$

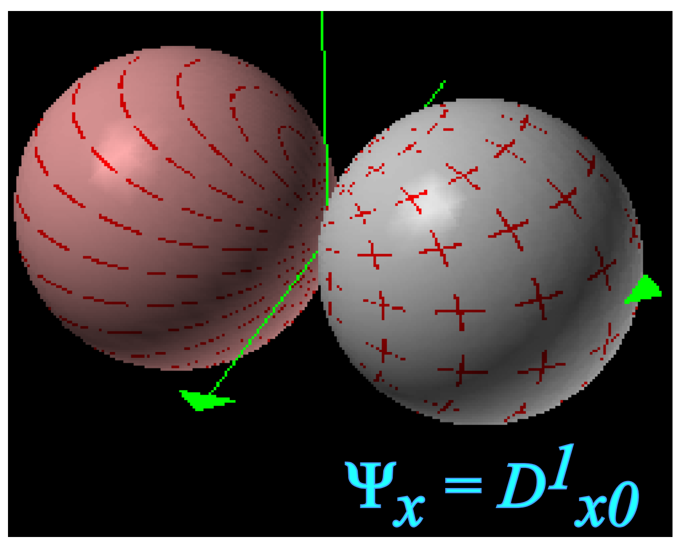






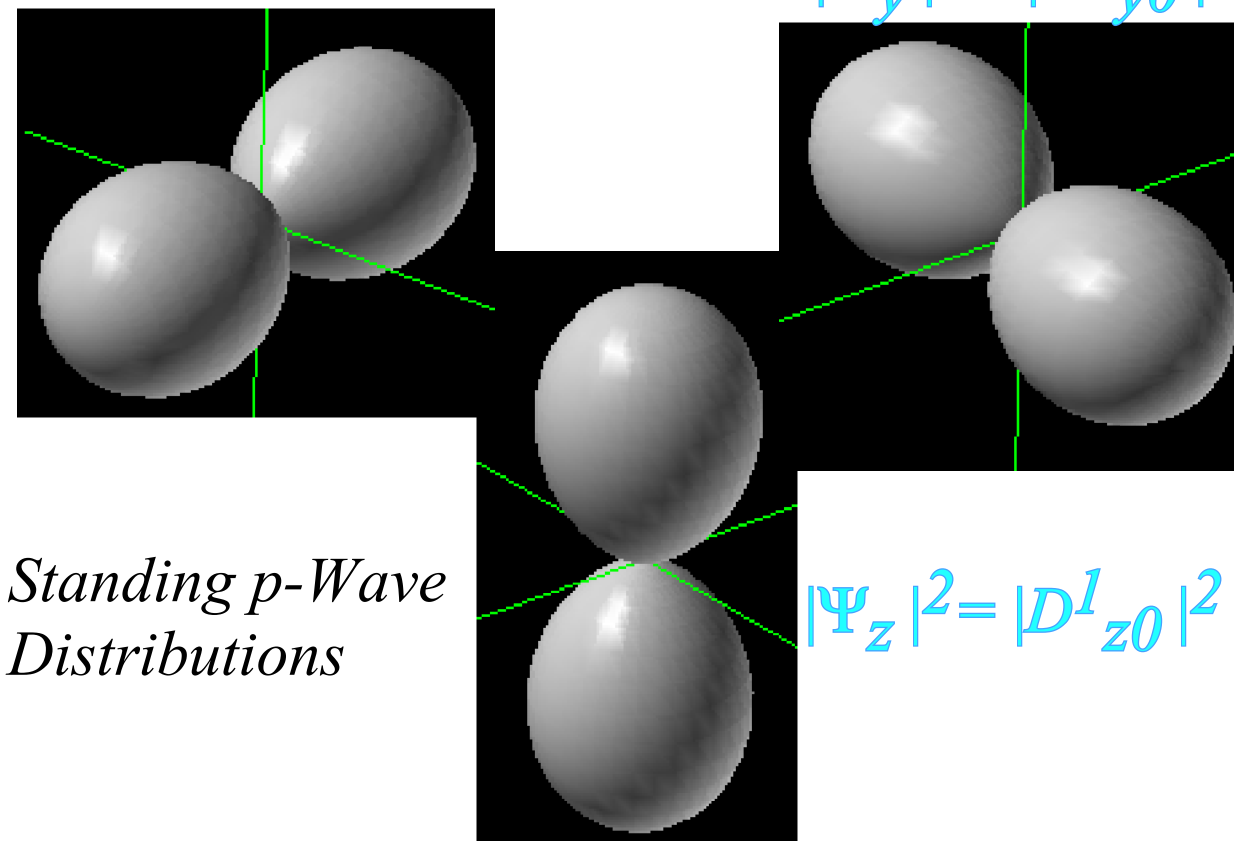
j = 1
Standing
p-Waves





$$\Psi^1_x(\phi,\theta) = D^1_{x,z}(\phi,\theta,0)$$
$$= \cos\phi\sin\theta$$
$$\Psi^1_y(\phi,\theta) = D^1_{y,z}(\phi,\theta,0)$$
$$= \sin\phi\sin\theta$$
$$\Psi^1_z(\phi,\theta) = D^1_{z,z}(\phi,\theta,0)$$
$$= \cos\theta$$

$|\Psi_x|^2 = |D^1_{x0}|^2$ $|\Psi_y|^2 = |D^1_{y0}|^2$

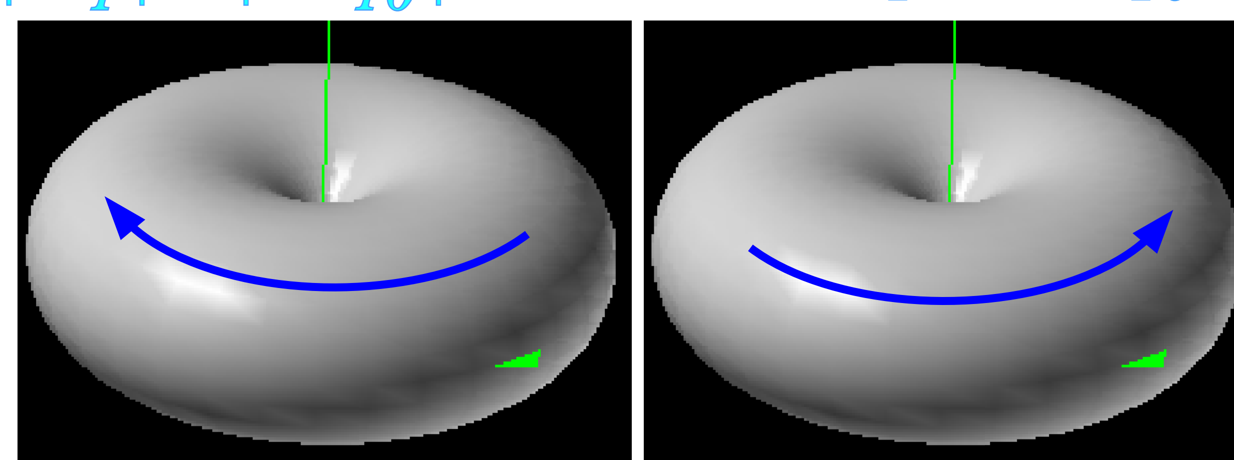


Standing p-Wave Distributions

$|\Psi_z|^2 = |D^1_{z0}|^2$

Moving p-Wave Distributions

$|\Psi_{-1}|^2 = |D^1_{-10}|^2$ $|\Psi_1|^2 = |D^1_{10}|^2$



1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

Tensor ($j=\ell=2$) representation

$$D^2(\alpha\beta 0)=\left(\begin{array}{cc|c|cc}
e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)^2 & e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & \sqrt{\frac{3}{8}}e^{-i2\alpha}\sin^2\beta & e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{-i2\alpha}\left(\frac{1-\cos\beta}{2}\right)^2 \\
e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)(2\cos\beta-1) & -\sqrt{\frac{3}{2}}e^{-i\alpha}\sin\beta\cos\beta & e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)(2\cos\beta+1) & -e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta \\
\sqrt{\frac{3}{8}}\sin^2\beta & \sqrt{\frac{3}{2}}\sin\beta\cos\beta & \frac{3\cos^2\beta-1}{2} & \sqrt{\frac{3}{2}}\sin\beta\cos\beta & \sqrt{\frac{3}{8}}\sin^2\beta \\
e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{i\alpha}\left(\frac{1-\cos\beta}{2}\right)(2\cos\beta+1) & \sqrt{\frac{3}{2}}e^{i\alpha}\sin\beta\cos\beta & e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)(2\cos\beta-1) & -e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta \\
e^{i2\alpha}\left(\frac{1-\cos\beta}{2}\right)^2 & e^{i2\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta & \sqrt{\frac{3}{8}}e^{i2\alpha}\sin^2\beta & e^{i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{i2\alpha}\left(\frac{1+\cos\beta}{2}\right)^2
\end{array}\right)$$

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Tensor ($j=\ell=2$) representation

$$D^2(\alpha\beta 0)=\left(\begin{array}{cc|c|cc}
e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)^2 & e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & \sqrt{\frac{3}{8}}e^{-i2\alpha}\sin^2\beta & e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{-i2\alpha}\left(\frac{1-\cos\beta}{2}\right)^2 \\
e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)(2\cos\beta-1) & -\sqrt{\frac{3}{2}}e^{-i\alpha}\sin\beta\cos\beta & e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)(2\cos\beta+1) & -e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta \\
\sqrt{\frac{3}{8}}\sin^2\beta & \sqrt{\frac{3}{2}}\sin\beta\cos\beta & \frac{3\cos^2\beta-1}{2} & \sqrt{\frac{3}{2}}\sin\beta\cos\beta & \sqrt{\frac{3}{8}}\sin^2\beta \\
e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{i\alpha}\left(\frac{1-\cos\beta}{2}\right)(2\cos\beta+1) & \sqrt{\frac{3}{2}}e^{i\alpha}\sin\beta\cos\beta & e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)(2\cos\beta-1) & -e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta \\
e^{i2\alpha}\left(\frac{1-\cos\beta}{2}\right)^2 & e^{i2\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta & \sqrt{\frac{3}{8}}e^{i2\alpha}\sin^2\beta & e^{i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{i2\alpha}\left(\frac{1+\cos\beta}{2}\right)^2
\end{array}\right)$$

Spherical 2^k*-multipole functions* X^k_q or *X-functions* are *D**-functions times the k^{th} power of radius (r^k).

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=2}(\phi\theta) = D^{2*}_{2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}}e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x+iy)^2}{r^2}$$

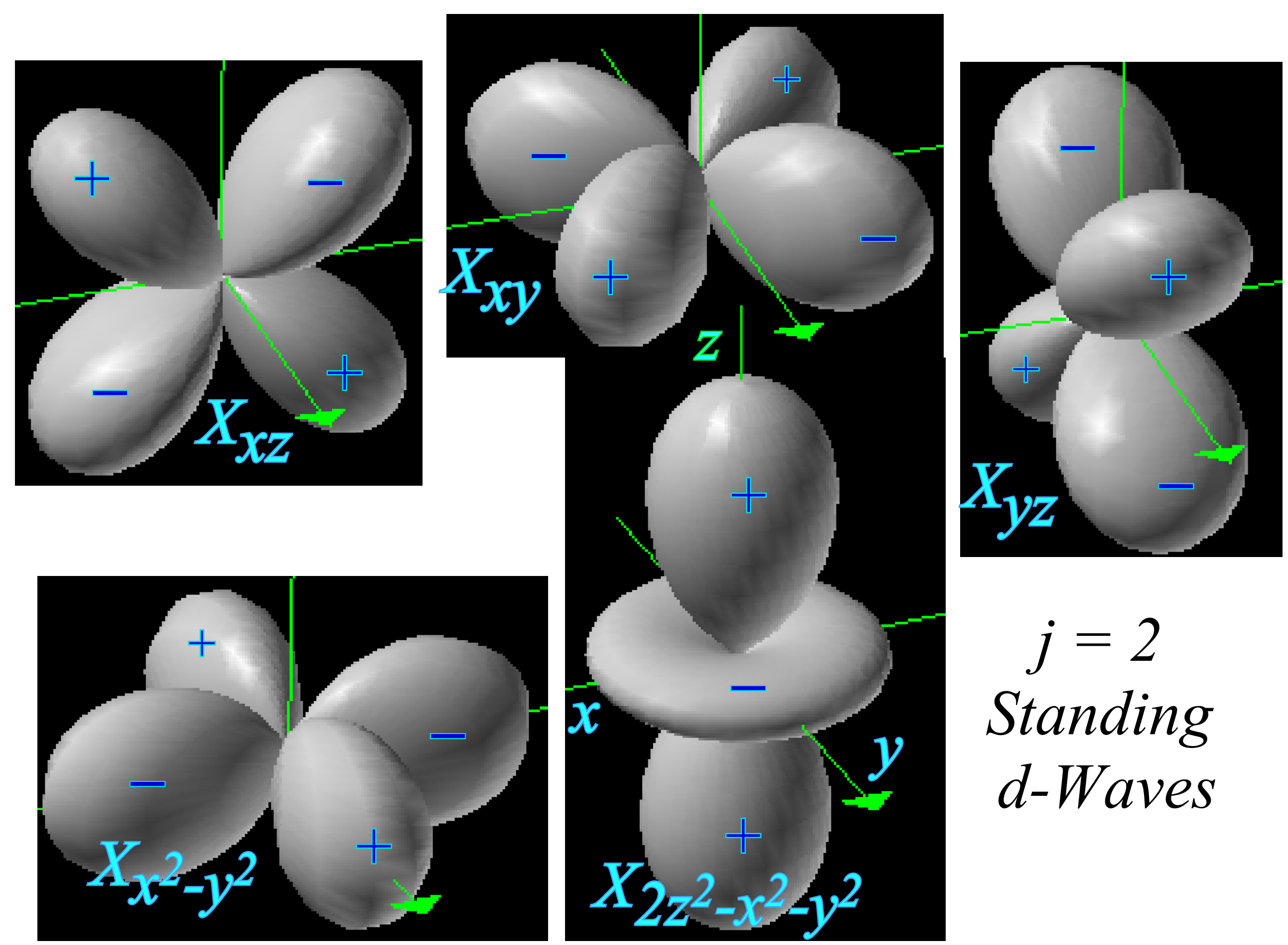
$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=1}(\phi\theta) = D^{2*}_{1,0}(\phi\theta 0) = -\sqrt{\frac{3}{2}}e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=0}(\phi\theta) = D^{2*}_{0,0}(\phi\theta 0) = \frac{3\cos^2\theta-1}{2} = \frac{3z^2-r^2}{2r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=-1}(\phi\theta) = D^{2*}_{-1,0}(\phi\theta 0) = \sqrt{\frac{3}{2}}e^{-i\phi}\sin\theta\cos\theta = \sqrt{\frac{3}{2}}\frac{(x-iy)z}{r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=-2}(\phi\theta) = D^{2*}_{-2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}}e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x-iy)^2}{r^2}$$

$$X^k_q = r^k D^{k*}_{q,0} = \sqrt{\frac{4\pi}{2k+1}}\,r^k Y^k_q$$



Notation Switch:

azimuth angle:

$\alpha\rightarrow\phi$

polar angle:

$\beta\rightarrow\theta$

1. *Atomic and molecular* $D^{J*}_{mn}(\alpha,\beta,\gamma)$*-wavefunctions*

Tensor ($j=\ell=2$) *representation*

Spherical 2^k*-multipole functions* X^k_q or *X-functions* are D^*-functions times the k^{th} power of radius (r^k).

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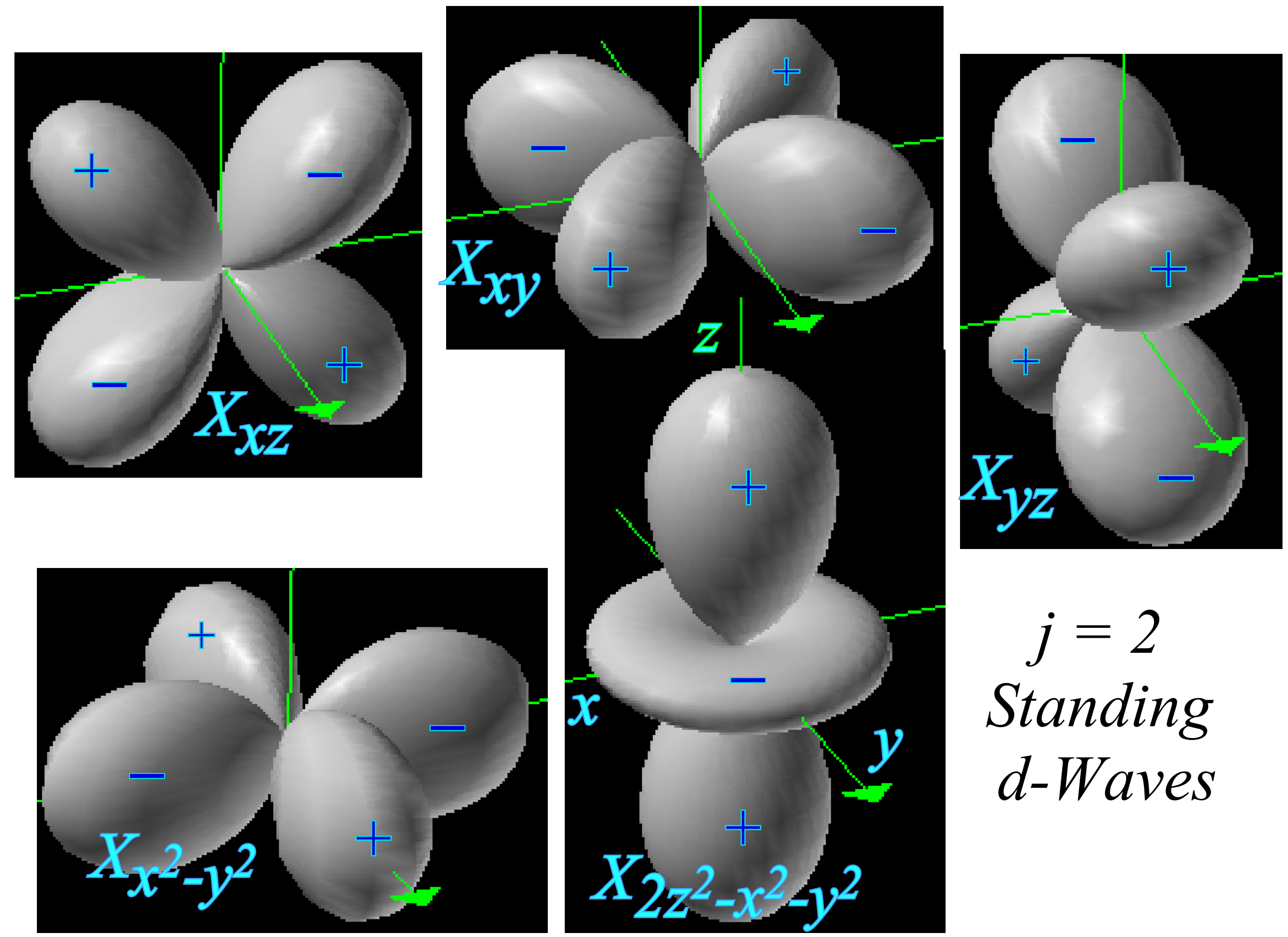
$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=1}(\phi\theta) = D^{2*}_{1,0}(\phi\theta 0) = -\sqrt{\frac{3}{2}}e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=0}(\phi\theta) = D^{2*}_{0,0}(\phi\theta 0) = \frac{3\cos^2\theta-1}{2} = \frac{3z^2-r^2}{2r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=-1}(\phi\theta) = D^{2*}_{-1,0}(\phi\theta 0) = \sqrt{\frac{3}{2}}e^{-i\phi}\sin\theta\cos\theta = \sqrt{\frac{3}{2}}\frac{(x-iy)z}{r^2}$$

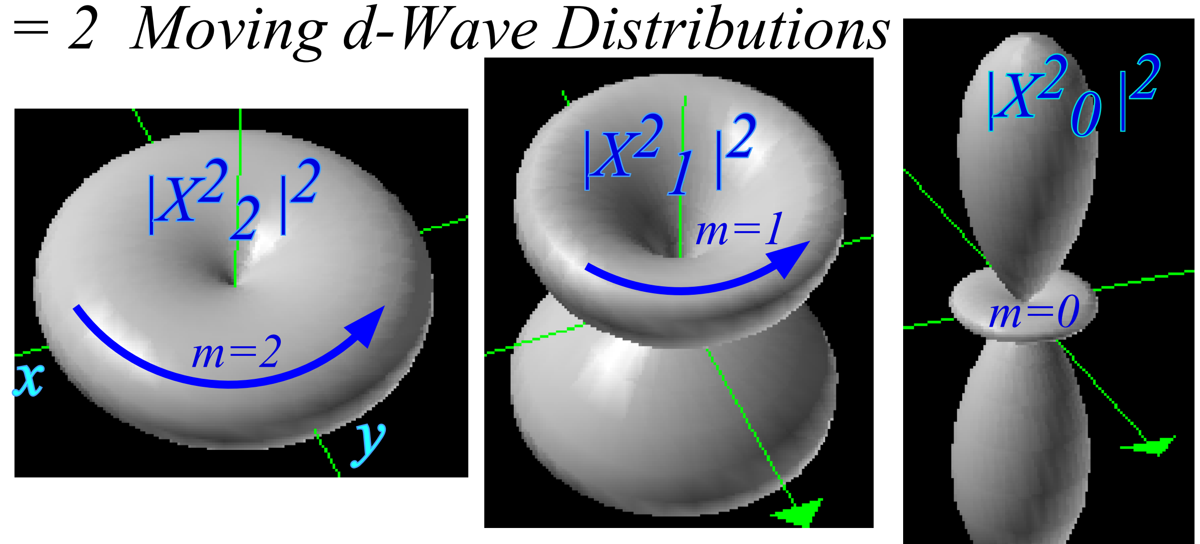
$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=-2}(\phi\theta) = D^{2*}_{-2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}}e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x-iy)^2}{r^2}$$

$$X^k_q = r^k D^{k*}_{q,0} = \sqrt{\frac{4\pi}{2k+1}}\,r^k Y^k_q$$



j = 2
Standing
d-Waves

j = 2 Moving d-Wave Distributions



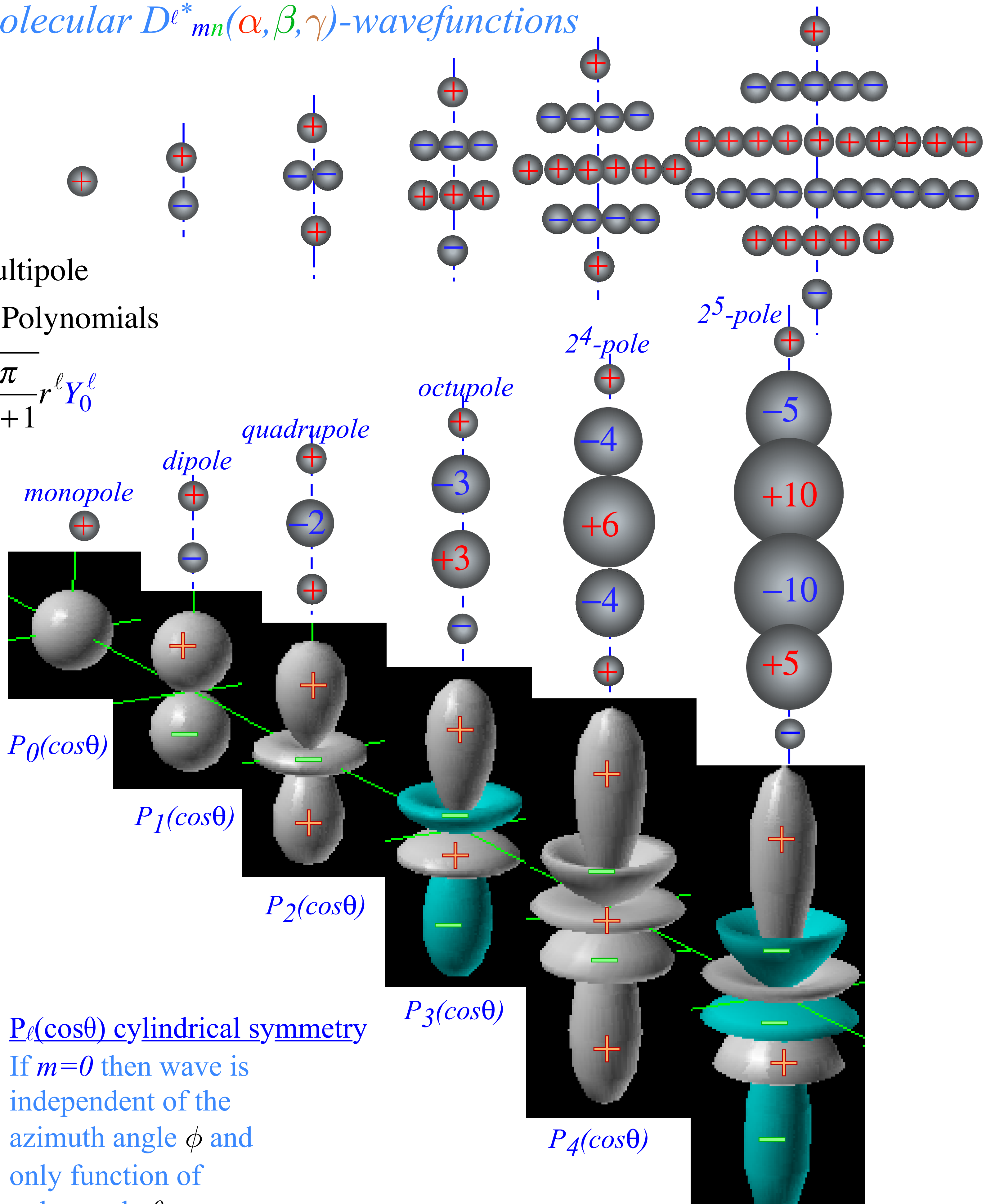
Notation Switch:
azimuth angle:
$\alpha \to \phi$
polar angle:
$\beta \to \theta$

1. Atomic and molecular $D^{\ell *}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

Legendre $P_\ell(\Theta)$ Multipole

Symmetric ($m = 0$) Polynomials

$$X^\ell_0 = r^\ell D^{\ell *}_{0,0} = \sqrt{\frac{4\pi}{2\ell+1}}\, r^\ell Y^\ell_0$$



Note
Pascal Triangle
of (+) and (-)
charges

Notation Switch:
azimuth angle:
$\alpha \to \phi$
polar angle:
$\beta \to \theta$

$P_\ell(\cos\theta)$ cylindrical symmetry

If $m=0$ then wave is independent of the azimuth angle ϕ and only function of polar angle θ.

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

Asymmetric Top eigensolutions for J=1-2

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

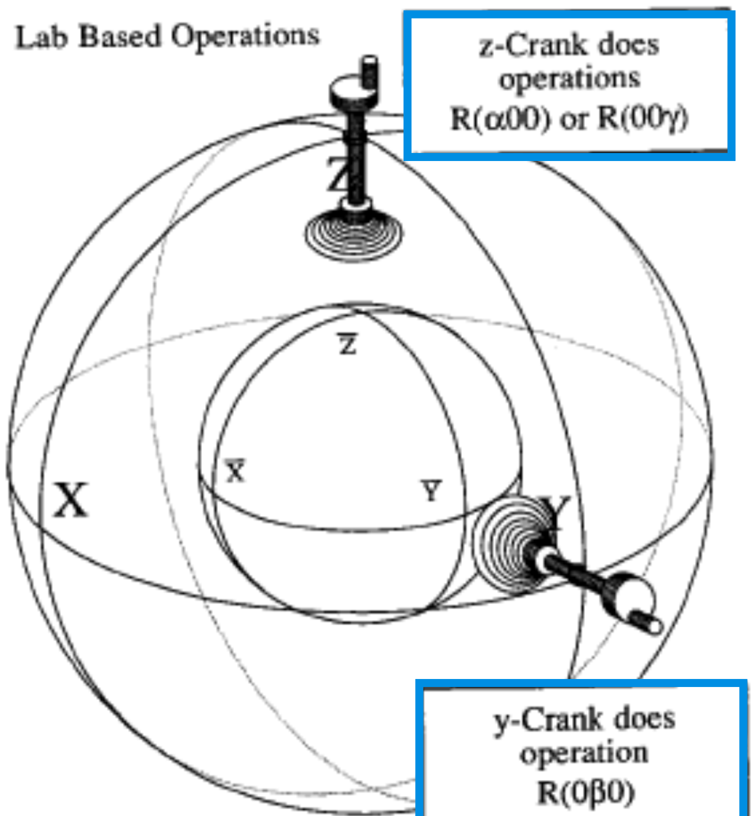
"Mock-Mach" lab-vs-body-defined states $|{}^{J}_{mn}\rangle = \mathbf{P}_{mn}^{J}|(0,0,0)\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|(0,0,0)\rangle$

From Lecture 14 p.47

"Give me a place to stand...
and I will move the Earth"
Archimedes 287-212 B.C.E

Ideas of duality/relativity go *way* back (...VanVleck, Casimir..., Mach, Newton, Archimedes...)

Lab-fixed(Extrinsic-Global)**R**,**S**,..*vs.* Body-fixed (Intrinsic-Local)$\bar{\mathbf{R}}$,$\bar{\mathbf{S}}$,..



all **R**,**S**,..
commute with
all $\bar{\mathbf{R}}$,$\bar{\mathbf{S}}$,..

"Mock-Mach" relativity principles

$$\mathbf{R}|1\rangle = \bar{\mathbf{R}}^{-1}|1\rangle$$
$$\mathbf{S}|1\rangle = \bar{\mathbf{S}}^{-1}|1\rangle$$
$$\vdots$$

...for *one* state |1) *only!*

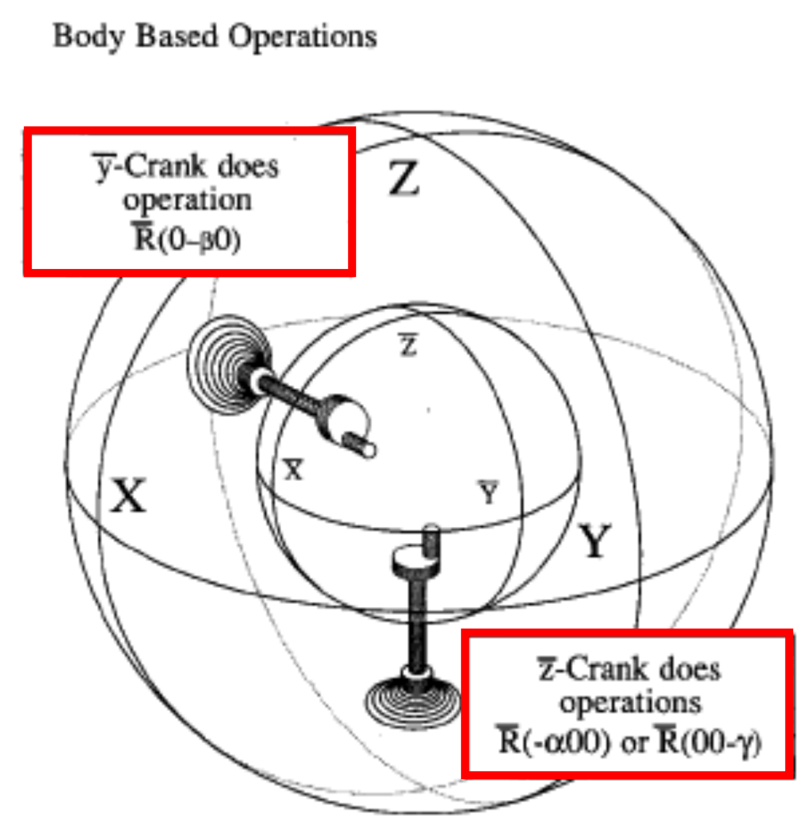


Figure from Ch. 5 of PSDS (Originally in Rev. Mod. Phys. 50, 1, p. 37-83 (1978) Fig. 2)

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $\left|{}^{J}_{mn}\right\rangle = \mathbf{P}_{mn}^{J}\left|(0,0,0)\right\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)\left|(0,0,0)\right\rangle$

For *SU(2)* and *R(3)*, sum over rotations is an integral over Euler angles *(αβγ)*.

For integral-*j=0, 1, 2,..* the *R(3)* integral over polar angle β ranges from 0 to π.

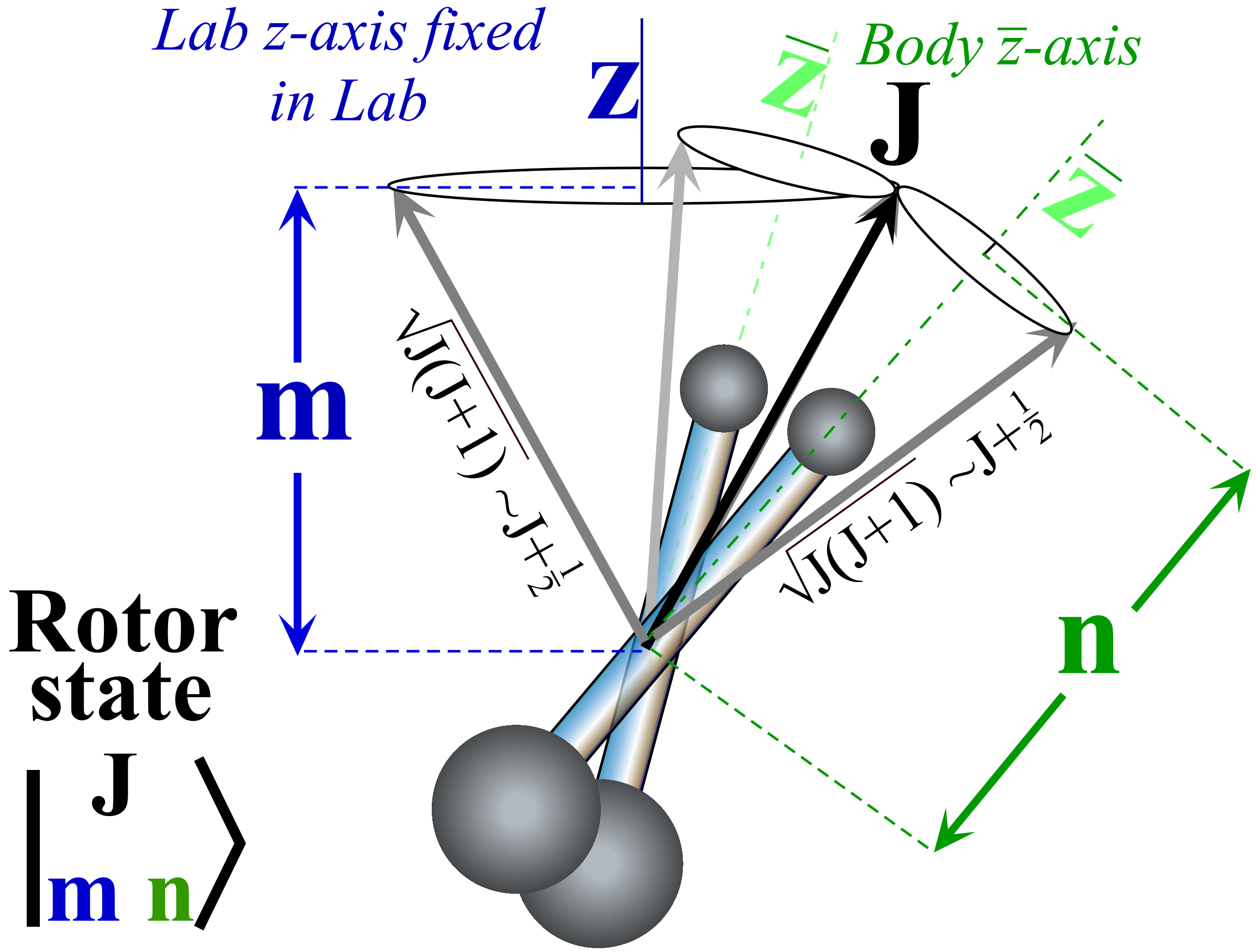
$$\text{for } R(3): \frac{\ell^j}{N}\int d(\alpha\beta\gamma) = \frac{2j+1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma = 2j+1 = \ell^j$$

For integral-*j=1/2, 3/2,..* the *U(2)* integral over polar angle β ranges from -π to π.

$$\text{for } SU(2): \frac{\ell^j}{N}\int d(\alpha\beta\gamma) = \frac{2j+1}{16\pi^2}\int_0^{2\pi} d\alpha \int_{-\pi}^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma = 2j+1 = \ell^j$$

Eigenstates of angular momentum are built from projected initial position states |000⟩.

$$\left|{}^{j}_{m,n}\right\rangle = \frac{\mathbf{P}^{j}_{m,n}\left|000\right\rangle}{\sqrt{\ell^j}} = \frac{1}{N}\int d(\alpha\beta\gamma) D^{j*}_{m,n}(\alpha\beta\gamma)\mathbf{R}(\alpha\beta\gamma)\left|000\right\rangle\sqrt{\ell^j} = \frac{1}{N}\int d(\alpha\beta\gamma) D^{j*}_{m,n}(\alpha\beta\gamma)\sqrt{\ell^j}\left|\alpha\beta\gamma\right\rangle$$



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General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

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Eigenstates of angular momentum are built from projected initial position states |000⟩.

$$\left|{}^{j}_{m,n}\right\rangle = \frac{\mathbf{P}^j_{m,n}|000\rangle}{\sqrt{\ell^j}} = \frac{1}{N}\int d(\alpha\beta\gamma) D^{j*}_{m,n}(\alpha\beta\gamma)\mathbf{R}(\alpha\beta\gamma)|000\rangle\sqrt{\ell^j} = \frac{1}{N}\int d(\alpha\beta\gamma) D^{j*}_{m,n}(\alpha\beta\gamma)\sqrt{\ell^j}|\alpha\beta\gamma\rangle$$

2. R(3) rotation and U(2) unitary $D^{J}_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|{}^{J}_{mn}\rangle = \Sigma_{m'} D^{J}_{m'n}(\alpha,\beta,\gamma)|{}^{J}_{m'n}\rangle$

Angular position is defined by a *rotational duality relativity relation* or "Mock-Mach" principle

$$\mathbf{R}(\alpha\beta\gamma)|000\rangle = |\alpha\beta\gamma\rangle = \bar{\mathbf{R}}^{\dagger}(\alpha\beta\gamma)|000\rangle \qquad \text{for all } (\alpha\beta\gamma) \text{ and } (\alpha'\beta'\gamma') \qquad \mathbf{R}(\alpha\beta\gamma)\bar{\mathbf{R}}(\alpha'\beta'\gamma') = \bar{\mathbf{R}}(\alpha'\beta'\gamma')\mathbf{R}(\alpha\beta\gamma)$$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|{}^J_{mn}\rangle = \mathbf{P}_{mn}{}^J|(0,0,0)\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|(0,0,0)\rangle$

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$$\text{for } SU(2): \frac{\ell^j}{N}\int d(\alpha\beta\gamma) = \frac{2j+1}{16\pi^2}\int_0^{2\pi} d\alpha \int_{-\pi}^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma = 2j+1 = \ell^j$$

Eigenstates of angular momentum are built from projected initial position states |000⟩.

$$\left|{}^j_{m,n}\right\rangle = \frac{\mathbf{P}^j_{m,n}|000\rangle}{\sqrt{\ell^j}} = \frac{1}{N}\int d(\alpha\beta\gamma) D^{j*}_{m,n}(\alpha\beta\gamma)\mathbf{R}(\alpha\beta\gamma)|000\rangle\sqrt{\ell^j} = \frac{1}{N}\int d(\alpha\beta\gamma) D^{j*}_{m,n}(\alpha\beta\gamma)\sqrt{\ell^j}|\alpha\beta\gamma\rangle$$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|{}^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|{}^J_{m'n}\rangle$

Angular position is defined by a *rotational duality relativity relation* or "Mock-Mach" principle

$$\mathbf{R}(\alpha\beta\gamma)|000\rangle = |\alpha\beta\gamma\rangle = \bar{\mathbf{R}}^\dagger(\alpha\beta\gamma)|000\rangle \qquad \text{for all } (\alpha\beta\gamma) \text{ and } (\alpha'\beta'\gamma') \qquad \mathbf{R}(\alpha\beta\gamma)\bar{\mathbf{R}}(\alpha'\beta'\gamma') = \bar{\mathbf{R}}(\alpha'\beta'\gamma')\mathbf{R}(\alpha\beta\gamma)$$

Left hand (LAB-*m*) and right hand (BODY-*n*) quantum numbers apply in turn.

LAB $m \leftrightarrow m'$ *transform*

$$\mathbf{R}(\alpha\beta\gamma)\left|{}^j_{m,n}\right\rangle = \sum_{m'=-j}^{j} D^j_{m',n}(\alpha\beta\gamma)\left|{}^j_{m',n}\right\rangle$$

BOD $n \leftrightarrow n'$ *transform*

$$\bar{\mathbf{R}}(\alpha\beta\gamma)\left|{}^j_{m,n}\right\rangle = \sum_{n'=-j}^{j} D^{j*}_{n',n}(\alpha\beta\gamma)\left|{}^j_{m,n'}\right\rangle$$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J |_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

For *SU(2)* and *R(3)*, sum over rotations is an integral over Euler angles *(αβγ)*.

For integral-j=0, 1, 2,.. the *R(3)* integral over polar angle β ranges from 0 to π.

$$\text{for } R(3): \frac{\ell^j}{N}\int d(\alpha\beta\gamma) = \frac{2j+1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma = 2j+1 = \ell^j$$

For integral-j=1/2, 3/2,.. the *U(2)* integral over polar angle β ranges from -π to π.

$$\text{for } SU(2): \frac{\ell^j}{N}\int d(\alpha\beta\gamma) = \frac{2j+1}{16\pi^2}\int_0^{2\pi} d\alpha \int_{-\pi}^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma = 2j+1 = \ell^j$$

Eigenstates of angular momentum are built from projected initial position states |000⟩.

$$\left|{}^{j}_{m,n}\right\rangle = \frac{\mathbf{P}^j_{m,n}|000\rangle}{\sqrt{\ell^j}} = \frac{1}{N}\int d(\alpha\beta\gamma)\, D^{j*}_{m,n}(\alpha\beta\gamma)\mathbf{R}(\alpha\beta\gamma)|000\rangle\sqrt{\ell^j} = \frac{1}{N}\int d(\alpha\beta\gamma)\, D^{j*}_{m,n}(\alpha\beta\gamma)\sqrt{\ell^j}\,|\alpha\beta\gamma\rangle$$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}_{(\alpha,\beta,\gamma)}|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

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$$\mathbf{R}(\alpha\beta\gamma)|000\rangle = |\alpha\beta\gamma\rangle = \bar{\mathbf{R}}^\dagger(\alpha\beta\gamma)|000\rangle$$

for all $(\alpha\beta\gamma)$ and $(\alpha'\beta'\gamma')$

$$\mathbf{R}(\alpha\beta\gamma)\bar{\mathbf{R}}(\alpha'\beta'\gamma') = \bar{\mathbf{R}}(\alpha'\beta'\gamma')\mathbf{R}(\alpha\beta\gamma)$$

Left hand (LAB-m) and right hand (BODY-n) quantum numbers apply in turn.

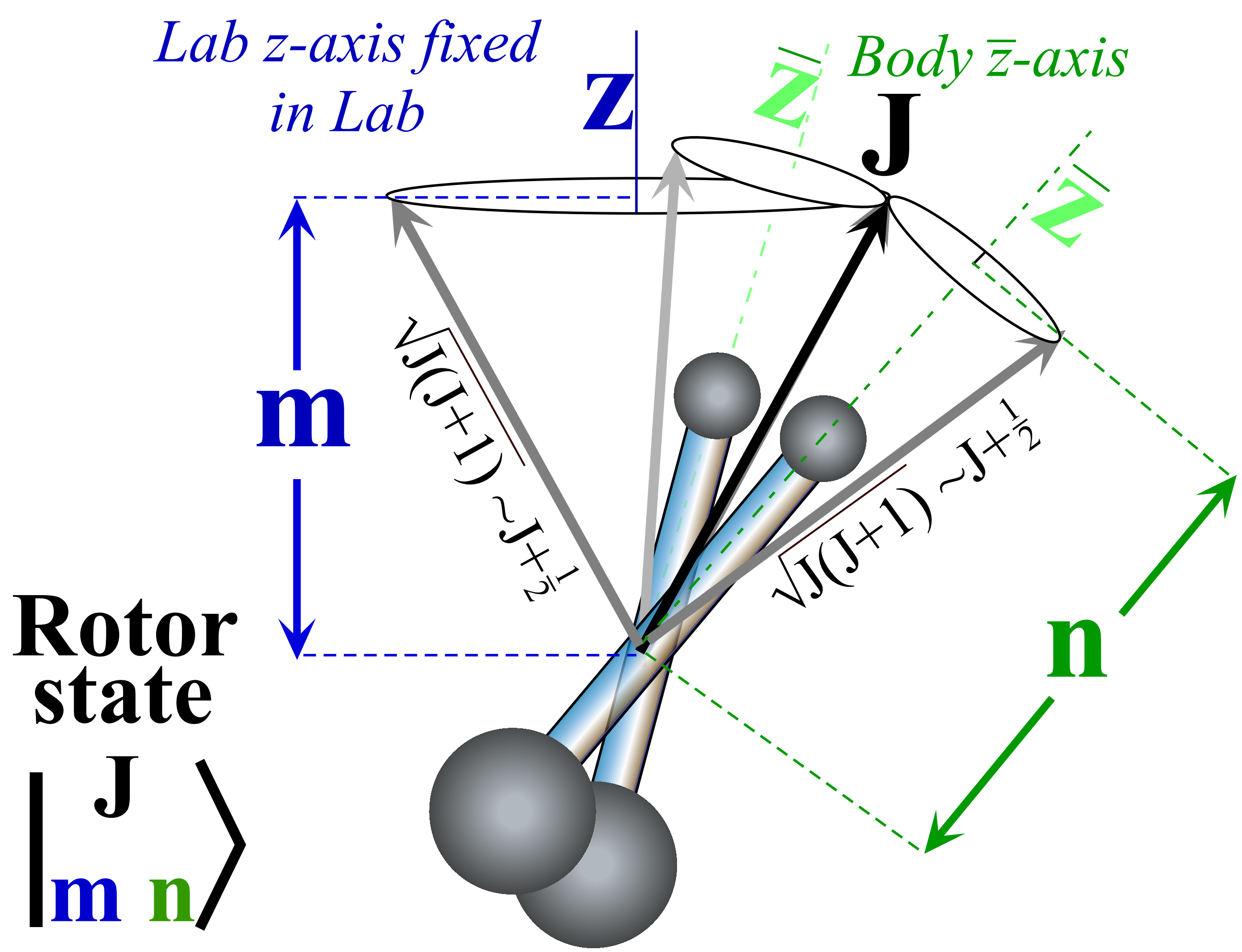
LAB $m \leftrightarrow m'$ *transform*
$$\mathbf{R}(\alpha\beta\gamma)\left|{}^{j}_{m,n}\right\rangle = \sum_{m'=-j}^{j} D^j_{m',n}(\alpha\beta\gamma)\left|{}^{j}_{m',n}\right\rangle$$

BOD $n \leftrightarrow n'$ *transform*
$$\bar{\mathbf{R}}(\alpha\beta\gamma)\left|{}^{j}_{m,n}\right\rangle = \sum_{n'=-j}^{j} D^{j*}_{n',n}(\alpha\beta\gamma)\left|{}^{j}_{m,n'}\right\rangle$$

Same applies to the generators $\mathbf{s}_Z$ or $\mathbf{J}_Z$ of *SU(2)* or *R(3)*.

LAB m *eigenvalues*
$$\mathbf{s}_Z\left|{}^{j}_{m,n}\right\rangle = m\left|{}^{j}_{m,n}\right\rangle$$

BOD n *eigenvalues*
$$\bar{\mathbf{s}}_{\bar{Z}}\left|{}^{j}_{m,n}\right\rangle = -n\left|{}^{j}_{m,n}\right\rangle$$



2. *R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices*

General Stern-Gerlach and polarization transformations $\mathbf{R}_{(\alpha,\beta,\gamma)}\left|{}^{J}_{mn}\right\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)\left|{}^{J}_{m'n}\right\rangle$

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$$\mathbf{R}(\alpha\beta\gamma)|000\rangle = |\alpha\beta\gamma\rangle = \bar{\mathbf{R}}^{\dagger}(\alpha\beta\gamma)|000\rangle \qquad \text{for all } (\alpha\beta\gamma) \text{ and } (\alpha'\beta'\gamma') \qquad \mathbf{R}(\alpha\beta\gamma)\bar{\mathbf{R}}(\alpha'\beta'\gamma') = \bar{\mathbf{R}}(\alpha'\beta'\gamma')\mathbf{R}(\alpha\beta\gamma)$$

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$$\mathbf{R}(\alpha\beta\gamma)\left|{}^{j}_{m,n}\right\rangle = \sum_{m'=-j}^{j} D^{j}_{m',n}(\alpha\beta\gamma)\left|{}^{j}_{m',n}\right\rangle$$

BOD $n \leftrightarrow n'$ *transform*
$$\bar{\mathbf{R}}(\alpha\beta\gamma)\left|{}^{j}_{m,n}\right\rangle = \sum_{n'=-j}^{j} D^{j*}_{n',n}(\alpha\beta\gamma)\left|{}^{j}_{m,n'}\right\rangle$$

Same applies to the generators $\mathbf{s}_Z$ or $\mathbf{J}_Z$ of *SU(2)* or *R(3)*.

LAB *m* *eigenvalues*
$$\mathbf{s}_Z\left|{}^{j}_{m,n}\right\rangle = m\left|{}^{j}_{m,n}\right\rangle$$

BOD *n* *eigenvalues*
$$\bar{\mathbf{s}}_{\bar{Z}}\left|{}^{j}_{m,n}\right\rangle = -n\left|{}^{j}_{m,n}\right\rangle$$

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|{}^J_{mn}\rangle = \mathbf{P}_{mn}{}^J|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|{}^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|{}^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

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2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

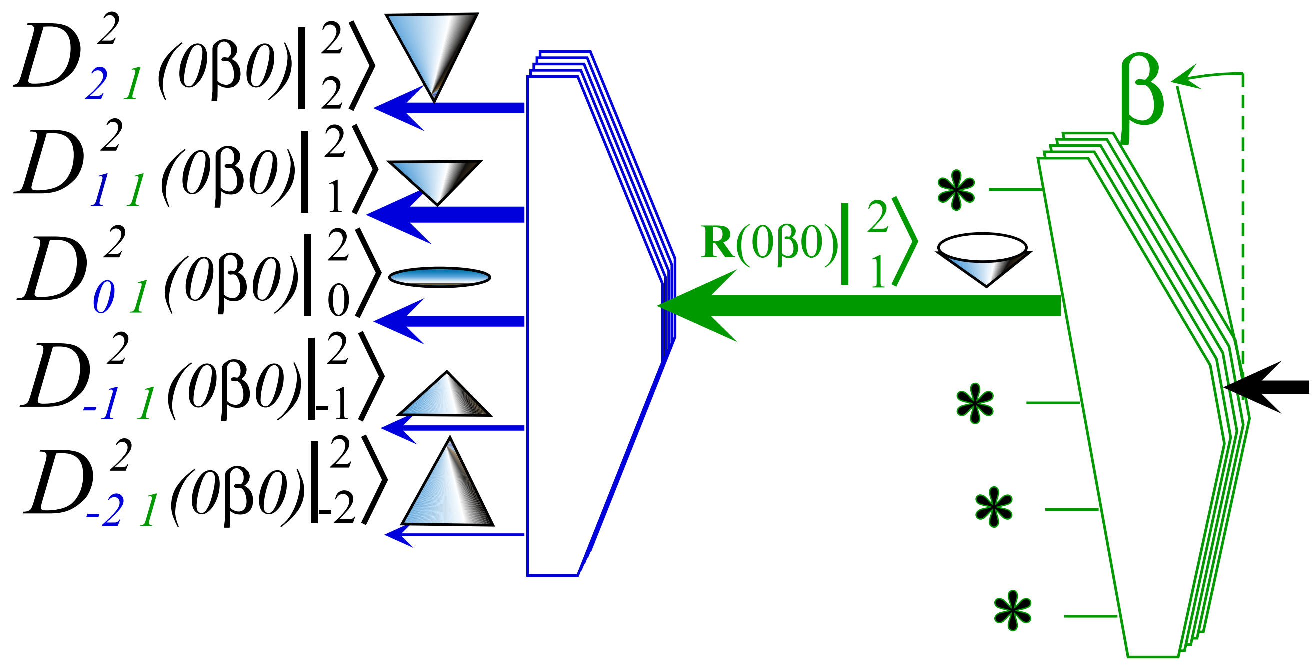
General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Polarization analysis: Suppose a spin-j state $\mathbf{R}(0\beta 0)\,|^{j=2}_{n=1}\rangle$ exits an analyzer rotated by β

and then enters a vertical ($\beta=0$) analyzer and forced to choose from unrotated states $|^{j=2}_{m'}\rangle$

$$\mathbf{R}(0\beta 0)\left|{}^{j}_{n}\right\rangle = \sum_{m'=-j}^{j}\left|{}^{j}_{m'}\right\rangle\left\langle{}^{j}_{m'}\right|\mathbf{R}(0\beta 0)\left|{}^{j}_{n}\right\rangle$$

$$= \sum_{m'=-j}^{j}\left|{}^{j}_{m'}\right\rangle D^{j}_{m'n}(0\beta 0)$$



QTforCA Unit 8. Ch. 23 Fig. 23.2.1

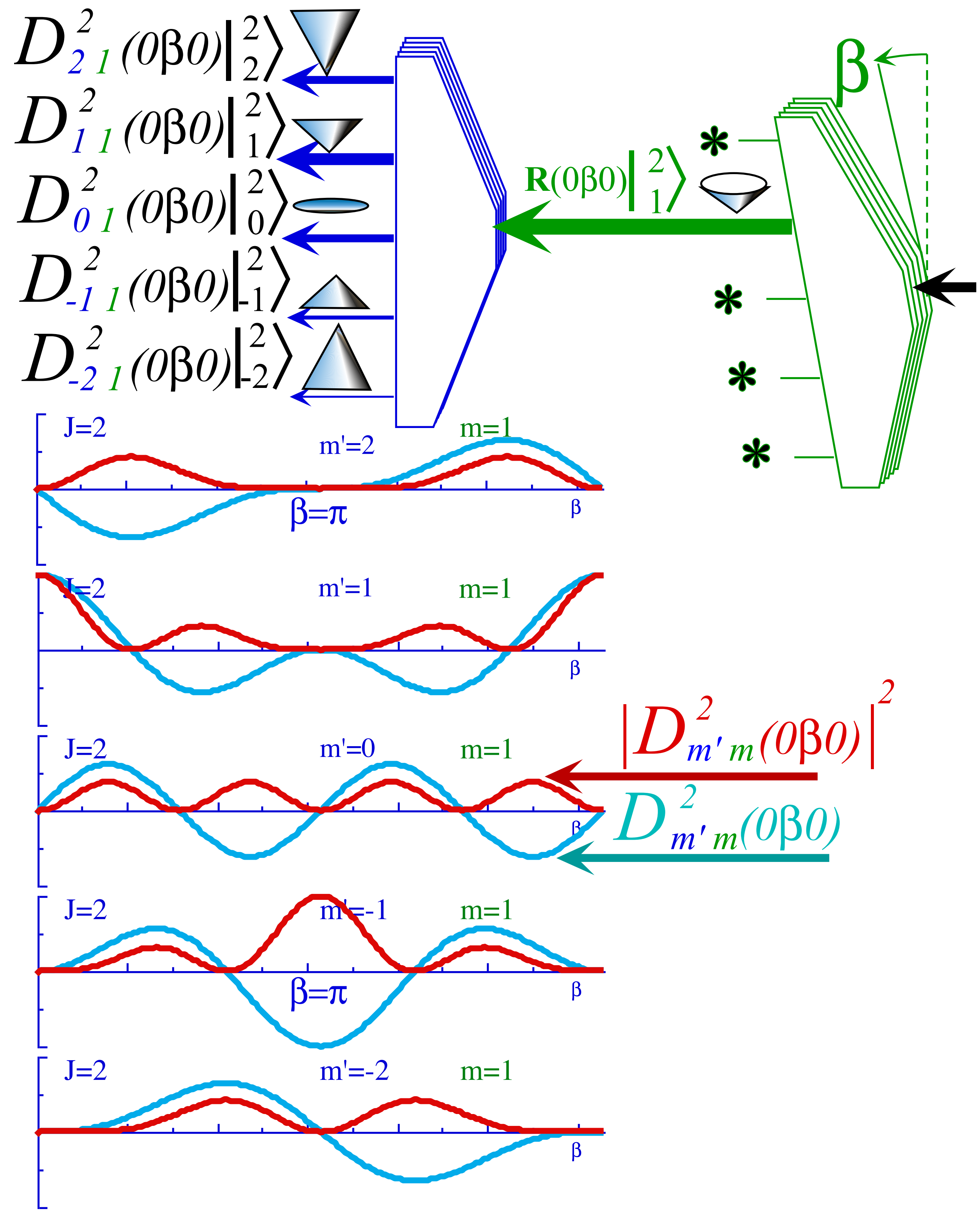
2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|{}^J_{mn}\rangle=\Sigma_{m'}D^J_{m'n}(\alpha,\beta,\gamma)|{}^J_{m'n}\rangle$

Polarization analysis: Suppose a spin-j state $\mathbf{R}(0\beta0)\,|{}^{j=2}_{n=1}\rangle$ exits an analyzer rotated by β and then enters a vertical ($\beta=0$) analyzer and forced to choose from unrotated states $|{}^{j=2}_{m'}\rangle$

$$\mathbf{R}(0\beta0)\left|{}^{j}_{n}\right\rangle = \sum_{m'=-j}^{j}\left|{}^{j}_{m'}\right\rangle\left\langle{}^{j}_{m'}\right|\mathbf{R}(0\beta0)\left|{}^{j}_{n}\right\rangle$$

$$= \sum_{m'=-j}^{j}\left|{}^{j}_{m'}\right\rangle D^{j}_{m'n}(0\beta0)$$



Overlap of state $\mathbf{R}(\alpha\beta\gamma)\,|{}^2_1\rangle$ with unrotated $|{}^{j=2}_{m'}\rangle$ is the corresponding D-matrix element.

$$\left\langle{}^{j'}_{m'}\right|\mathbf{R}(\alpha\beta\gamma)\left|{}^2_1\right\rangle = \delta^{j'2}D^2_{m'1}(\alpha\beta\gamma) = \left\langle{}^{j'}_{m'}\middle|{}^2_1\right\rangle_R$$

$D^j_{m'n}(0\beta0)$ plotted vs. β for fixed j,m',n

QTforCA Unit 8. Ch. 23 Fig. 23.2.1

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)\left|{}^J_{mn}\right\rangle=\Sigma_{m'}D^J_{m'n}(\alpha,\beta,\gamma)\left|{}^J_{m'n}\right\rangle$

$$D^2(\alpha\beta 0)=\begin{pmatrix}
e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)^2 & e^{-i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & \sqrt{\frac{3}{8}}e^{-i2\alpha}\sin^2\beta & e^{-i2\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta & e^{-i2\alpha}\left(\frac{1-\cos\beta}{2}\right)^2 \\
e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{-i\alpha}\left(\frac{1+\cos\beta}{2}\right)(2\cos\beta-1) & -\sqrt{\frac{3}{2}}e^{-i\alpha}\sin\beta\cos\beta & e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)(2\cos\beta+1) & -e^{-i\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta \\
\sqrt{\frac{3}{8}}\sin^2\beta & \sqrt{\frac{3}{2}}\sin\beta\cos\beta & \frac{3\cos^2\beta-1}{2} & \sqrt{\frac{3}{2}}\sin\beta\cos\beta & \sqrt{\frac{3}{8}}\sin^2\beta \\
e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{i\alpha}\left(\frac{1-\cos\beta}{2}\right)(2\cos\beta+1) & \sqrt{\frac{3}{2}}e^{i\alpha}\sin\beta\cos\beta & e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)(2\cos\beta-1) & -e^{i\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta \\
e^{i2\alpha}\left(\frac{1-\cos\beta}{2}\right)^2 & e^{i2\alpha}\left(\frac{1-\cos\beta}{2}\right)\sin\beta & \sqrt{\frac{3}{8}}e^{i2\alpha}\sin^2\beta & e^{i2\alpha}\left(\frac{1+\cos\beta}{2}\right)\sin\beta & e^{i2\alpha}\left(\frac{1+\cos\beta}{2}\right)^2
\end{pmatrix}$$

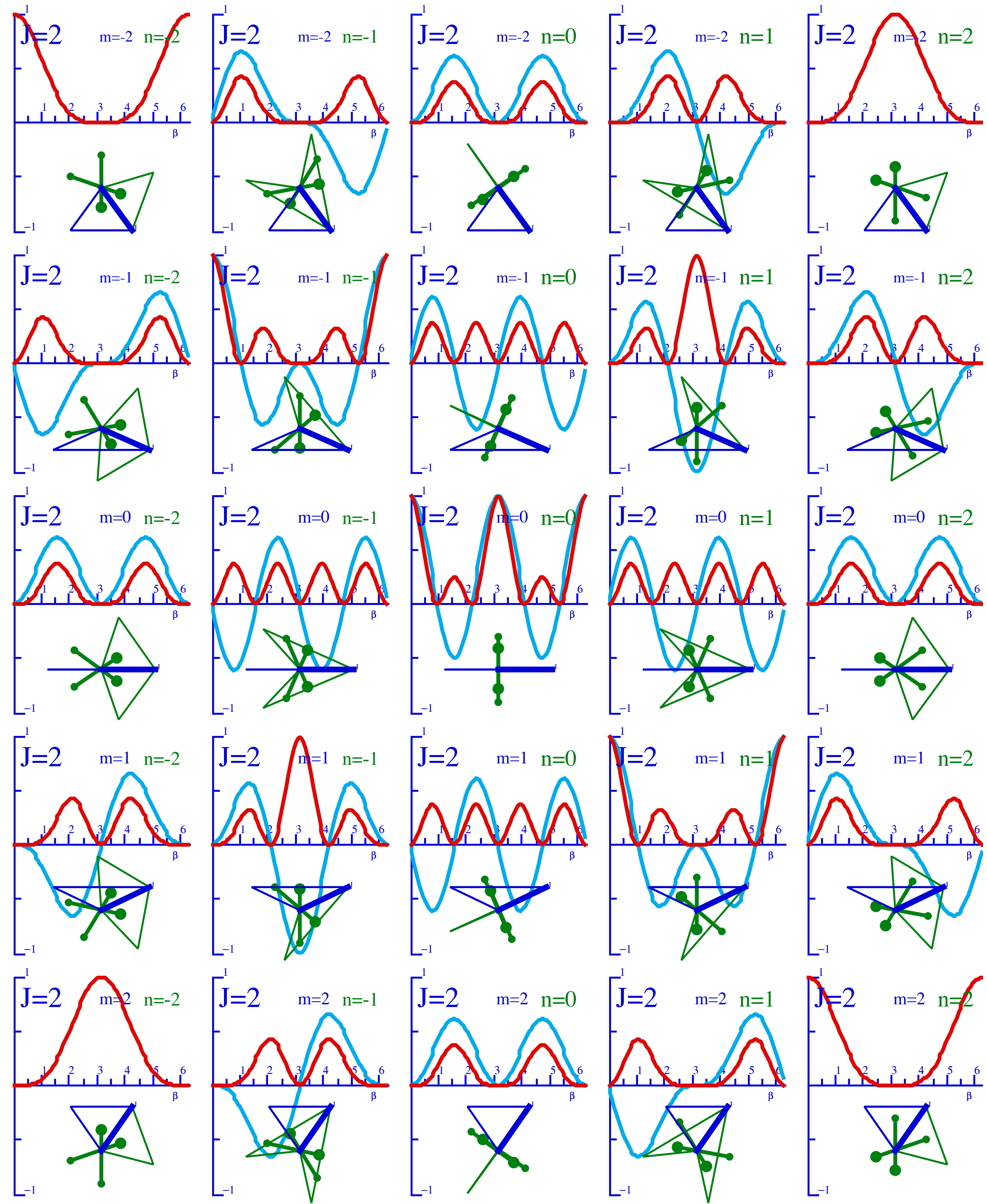
$$\mathbf{R}(0\beta 0)\left|{}^j_n\right\rangle=\sum_{m'=-j}^{j}\left|{}^j_{m'}\right\rangle\left\langle{}^j_{m'}\right|\mathbf{R}(0\beta 0)\left|{}^j_n\right\rangle$$

$$=\sum_{m'=-j}^{j}\left|{}^j_{m'}\right\rangle D^j_{m'n}(0\beta 0)$$

Overlap of state $\mathbf{R}(\alpha\beta\gamma)\left|{}^2_1\right\rangle$ with unrotated $\left|{}^{j=2}_{m'}\right\rangle$ is the corresponding D-matrix element.

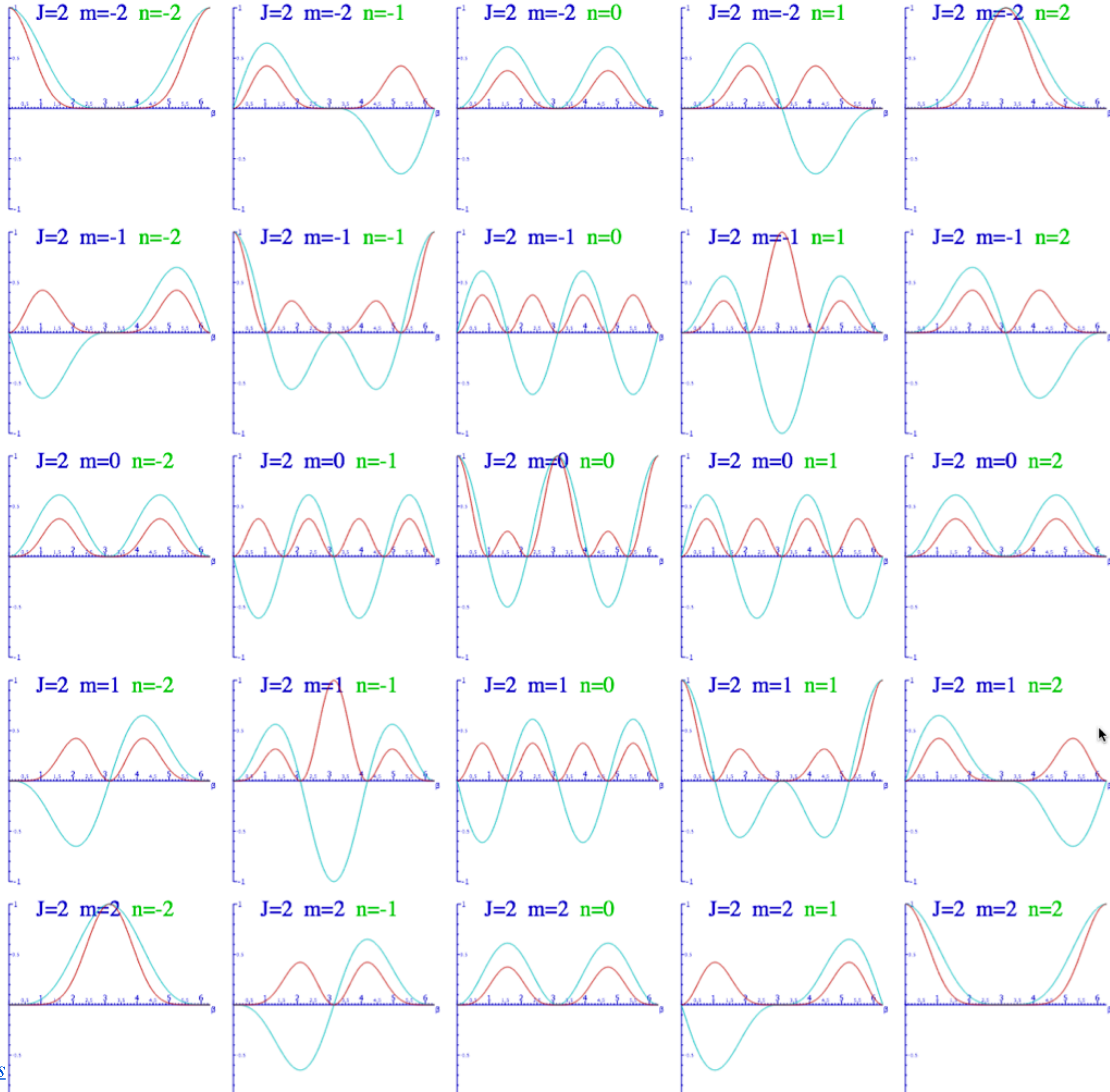
$$\left\langle{}^{j'}_{m'}\right|\mathbf{R}(\alpha\beta\gamma)\left|{}^2_1\right\rangle=\delta^{j'2}D^2_{m'1}(\alpha\beta\gamma)=\left\langle{}^{j'}_{m'}\middle|{}^2_1\right\rangle_R$$

$D^j_{m'n}(0\beta 0)$ plotted vs. β for fixed j,m',n



QTforCA Unit 8. Ch. 23 Fig. 23.2.5

$D^J_{m'n}(0\beta 0)$ plotted vs. β for fixed J, m', n



QuantIt web simulation: Visualizing D representations

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$*-wavefunctions*

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$*-transformation matrices*

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ *and eigenvalues*

Multipole $\mathbf{T}_q^k$ *expansion of asymmetric-rotor Hamiltonians* $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ *expansion of symmetric-rotor Hamiltonians* $\mathbf{H} = B\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

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

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Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

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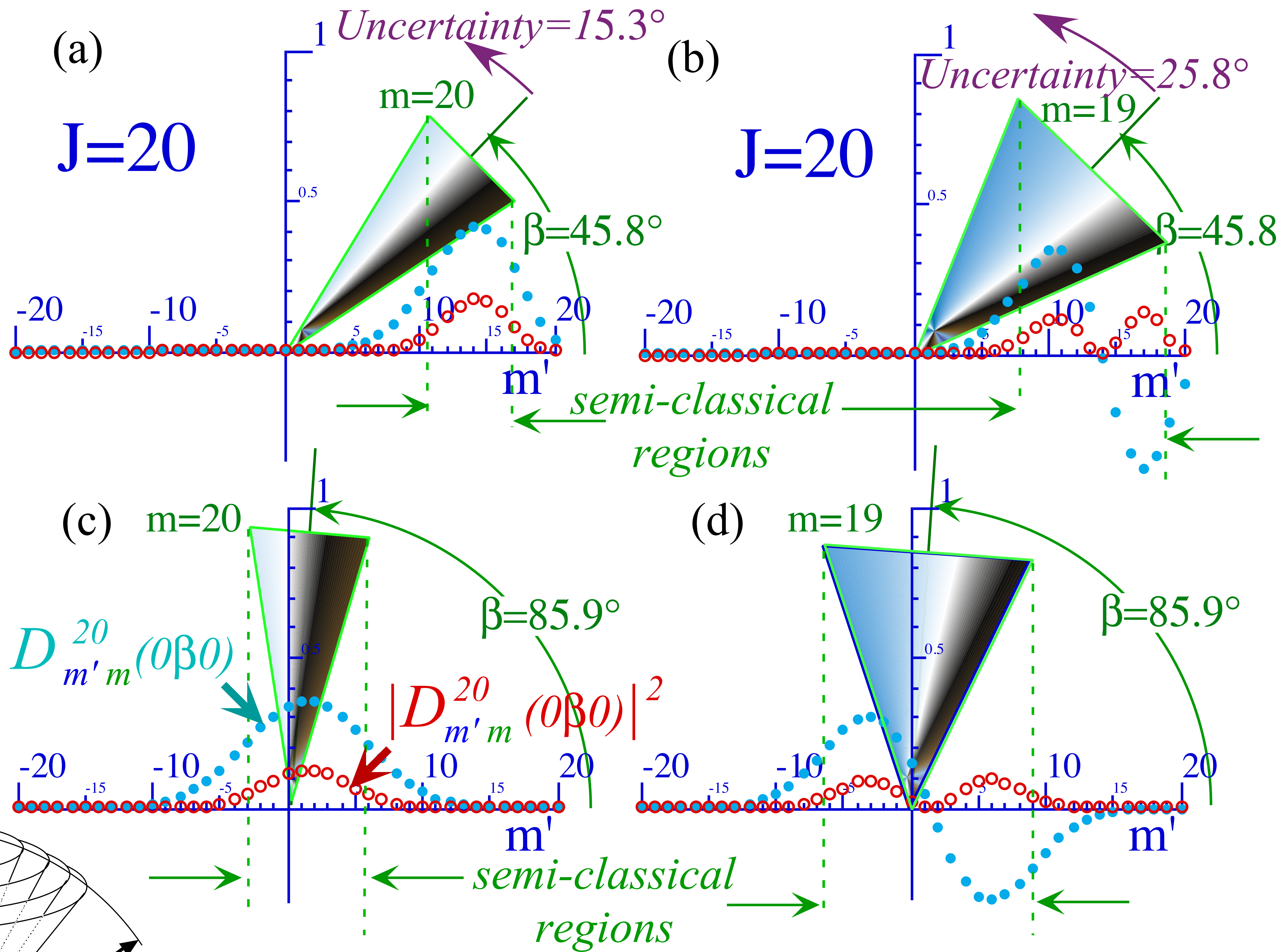
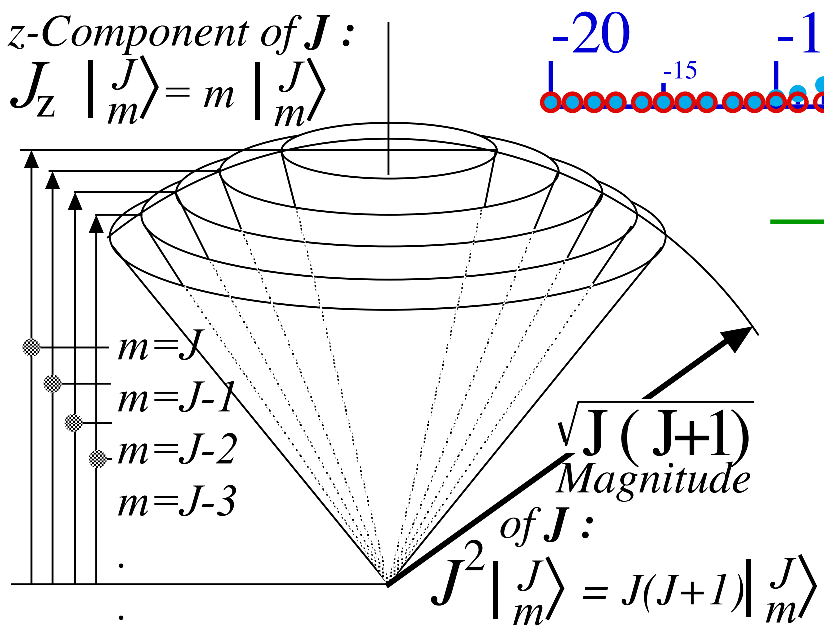
Angular momentum cones and high J properties

$D^J_{m'm}(0\beta 0)$ plotted vs. m' for fixed J,β,m

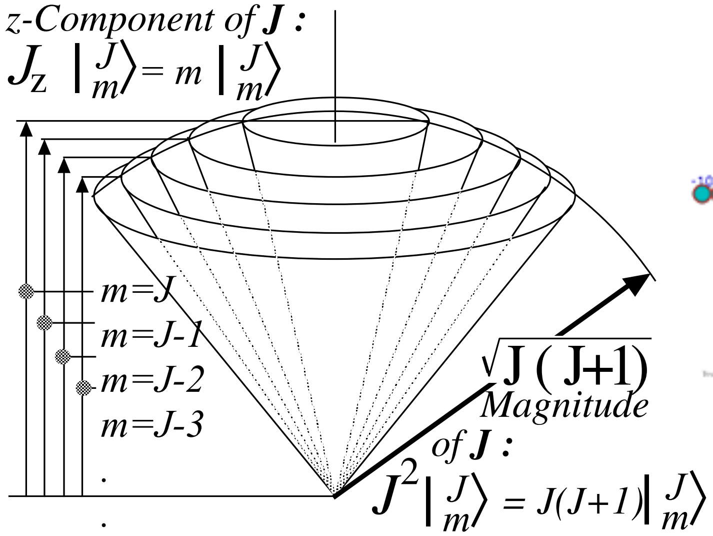


QTforCA Unit 8. Ch. 23 Fig. 23.1.1



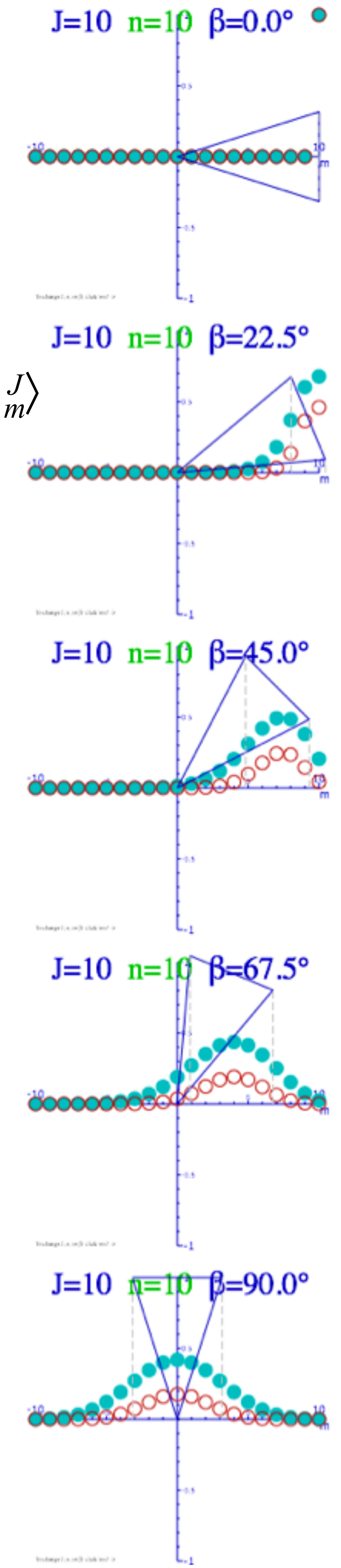
[QuantIt web simulation: Visualizing D representations]

QTforCA Unit 8. Ch. 23 Fig. 23.2.2

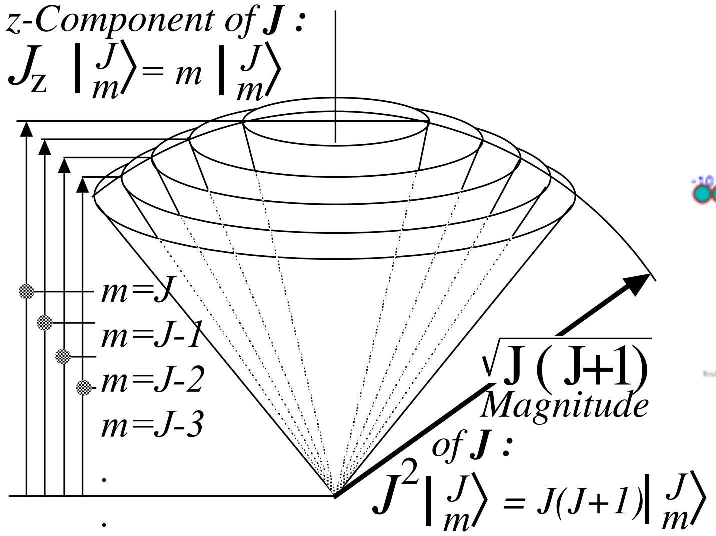


$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10,\beta,n$

$n=10$

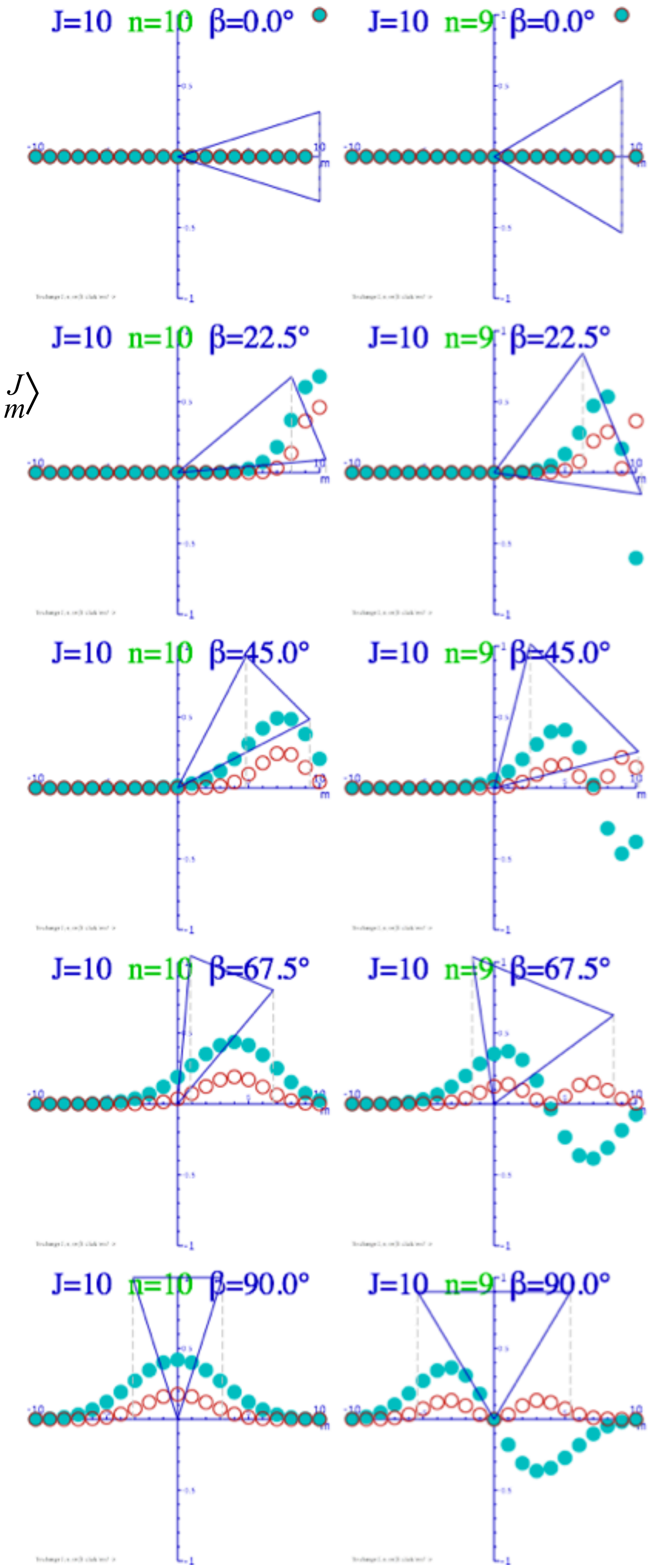


[QuantIt web simulation:
Visualizing D representations]

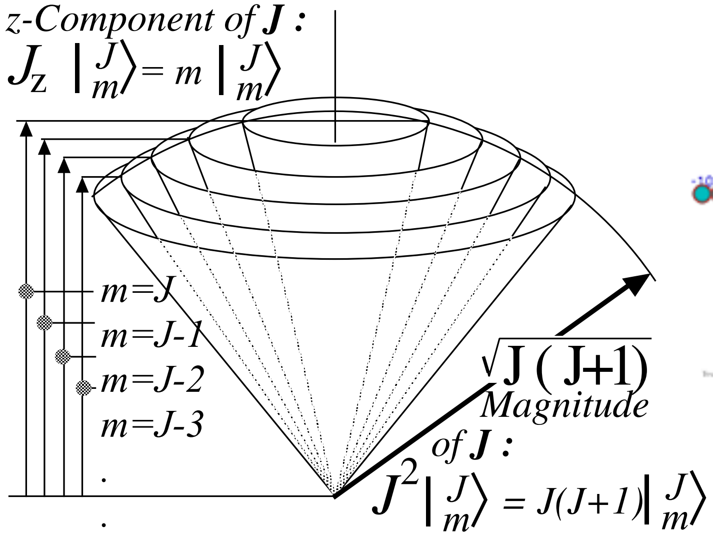


$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
J=10, β, n

n=9

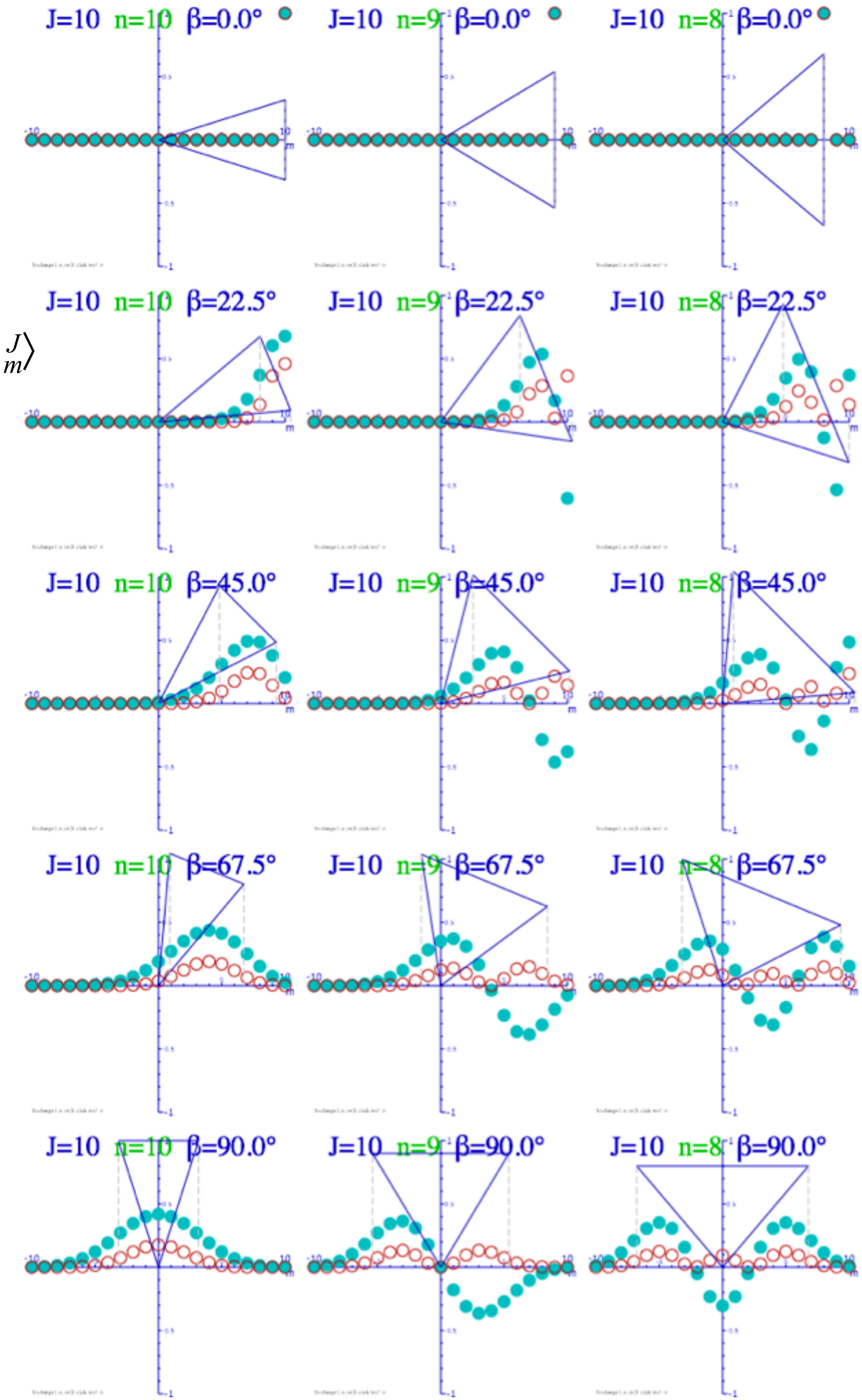


[QuantIt web simulation: Visualizing D representations]

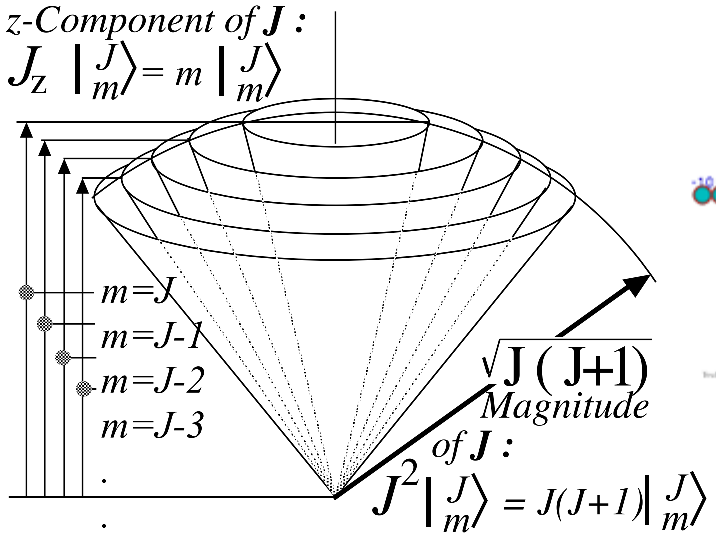


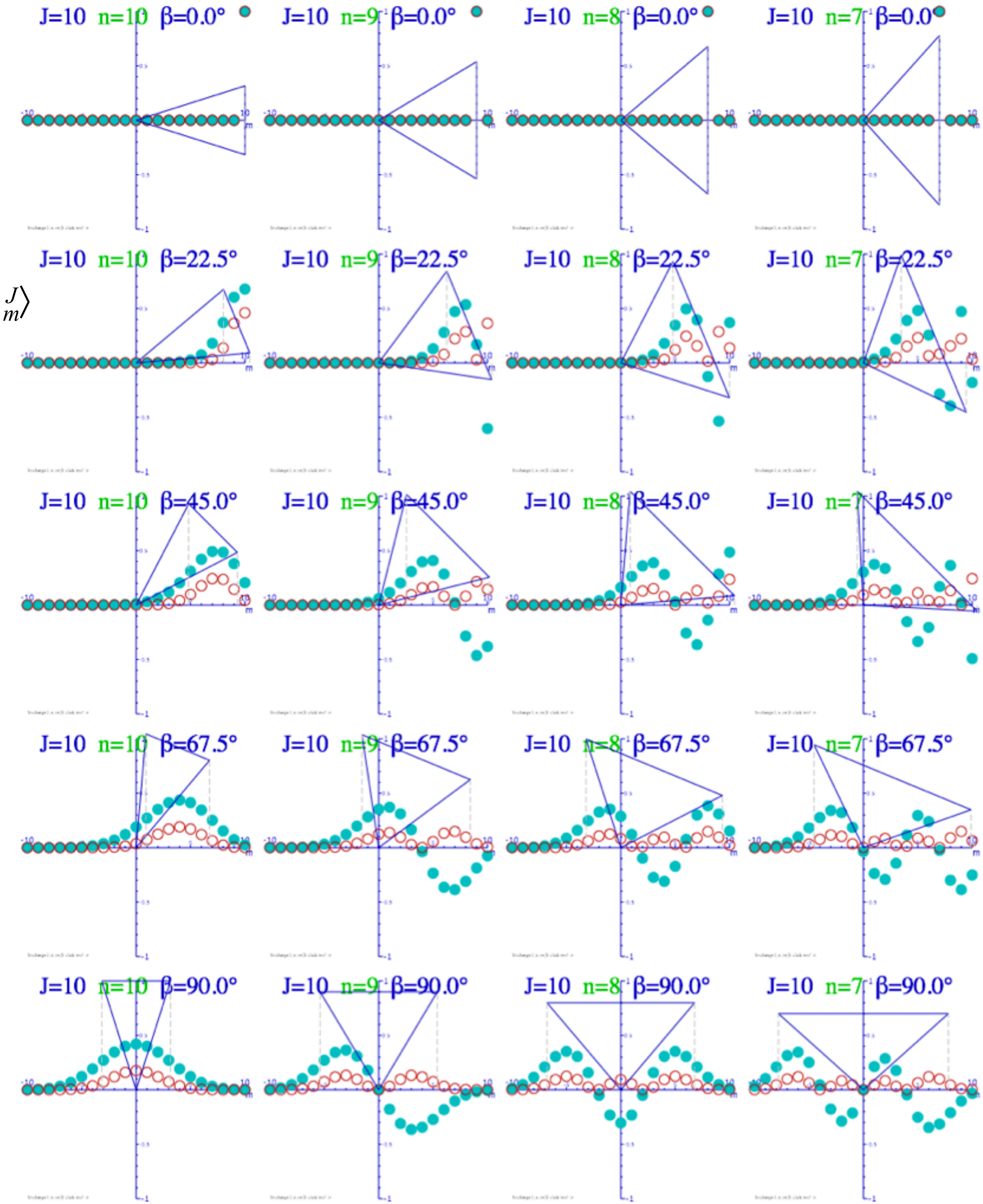
$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

$n=8$



QuantIt web simulation:
Visualizing D representations

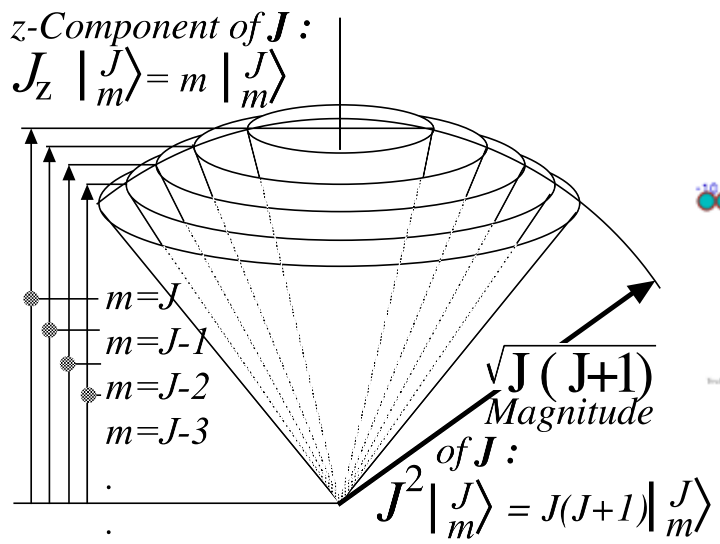




$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

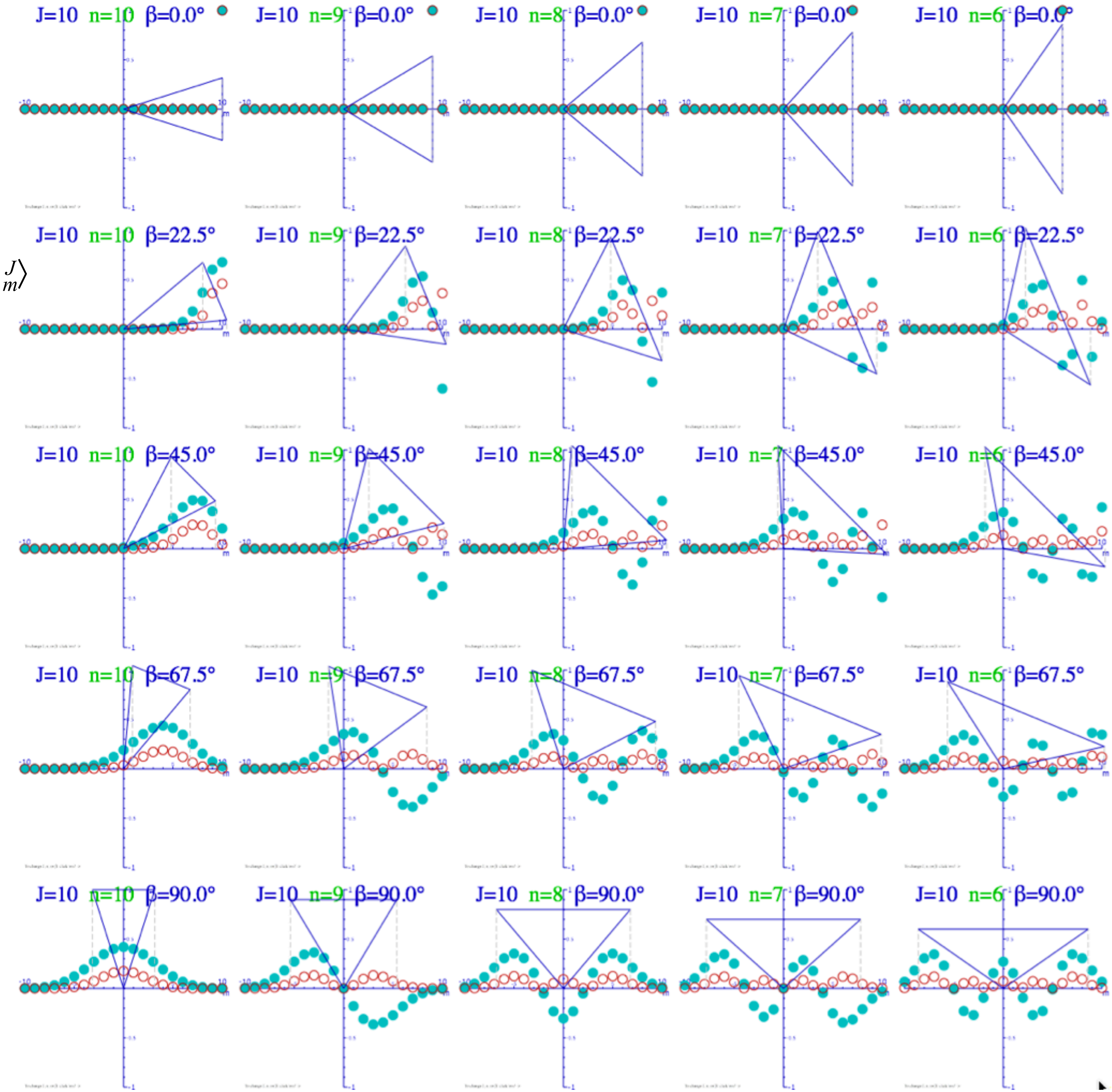
$n=7$

QuantIt web simulation: Visualizing D representations

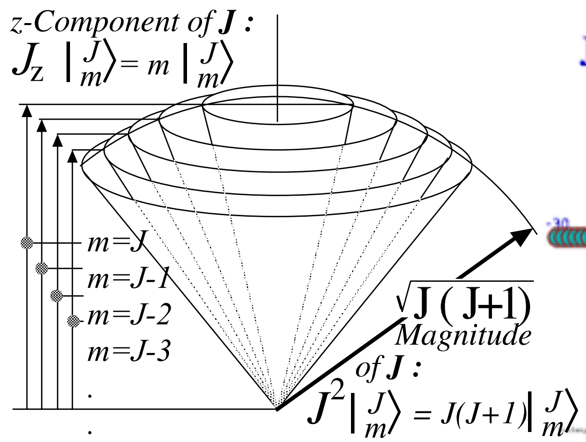


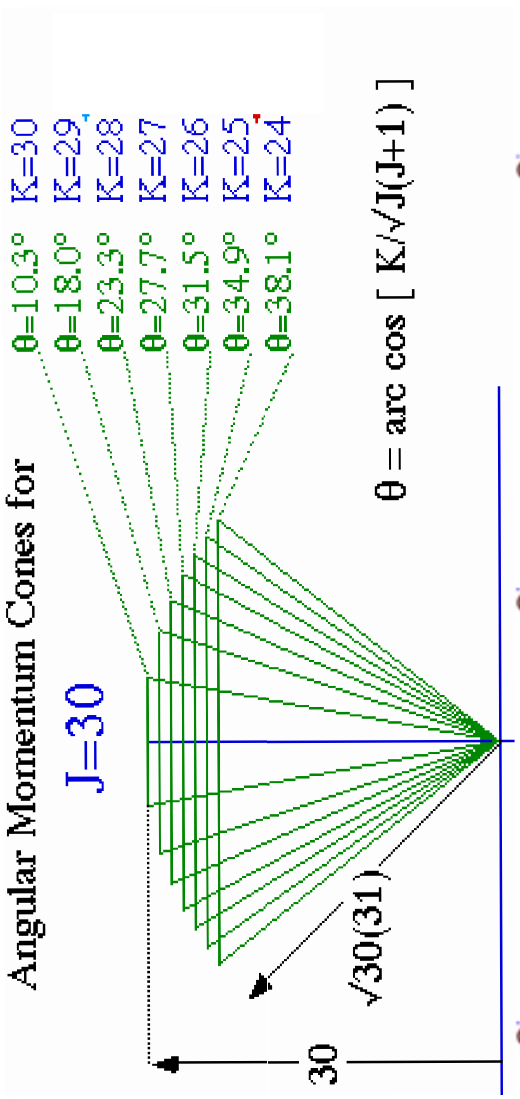
$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

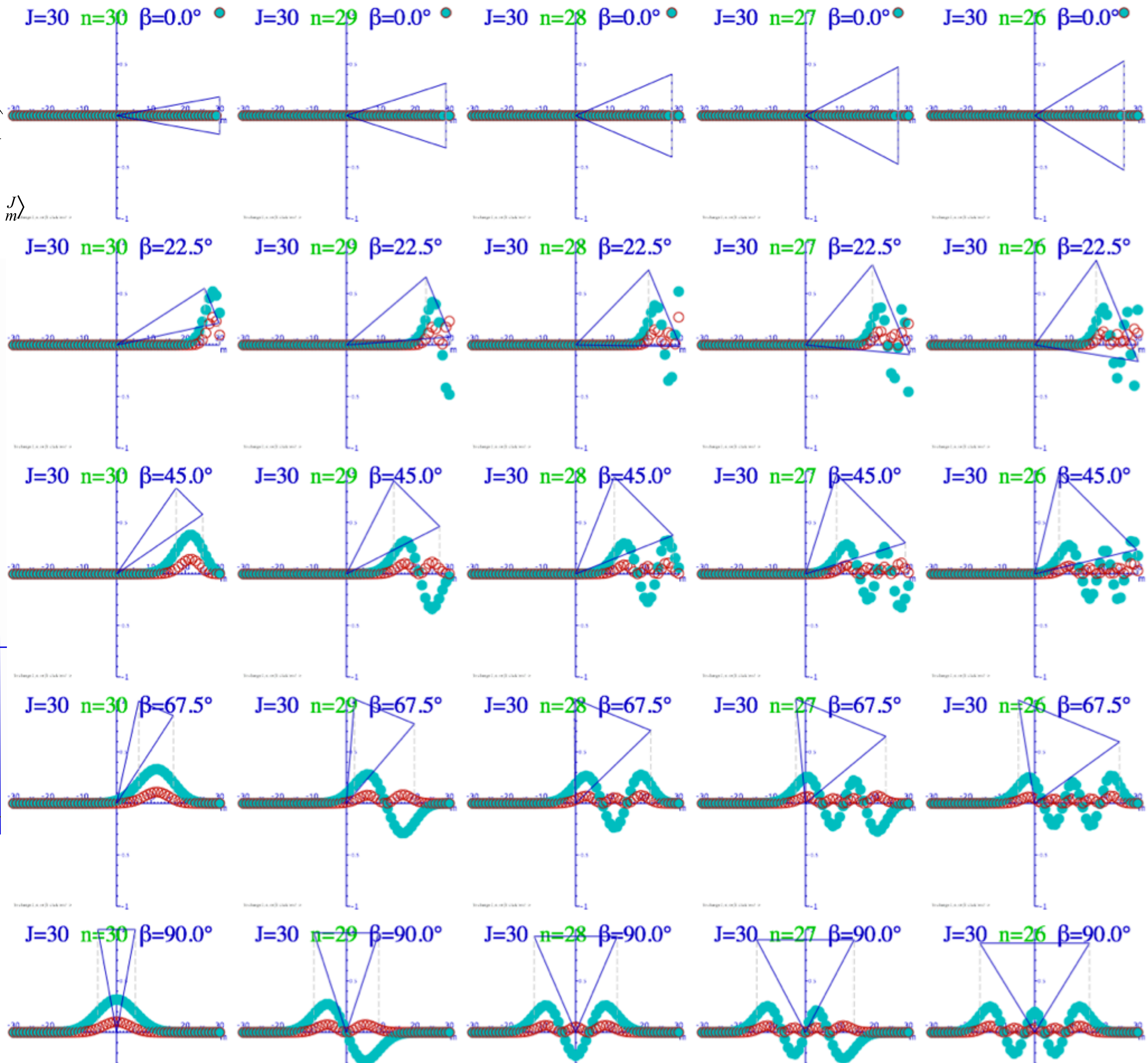
$n=6$



[QuantIt web simulation: Visualizing D representations]







QuantIt web simulation: Visualizing D representations

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$*-wavefunctions*

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Multipole $\mathbf{T}^k_q$ *expansion of asymmetric-rotor Hamiltonians* $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

Multipole $\mathbf{T}^k_q$ *expansion of symmetric-rotor Hamiltonians* $\mathbf{H} = B\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

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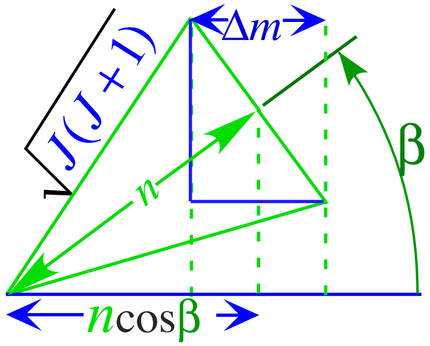
Example of CO_2 *rovibration* $(\upsilon=0)\Leftrightarrow(\upsilon=1)$*bands*

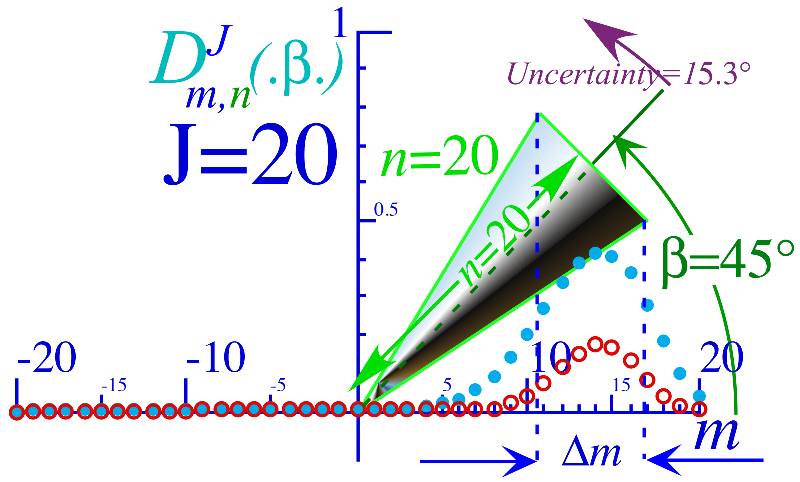
Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

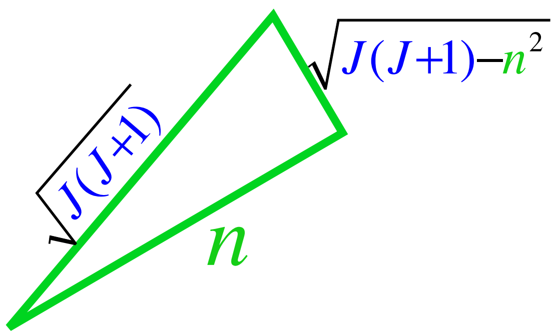
Asymmetric Top eigensolutions for J=1-2

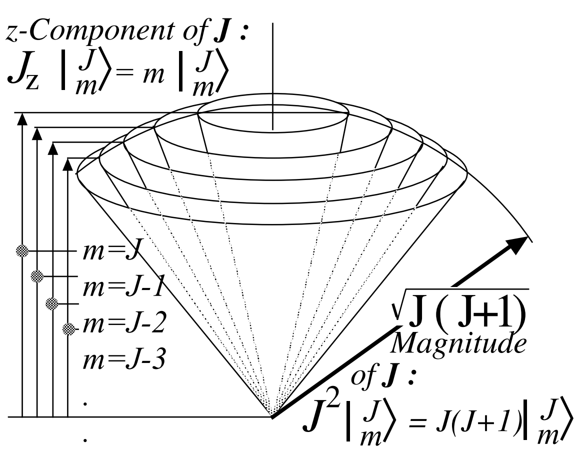
Using literal interpretation of $\left|\begin{smallmatrix}J\\m\end{smallmatrix}\right\rangle$ to derive approximate number Δm of "most-busy" counters and determine most probable m-values.

$$\Delta m = 2\sqrt{J(J+1)-n^2}\cdot\sin\beta$$









[QuantIt web simulation:
Visualizing D representations]()

http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

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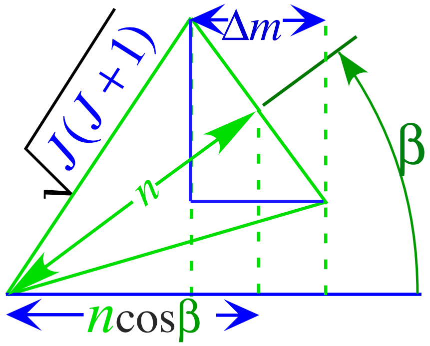
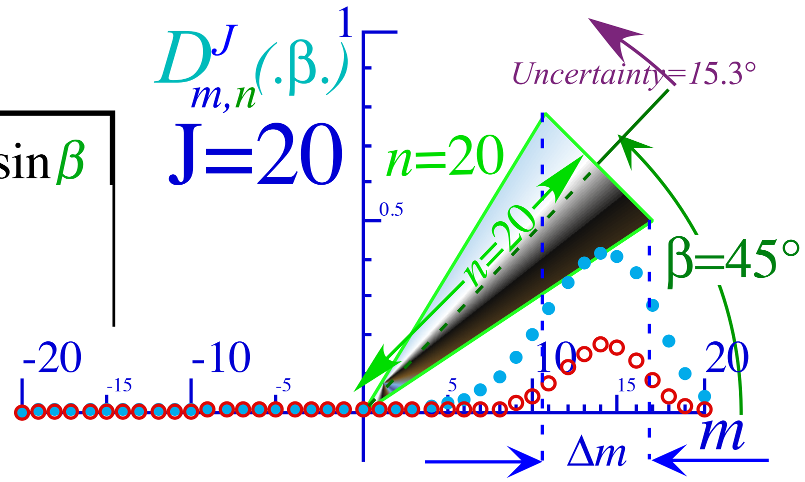


$n=J$: $\Delta m = 2\sqrt{J}\ \sin\beta$

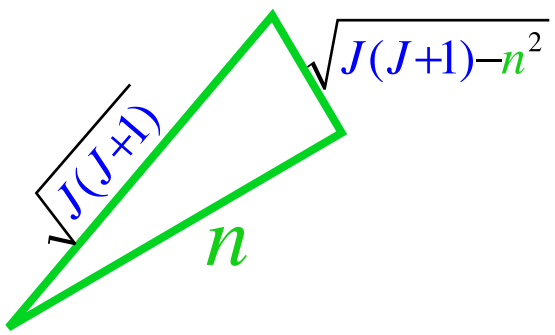
$n=J-1$:

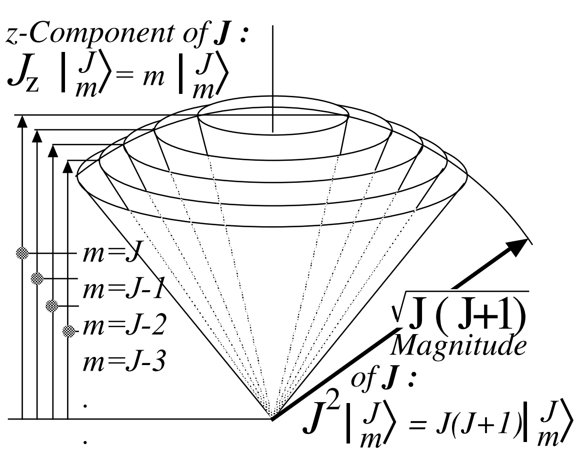
$n=J-2$:



$$\Delta m = 2\sqrt{20}\sin 45° = \sqrt{40} = 6.2$$

Testing formula with $J=20$ for $\beta=45°$...





[*QuantIt web simulation: Visualizing D representations*](http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm)

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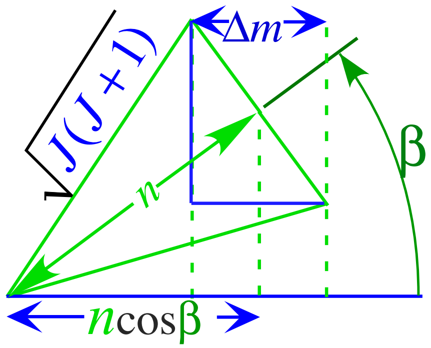
Angular momentum cones and high J properties

Using literal interpretation of $\left|\begin{matrix}J\\m\end{matrix}\right\rangle$ to derive approximate number Δm of "most-busy" counters and determine most probable m-values.

$$\Delta m = 2\sqrt{J(J+1)-n^2}\cdot\sin\beta$$



$n=J$: $\Delta m = 2\sqrt{J}\ \sin\beta$

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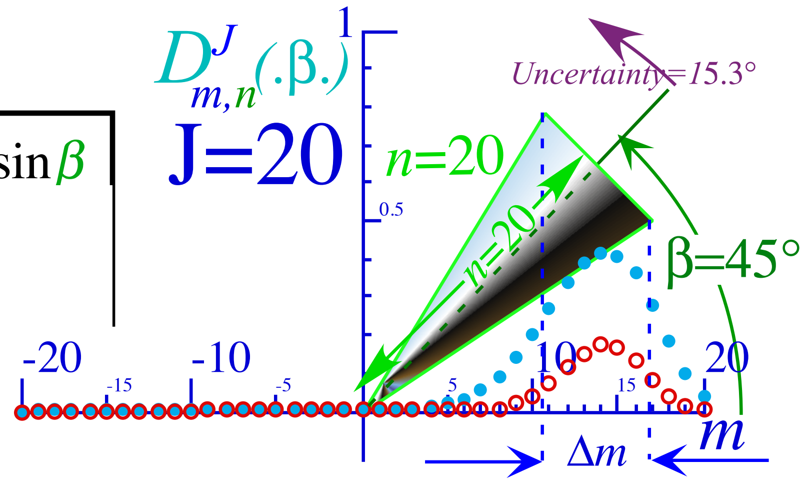

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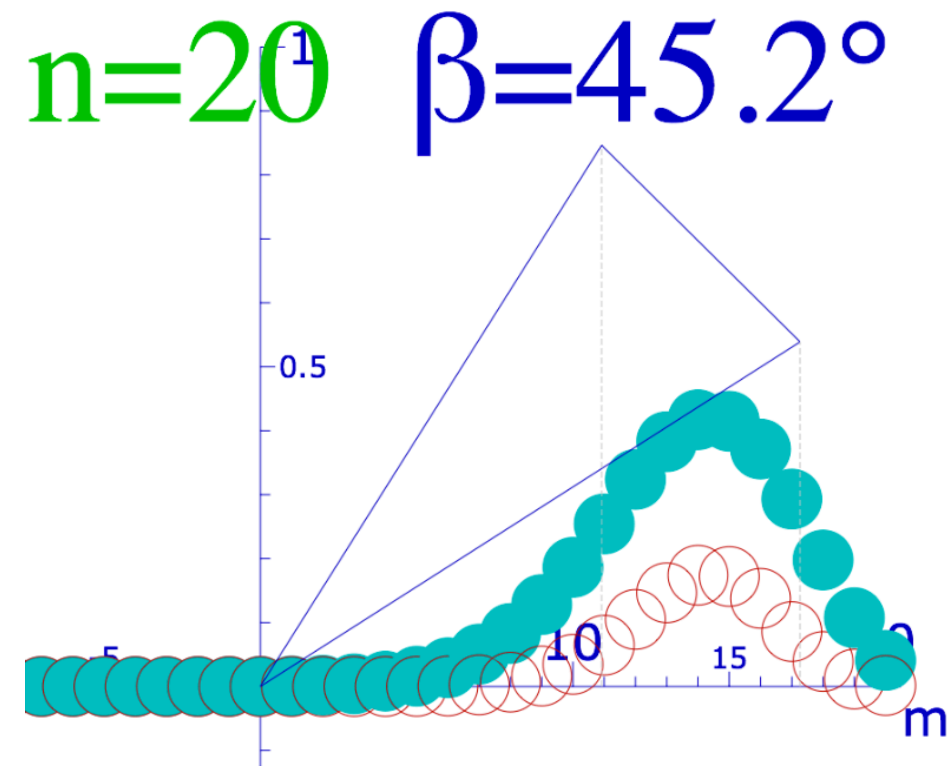

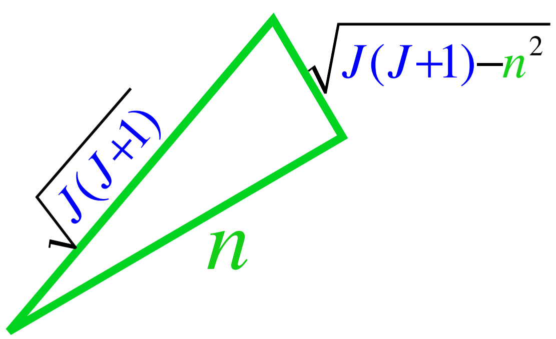

Testing formula with $J=20$ for $\beta=45°$...

[QuantIt web simulation: Visualizing D representations](http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm)

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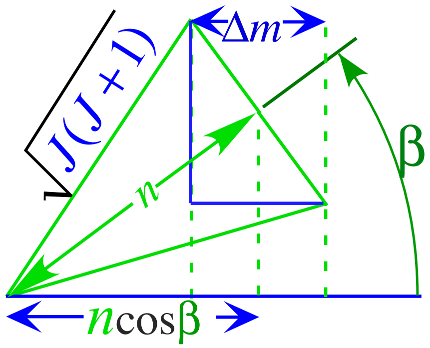

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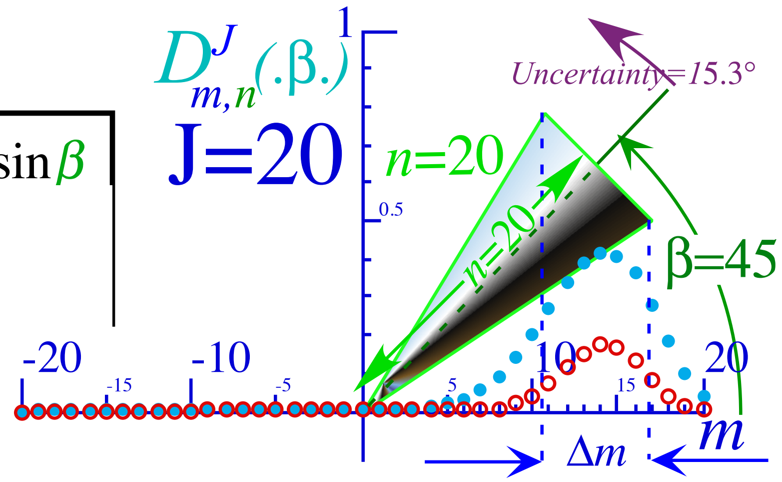
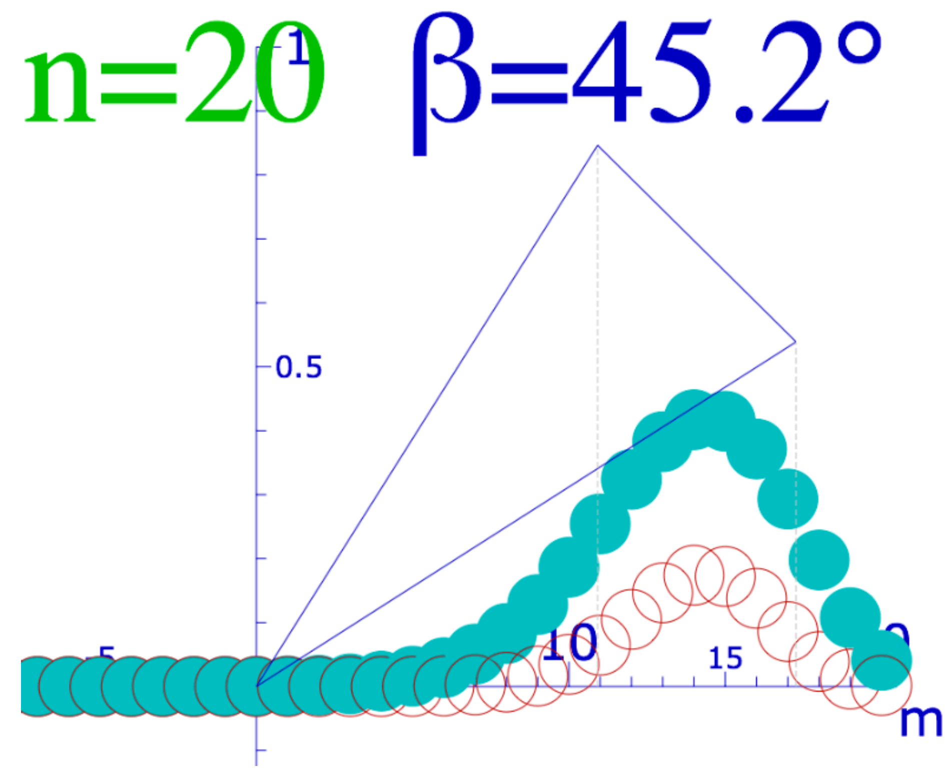
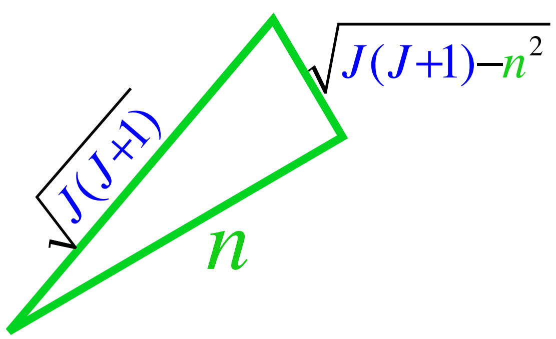


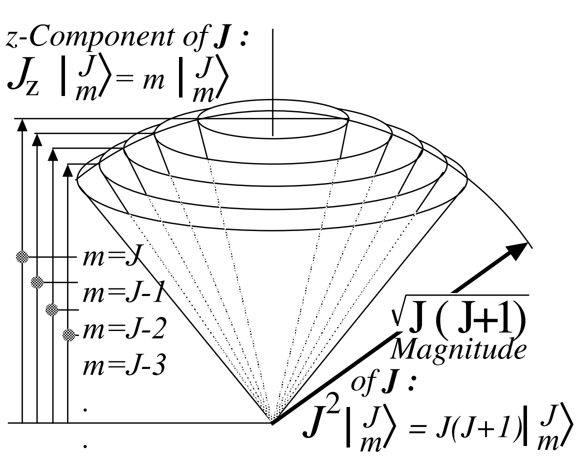
$\Delta m = 2\sqrt{20}\sin 45° = \sqrt{40} = 6.2$

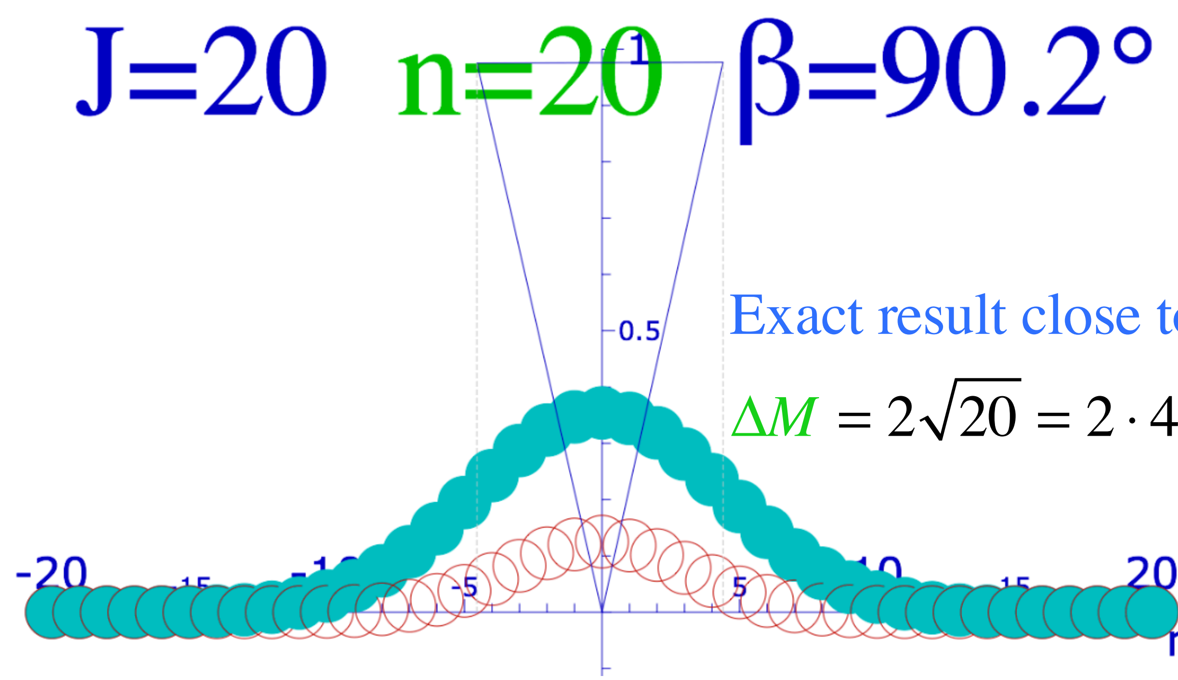




Testing formula with $J=20$ for $\beta=45°$...

...and for $\beta=90°$



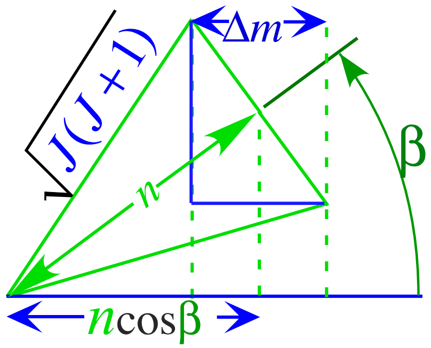


Exact result close to:

$$\Delta M = 2\sqrt{20} = 2\cdot 4.47 = 8.94$$

Using literal interpretation of $\left|\begin{smallmatrix}J\\m\end{smallmatrix}\right\rangle$ to derive approximate number Δm of "most-busy" counters and determine most probable *m*-values.

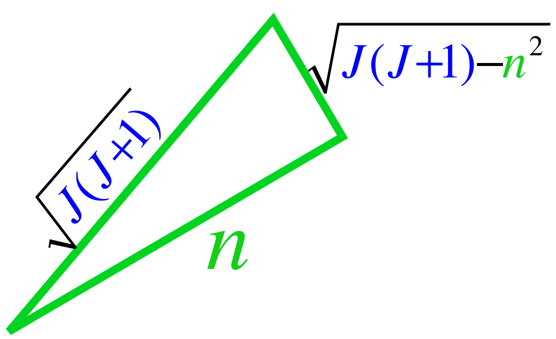
$$\Delta m = 2\sqrt{J(J+1)-n^2}\cdot\sin\beta$$

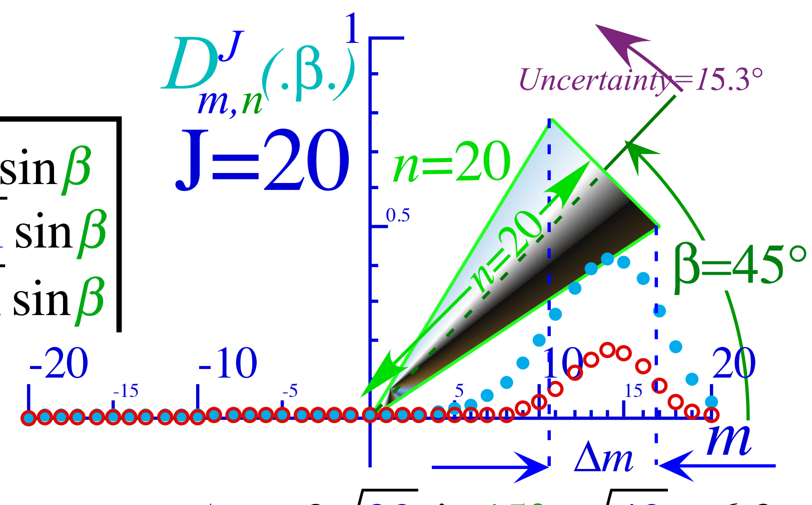


$n=J$: $\Delta m = 2\sqrt{J}\ \sin\beta$

$n=J-1$: $\Delta m = 2\sqrt{3J-1}\ \sin\beta$

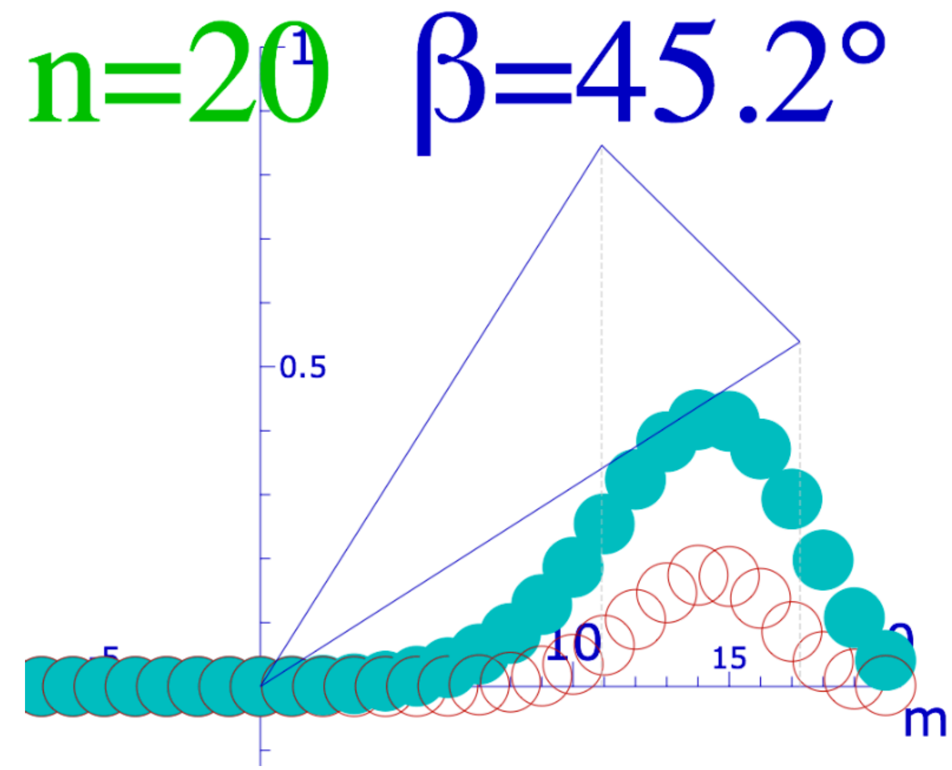
$n=J-2$: $\Delta m = 2\sqrt{5J-1}\ \sin\beta$



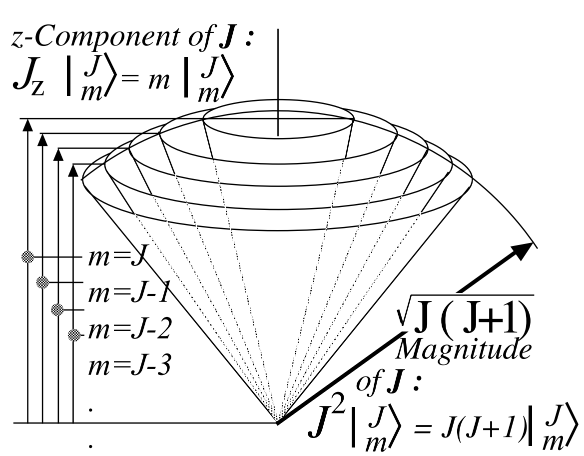


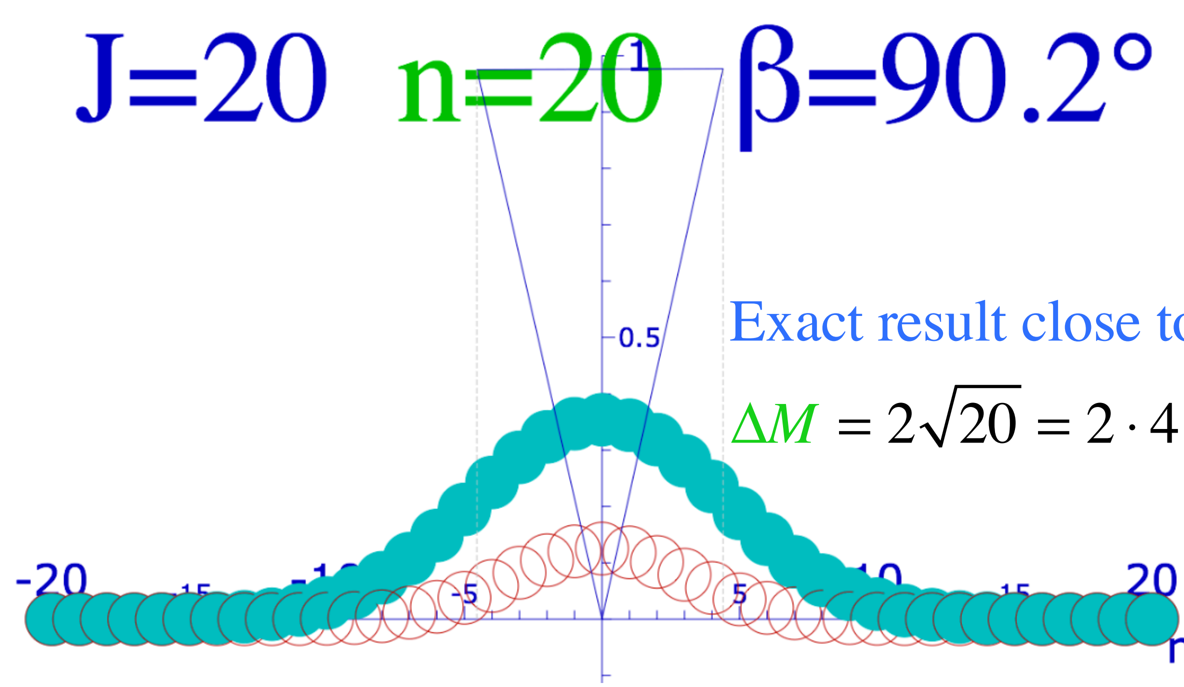
$\Delta m = 2\sqrt{20}\sin 45° = \sqrt{40} = 6.2$

Testing formula with $J=20$ for $\beta=45°$...



...and for $\beta=90°$





Exact result close to:

$$\Delta M = 2\sqrt{20} = 2\cdot 4.47 = 8.94$$

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J |_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma) \mathbf{R}(\alpha,\beta,\gamma) |_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

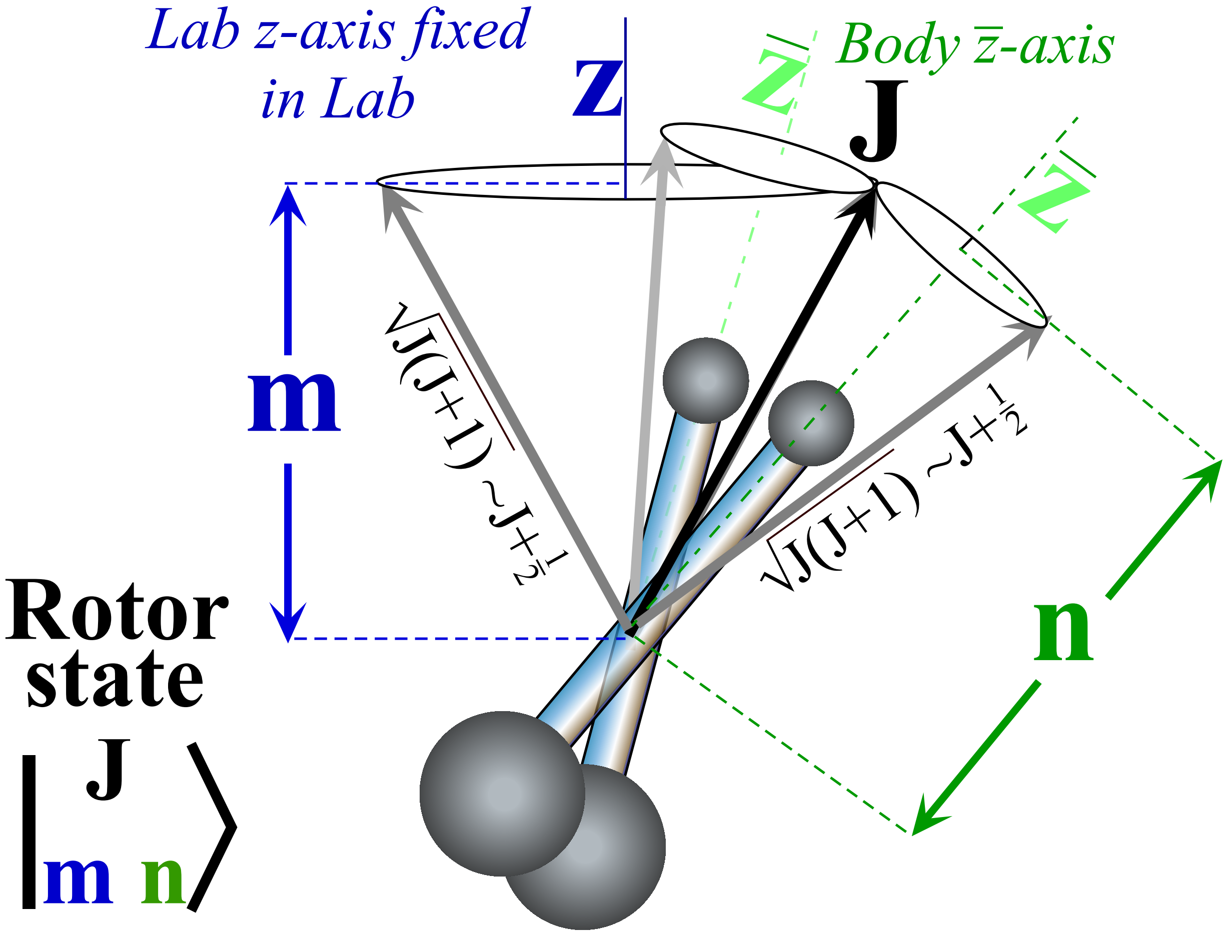
Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

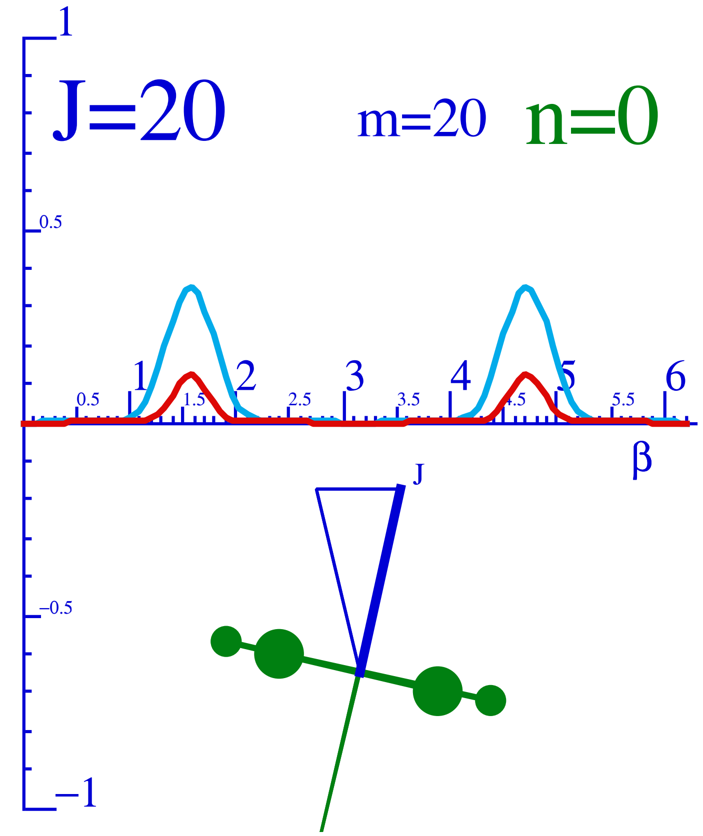
Asymmetric Top eigensolutions for J=1-2

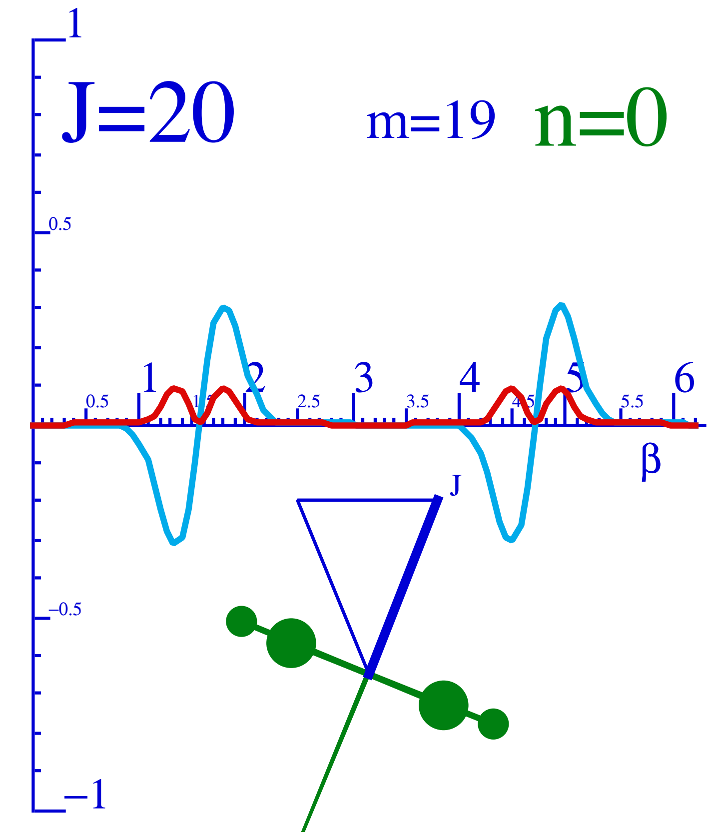
Angular momentum cones and high J properties of LAB vs BOD wavefunctions

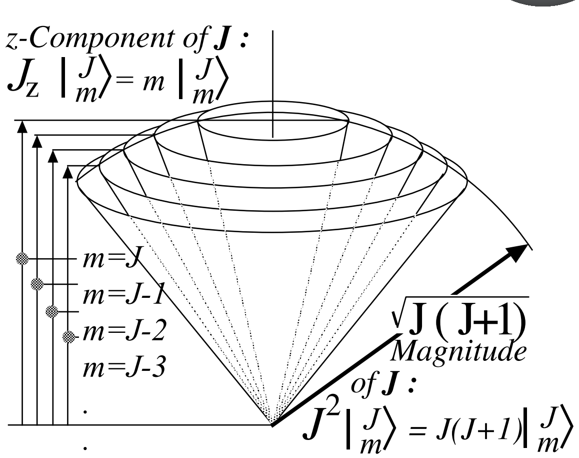
$D^{J=20}_{m,n}(0\beta 0)$
plotted
vs. β
for fixed
$J=20, m, n$

Using literal interpretation of $\left|\begin{smallmatrix} J \\ m\ n \end{smallmatrix}\right\rangle$ to describe approximate rotor wave-functions









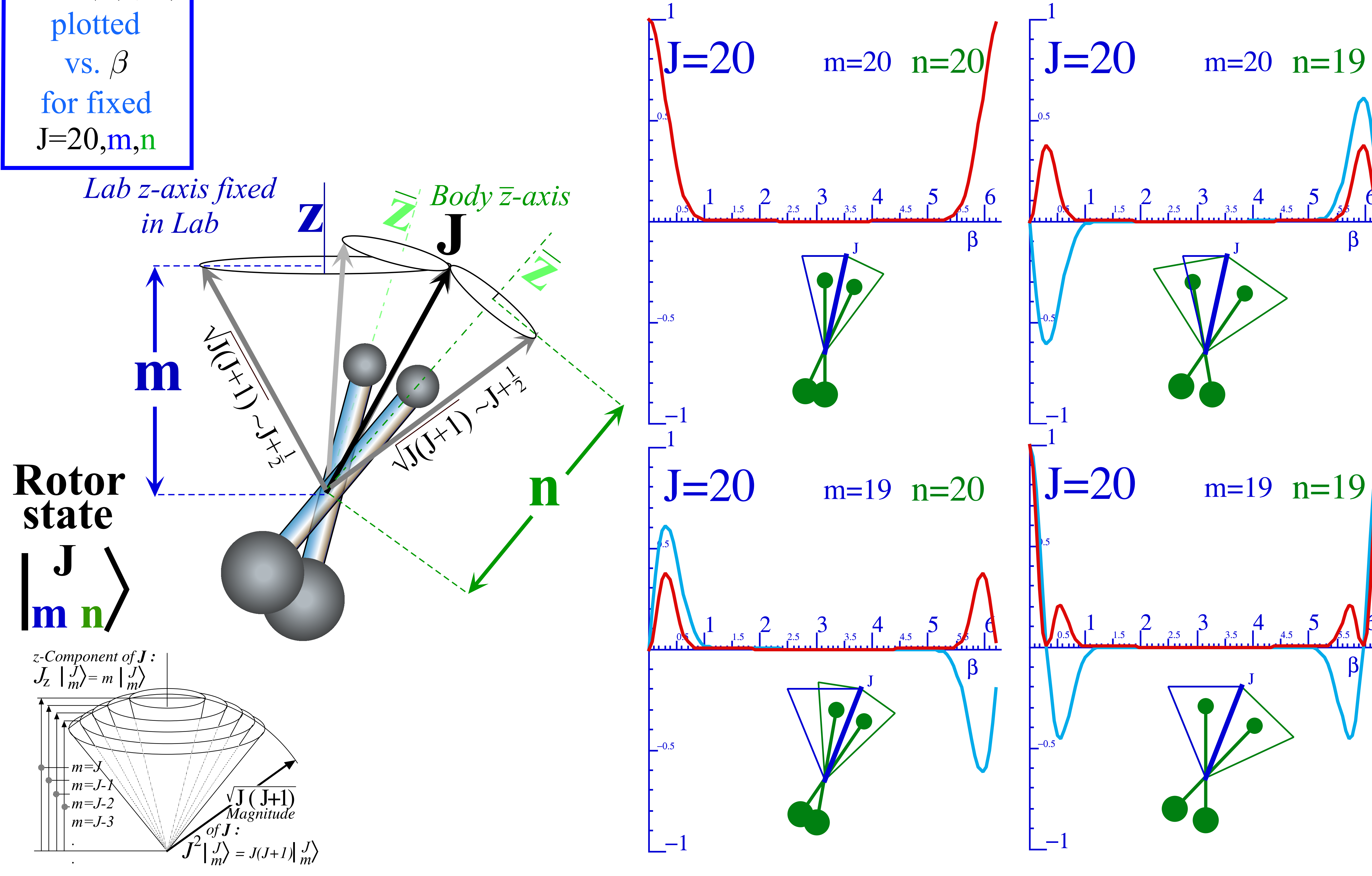
QTforCA Unit 8. Ch. 23 Fig. 23.2.4

[*QuantIt web simulation: Visualizing D representations*]

QTforCA Unit 8. Ch. 23 Fig. 23.2.7

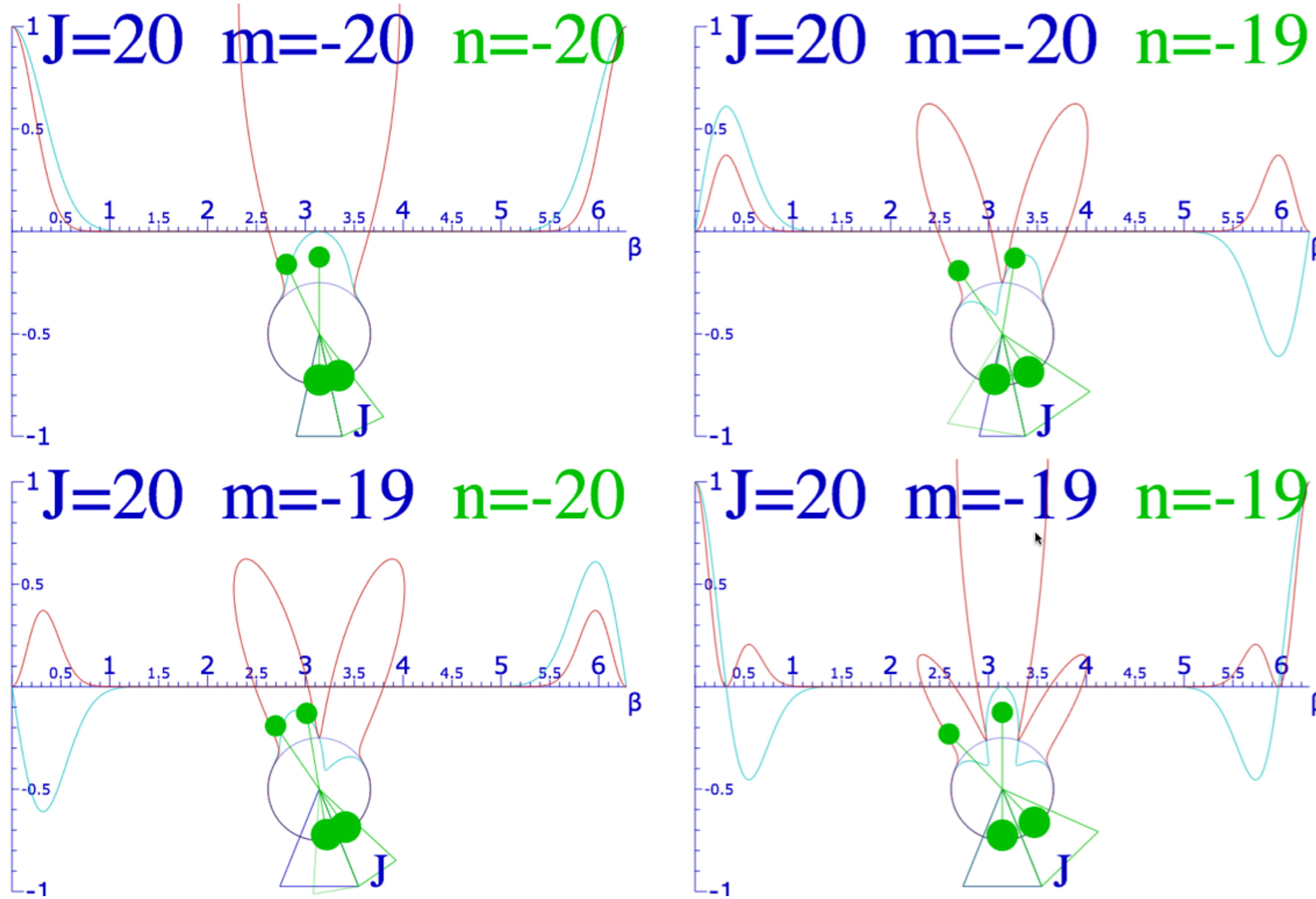
Angular momentum cones and high J properties of LAB vs BOD wavefunctions

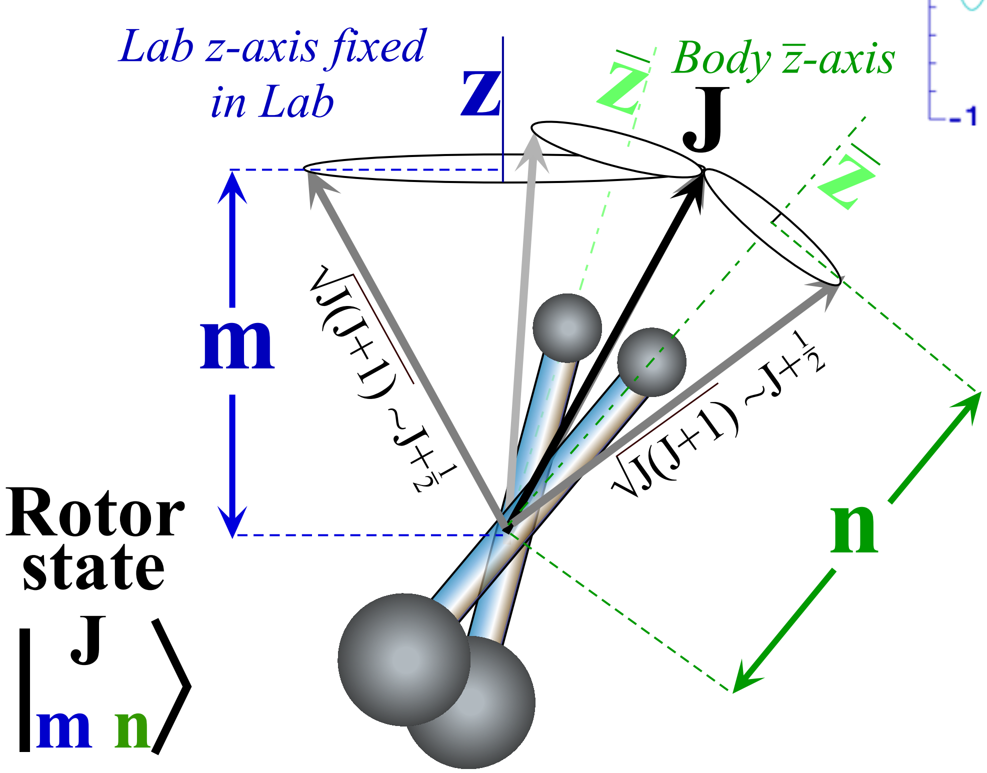
$D^{J=20}_{m,n}(0\beta 0)$ plotted vs. β for fixed J=20,m,n



Angular momentum cones and high J properties of LAB vs BOD wavefunctions

$D^{J=20}_{m,n}(0\beta 0)$
plotted
vs. β
for fixed
J=20,m,n





[QuantIt web simulation:
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Asymmetric Top eigensolutions for J=1-2

Building Hamiltonian $\mathbf{H}=A\mathbf{J}_x{}^2+B\mathbf{J}_y{}^2+C\mathbf{J}_z{}^2$ *out of scalar and tensor operators*

Spherical 2^k*-multipole functions* $X^k{}_q$ or *X-functions* are D*-functions times the k^{th} power of radius (r^k).

Consider k=2 "quadrupole" functions

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

$$\sqrt{4\pi/5}\, Y_{m=2}^{\ell=2}(\phi\theta) = D_{2,0}^{2*}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x+iy)^2}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=1}^{\ell=2}(\phi\theta) = D_{1,0}^{2*}(\phi\theta 0) = -\sqrt{\frac{3}{2}} e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=0}^{\ell=2}(\phi\theta) = D_{0,0}^{2*}(\phi\theta 0) = \frac{3\cos^2\theta-1}{2} = \frac{3z^2-r^2}{2r^2}$$

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→

$$\sqrt{4\pi/5}\, Y^{\ell=2}_{m=0}(\phi\theta) = X^2_0(\phi\theta 0) = r^2\frac{3\cos^2\theta-1}{2} = \frac{3z^2-r^2}{2} = \frac{2z^2-x^2-y^2}{2}$$

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$$\sqrt{4\pi/5}\, Y^{\ell=2}_{m=-2}(\phi\theta) = D^{2*}_{-2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x-iy)^2}{r^2}$$

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$$\sqrt{4\pi/5}\, Y_{m=0}^{\ell=2}(\phi\theta) = X_0^2(\phi\theta 0) = r^2\frac{3\cos^2\theta - 1}{2} = \frac{3z^2 - r^2}{2} = \frac{2z^2 - x^2 - y^2}{2}$$

The (x,y,z) polynomials become $(\mathbf{J}_x,\mathbf{J}_y,\mathbf{J}_z)$ rotor tensor operators

$$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z^{\;2} - \mathbf{J}_x^{\;2} - \mathbf{J}_y^{\;2}}{2} = \mathbf{J}^2\frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$$

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Spherical 2^k*-multipole functions* X^k_q or *X-functions* are D^*-functions times the k^{th} power of radius (r^k).

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$$X^k_q = r^k D^{k*}_{q,0} = \sqrt{\frac{4\pi}{2k+1}} r^k Y^k_q$$

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$$\mathbf{T}^2_2+\mathbf{T}^2_{-2} = \sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

-

$$= X^2_2(\phi\theta 0)-X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{2}} r^2\frac{e^{i2\phi}-e^{-i2\phi}}{2}\sin^2\theta = \sqrt{\frac{3}{8}}(i4xy) = i\sqrt{6}xy = i\sqrt{\frac{3}{2}} r^2\sin 2\phi\sin^2\theta$$

$$\mathbf{T}^2_2-\mathbf{T}^2_{-2} = i\sqrt{6}\,\mathbf{J}_x\mathbf{J}_y$$

etc.

And, don't forget scalar: $\mathbf{T}^0_0 = \mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2 = \mathbf{J}^2$

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

Asymmetric Top eigensolutions for J=1-2

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

$$\mathbf{T}_0^0=\mathbf{J}_x^{\ 2}+\mathbf{J}_y^{\ 2}+\mathbf{J}_z^{\ 2}=\mathbf{J}^2$$

$$\mathbf{T}_0^2=\frac{2\mathbf{J}_z^{\ 2}-\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$$

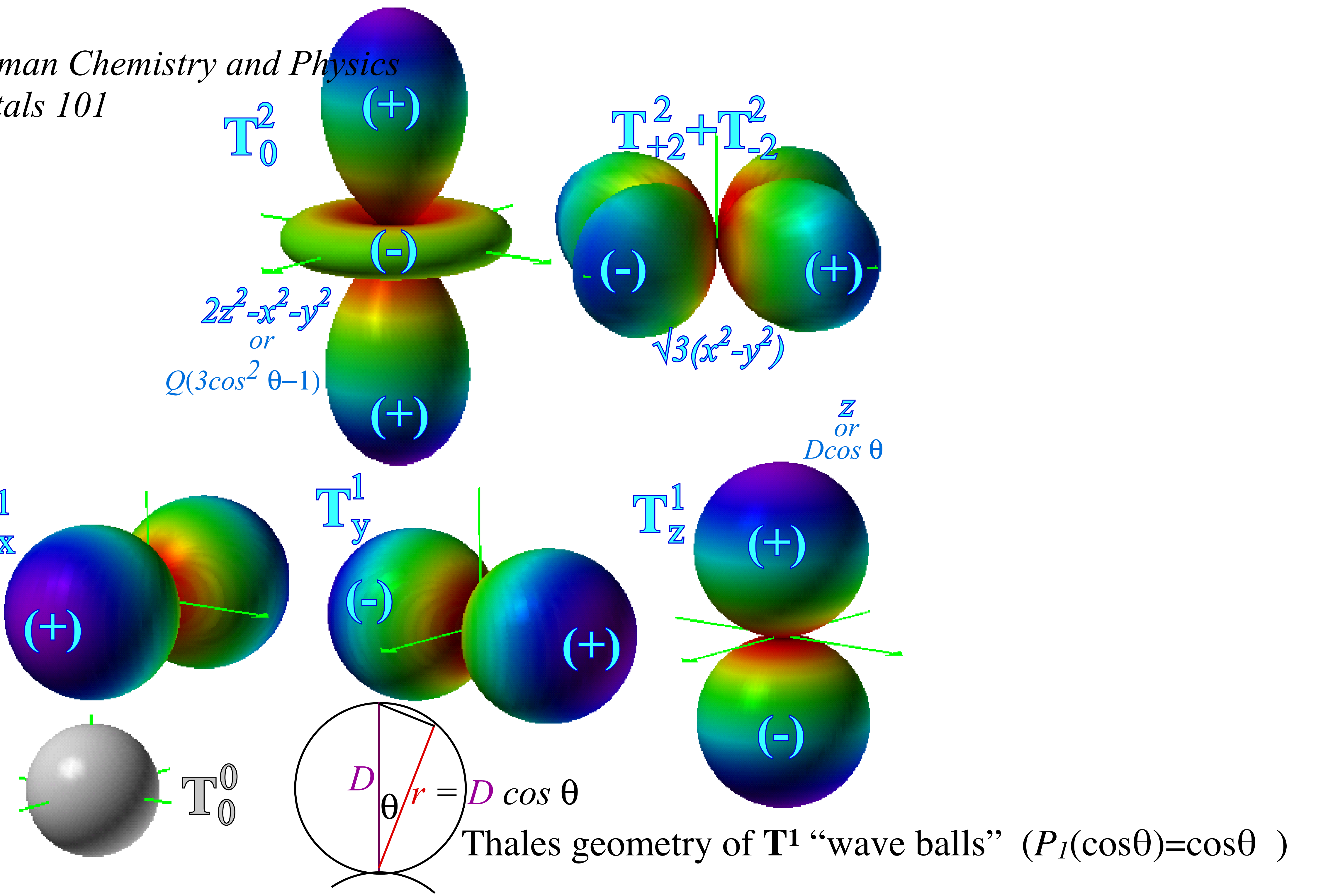
$$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\,\frac{\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

Review of freshman Chemistry and Physics
Electronic orbitals 101

Quadrupoles
(d-orbitals)

Dipoles
(p-orbitals)

Monopole
(s-orbital)



Thales geometry of $\mathbf{T}^1$ "wave balls" ($P_1(\cos\theta)=\cos\theta$)

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

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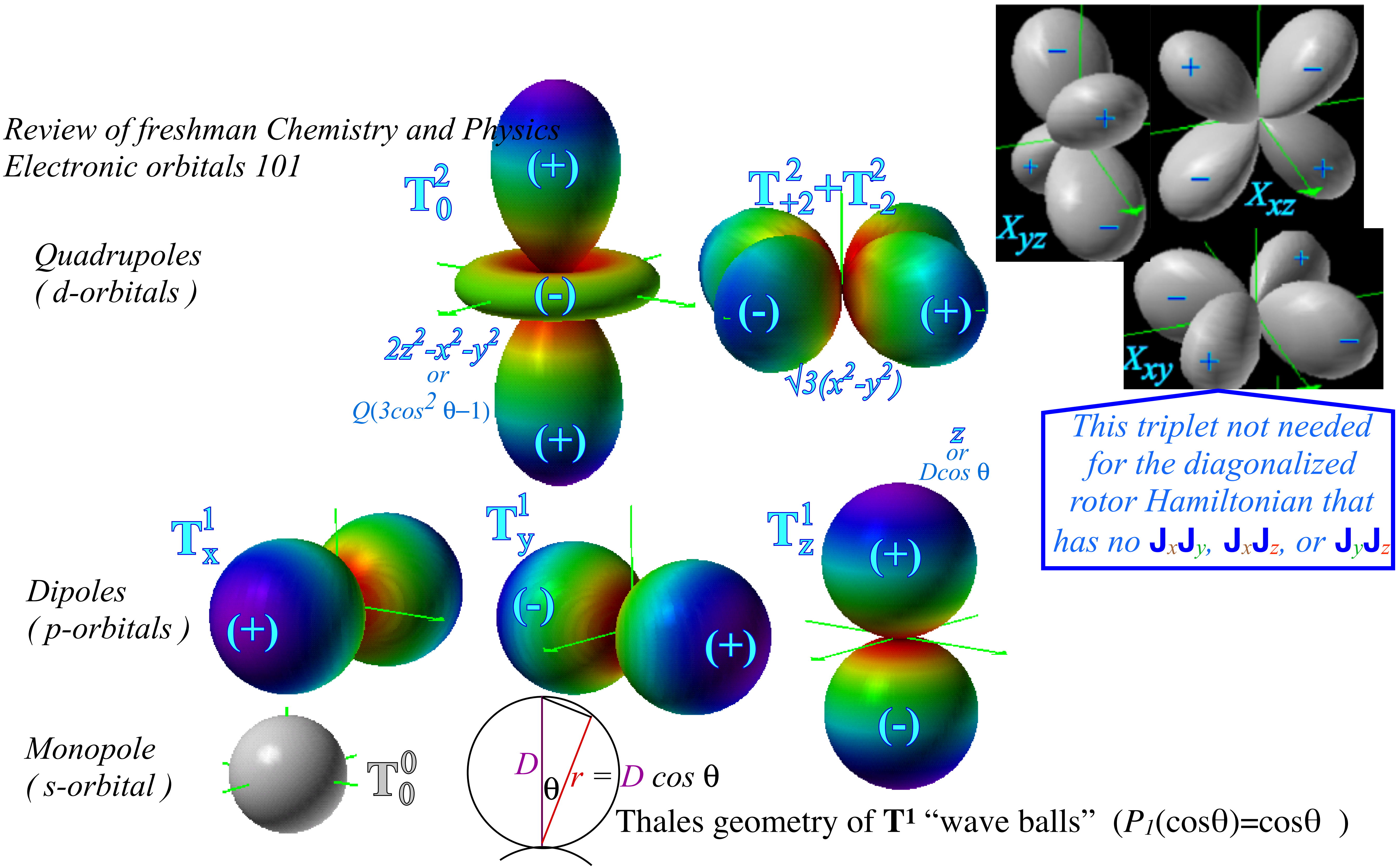

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$$\mathbf{H}=A\mathbf{J}_x^{\ 2}+B\mathbf{J}_y^{\ 2}+C\mathbf{J}_z^{\ 2}$$

Kinetic energy inertial coefficients: $A=\frac{1}{2I_x},B=\frac{1}{2I_y},C=\frac{1}{2I_z}$

$$=(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C)(\mathbf{J}_x^{\ 2}+\mathbf{J}_y^{\ 2}+\mathbf{J}_z^{\ 2})$$

$$+(\frac{-1}{6}A+\frac{-1}{6}B+\frac{2}{6}C)(-\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}+2\mathbf{J}_z^{\ 2})$$

$$+(\frac{1}{2}A+\frac{-1}{2}B+0\cdot C)(\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}+0)$$

Making symmetric rotor Hamiltonian $\mathbf{H} = B\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

$$\mathbf{T}_0^0 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2 = \mathbf{J}^2$$

$$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$$

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$$+(\tfrac{-1}{6}A + \tfrac{-1}{6}B + \tfrac{2}{6}C)(-\mathbf{J}_x^2 - \mathbf{J}_y^2 + 2\mathbf{J}_z^2)$$

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$$+(\tfrac{-1}{3}A + \tfrac{-1}{3}B + \tfrac{2}{3}C)\left(\frac{2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2}{2}\right)$$

$$+(\tfrac{1}{\sqrt{6}}A + \tfrac{-1}{\sqrt{6}}B + 0 \cdot C)\left(\sqrt{6}\,\frac{\mathbf{J}_x^2 - \mathbf{J}_y^2}{2}\right)$$

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

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$$+(\frac{1}{\sqrt{6}}A+\frac{-1}{\sqrt{6}}B+0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2})$$

$$=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)$$
$$+\frac{1}{3}(-A-B+2C)(\mathbf{T}_0^2)$$
$$+\frac{1}{\sqrt{6}}(A-B)(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

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$$\mathbf{T}_0^0=\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2=\mathbf{J}^2$$

$$\mathbf{T}_0^2=\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$$

$$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

Kinetic energy inertial coefficients: $A=\frac{1}{2I_x},\ B=\frac{1}{2I_y},\ C=\frac{1}{2I_z}$

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

$$=\left(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C\right)\left(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2\right)=\left(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C\right)\left(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2\right)=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)$$

$$+\left(\frac{-1}{6}A+\frac{-1}{6}B+\frac{2}{6}C\right)\left(-\mathbf{J}_x^2-\mathbf{J}_y^2+2\mathbf{J}_z^2\right)\quad+\left(\frac{-1}{3}A+\frac{-1}{3}B+\frac{2}{3}C\right)\left(\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}\right)\quad+\frac{1}{3}(-A-B+2C)(\mathbf{T}_0^2)$$

$$+\left(\frac{1}{2}A+\frac{-1}{2}B+0\cdot C\right)\left(\mathbf{J}_x^2-\mathbf{J}_y^2+0\right)\quad+\left(\frac{1}{\sqrt{6}}A+\frac{-1}{\sqrt{6}}B+0\cdot C\right)\left(\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2}\right)\quad+\frac{1}{\sqrt{6}}(A-B)(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)+\frac{1}{3}(2C-A-B)(\mathbf{T}_0^2)+\frac{A-B}{\sqrt{6}}(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

$$\mathbf{T}_0^0=\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2=\mathbf{J}^2$$

$$\mathbf{T}_0^2=\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$$

$$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

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

Kinetic energy inertial coefficients : $A=\frac{1}{2I_x},B=\frac{1}{2I_y},C=\frac{1}{2I_z}$

$$\begin{aligned}
&=(\tfrac{1}{3}A+\tfrac{1}{3}B+\tfrac{1}{3}C)(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2) \\
&+(\tfrac{-1}{6}A+\tfrac{-1}{6}B+\tfrac{2}{6}C)(-\mathbf{J}_x^2-\mathbf{J}_y^2+2\mathbf{J}_z^2) \\
&+(\tfrac{1}{2}A+\tfrac{-1}{2}B+0\cdot C)(\mathbf{J}_x^2-\mathbf{J}_y^2+0)
\end{aligned}$$

$$\begin{aligned}
&=(\tfrac{1}{3}A+\tfrac{1}{3}B+\tfrac{1}{3}C)(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2) \\
&+(\tfrac{-1}{3}A+\tfrac{-1}{3}B+\tfrac{2}{3}C)(\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}) \\
&+(\tfrac{1}{\sqrt{6}}A+\tfrac{-1}{\sqrt{6}}B+0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2})
\end{aligned}$$

$$\begin{aligned}
&=\tfrac{1}{3}(A+B+C)(\mathbf{T}_0^0) \\
&+\tfrac{1}{3}(-A-B+2C)(\mathbf{T}_0^2) \\
&+\tfrac{1}{\sqrt{6}}(A-B)(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)
\end{aligned}$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)+\frac{1}{3}(2C-A-B)(\mathbf{T}_0^2)+\frac{A-B}{\sqrt{6}}(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{J}^2)+\frac{1}{3}(2C-A-B)(\mathbf{J}^2\frac{3\cos^2\theta-1}{2})+\frac{A-B}{\sqrt{6}}(\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi)$$

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

$$\mathbf{T}_0^0=\mathbf{J}_x^{\ 2}+\mathbf{J}_y^{\ 2}+\mathbf{J}_z^{\ 2}=\mathbf{J}^2$$

$$\mathbf{T}_0^2=\frac{2\mathbf{J}_z^{\ 2}-\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$$

$$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\frac{\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

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

Kinetic energy inertial coefficients : $A=\frac{1}{2I_x}, B=\frac{1}{2I_y}, C=\frac{1}{2I_z}$

$$=\left(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C\right)(\mathbf{J}_x^{\ 2}+\mathbf{J}_y^{\ 2}+\mathbf{J}_z^{\ 2})\quad=\left(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C\right)(\mathbf{J}_x^{\ 2}+\mathbf{J}_y^{\ 2}+\mathbf{J}_z^{\ 2})\quad=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)$$

$$+\left(\frac{-1}{6}A+\frac{-1}{6}B+\frac{2}{6}C\right)(-\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}+2\mathbf{J}_z^{\ 2})\quad+\left(\frac{-1}{3}A+\frac{-1}{3}B+\frac{2}{3}C\right)\left(\frac{2\mathbf{J}_z^{\ 2}-\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}}{2}\right)\quad+\frac{1}{3}(-A-B+2C)(\mathbf{T}_0^2)$$

$$+\left(\frac{1}{2}A+\frac{-1}{2}B+0\cdot C\right)(\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}+0)\quad+\left(\frac{1}{\sqrt{6}}A+\frac{-1}{\sqrt{6}}B+0\cdot C\right)\left(\sqrt{6}\frac{\mathbf{J}_x^{\ 2}-\mathbf{J}_y^{\ 2}}{2}\right)\quad+\frac{1}{\sqrt{6}}(A-B)(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^{\ 2}+B\mathbf{J}_y^{\ 2}+C\mathbf{J}_z^{\ 2}=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)+\frac{1}{3}(2C-A-B)(\mathbf{T}_0^2)+\frac{A-B}{\sqrt{6}}(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^{\ 2}+B\mathbf{J}_y^{\ 2}+C\mathbf{J}_z^{\ 2}=\frac{1}{3}(A+B+C)(\mathbf{J}^2)+\frac{1}{3}(2C-A-B)\left(\mathbf{J}^2\frac{3\cos^2\theta-1}{2}\right)+\frac{A-B}{\sqrt{6}}\left(\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi\right)$$

$$\mathbf{H}=A\mathbf{J}_x^{\ 2}+B\mathbf{J}_y^{\ 2}+C\mathbf{J}_z^{\ 2}=\mathbf{J}^2\left[\frac{A+B+C}{3}+\frac{2C-A-B}{6}(3\cos^2\theta-1)+\frac{A-B}{2}\sin^2\theta\cos 2\phi\right]$$

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

$$\mathbf{T}_0^0=\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2=\mathbf{J}^2$$

$$\mathbf{T}_0^2=\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$$

$$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

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

Kinetic energy inertial coefficients: $A=\frac{1}{2I_x},\ B=\frac{1}{2I_y},\ C=\frac{1}{2I_z}$

$$=(\tfrac{1}{3}A+\tfrac{1}{3}B+\tfrac{1}{3}C)(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2)\quad=(\tfrac{1}{3}A+\tfrac{1}{3}B+\tfrac{1}{3}C)(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2)\quad=\tfrac{1}{3}(A+B+C)(\mathbf{T}_0^0)$$

$$+(\tfrac{-1}{6}A+\tfrac{-1}{6}B+\tfrac{2}{6}C)(-\mathbf{J}_x^2-\mathbf{J}_y^2+2\mathbf{J}_z^2)\quad+(\tfrac{-1}{3}A+\tfrac{-1}{3}B+\tfrac{2}{3}C)(\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2})\quad+\tfrac{1}{3}(-A-B+2C)(\mathbf{T}_0^2)$$

$$+(\tfrac{1}{2}A+\tfrac{-1}{2}B+0\cdot C)(\mathbf{J}_x^2-\mathbf{J}_y^2+0)\quad+(\tfrac{1}{\sqrt{6}}A+\tfrac{-1}{\sqrt{6}}B+0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2})\quad+\tfrac{1}{\sqrt{6}}(A-B)(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)+\frac{1}{3}(2C-A-B)(\mathbf{T}_0^2)+\frac{A-B}{\sqrt{6}}(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{J}^2)+\frac{1}{3}(2C-A-B)(\mathbf{J}^2\frac{3\cos^2\theta-1}{2})+\frac{A-B}{\sqrt{6}}(\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi)$$

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\mathbf{J}^2\left[\frac{A+B+C}{3}+\frac{2C-A-B}{6}(3\cos^2\theta-1)+\frac{A-B}{2}\sin^2\theta\cos 2\phi\right]$$

Resulting semi-classical symmetric top Hamiltonian expansion: $(A=B)$

$$\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\mathbf{J}^2\left[\frac{B+B+C}{3}+\frac{2C-B-B}{6}(3\cos^2\theta-1)+\frac{B-B}{2}\sin^2\theta\cos 2\phi\right]=\mathbf{J}^2\left[B+\frac{C-B}{3}3\cos^2\theta\right]$$

Making symmetric rotor Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *out of scalar* $\mathbf{T}_0^2$ *and tensor* $\mathbf{T}_q^2$ *operators*

$$\mathbf{T}_0^0=\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2=\mathbf{J}^2 \qquad \mathbf{T}_0^2=\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta) \qquad \mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

Kinetic energy inertial coefficients: $A=\frac{1}{2I_x}, B=\frac{1}{2I_y}, C=\frac{1}{2I_z}$

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

$$=(\tfrac{1}{3}A+\tfrac{1}{3}B+\tfrac{1}{3}C)(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2) \quad =(\tfrac{1}{3}A+\tfrac{1}{3}B+\tfrac{1}{3}C)(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2) \quad =\tfrac{1}{3}(A+B+C)(\mathbf{T}_0^0)$$

$$+(\tfrac{-1}{6}A+\tfrac{-1}{6}B+\tfrac{2}{6}C)(-\mathbf{J}_x^2-\mathbf{J}_y^2+2\mathbf{J}_z^2) \quad +(\tfrac{-1}{3}A+\tfrac{-1}{3}B+\tfrac{2}{3}C)(\frac{2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2}{2}) \quad +\tfrac{1}{3}(-A-B+2C)(\mathbf{T}_0^2)$$

$$+(\tfrac{1}{2}A+\tfrac{-1}{2}B+0\cdot C)(\mathbf{J}_x^2-\mathbf{J}_y^2+0) \quad +(\tfrac{1}{\sqrt{6}}A+\tfrac{-1}{\sqrt{6}}B+0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^2-\mathbf{J}_y^2}{2}) \quad +\tfrac{1}{\sqrt{6}}(A-B)(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{T}_0^0)+\frac{1}{3}(2C-A-B)(\mathbf{T}_0^2)+\frac{A-B}{\sqrt{6}}(\mathbf{T}_2^2+\mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\frac{1}{3}(A+B+C)(\mathbf{J}^2)+\frac{1}{3}(2C-A-B)(\mathbf{J}^2\frac{3\cos^2\theta-1}{2})+\frac{A-B}{\sqrt{6}}(\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi)$$

$$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\mathbf{J}^2\left[\frac{A+B+C}{3}+\frac{2C-A-B}{6}(3\cos^2\theta-1)+\frac{A-B}{2}\sin^2\theta\cos 2\phi\right]$$

Resulting semi-classical symmetric top Hamiltonian expansion: $(A=B)$

$$\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2=\mathbf{J}^2\left[\frac{B+B+C}{3}+\frac{2C-B-B}{6}(3\cos^2\theta-1)+\frac{B-B}{2}\sin^2\theta\cos 2\phi\right]=\mathbf{J}^2\left[B+(C-B)\cos^2\theta\right]$$

$$=B\mathbf{J}^2+(C-B)\mathbf{J}_z^2=B\mathbf{J}^2+(C-B)\mathbf{J}^2\cos^2\theta$$

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J |_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma) \mathbf{R}(\alpha,\beta,\gamma) |_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H} = B\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

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

Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

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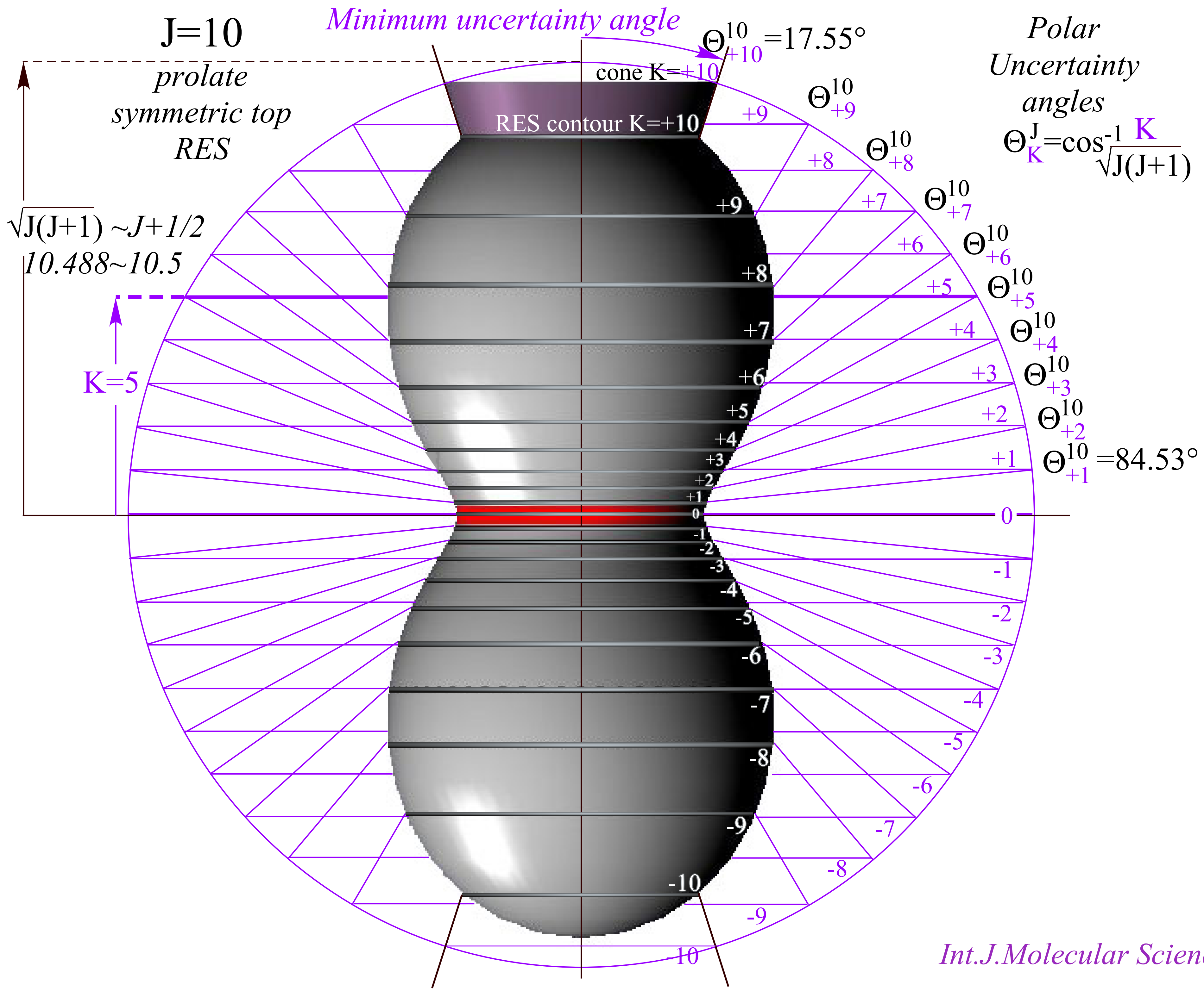
Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions

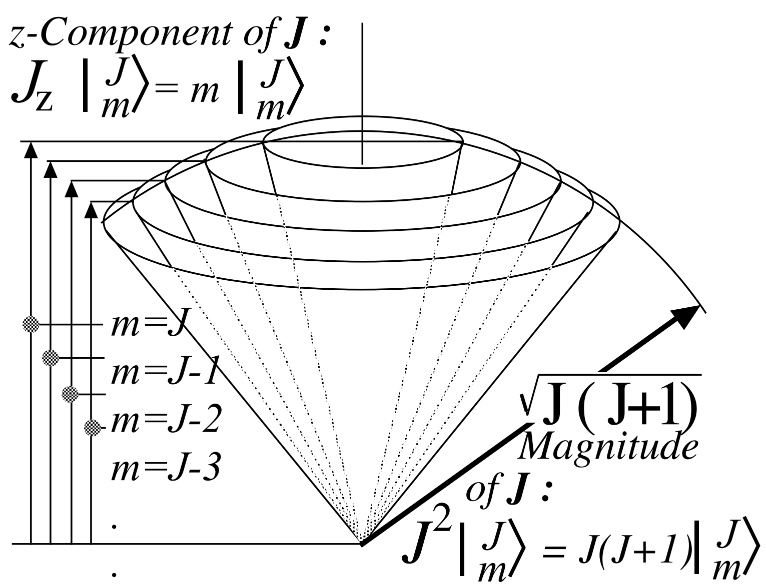
Plot Hamiltonian $\mathbf{H}=B\mathbf{J}^2+(C-B)\mathbf{J}_z^{\,2}$ radially as $H(\Theta)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta$

where: $\mathbf{J}_z = |\mathbf{J}|\cos\Theta = \sqrt{J(J+1)}\cos\Theta$

$\left|\begin{matrix} j \\ m, n \end{matrix}\right\rangle$ *Conventional notation:* $n=K$

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





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

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

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

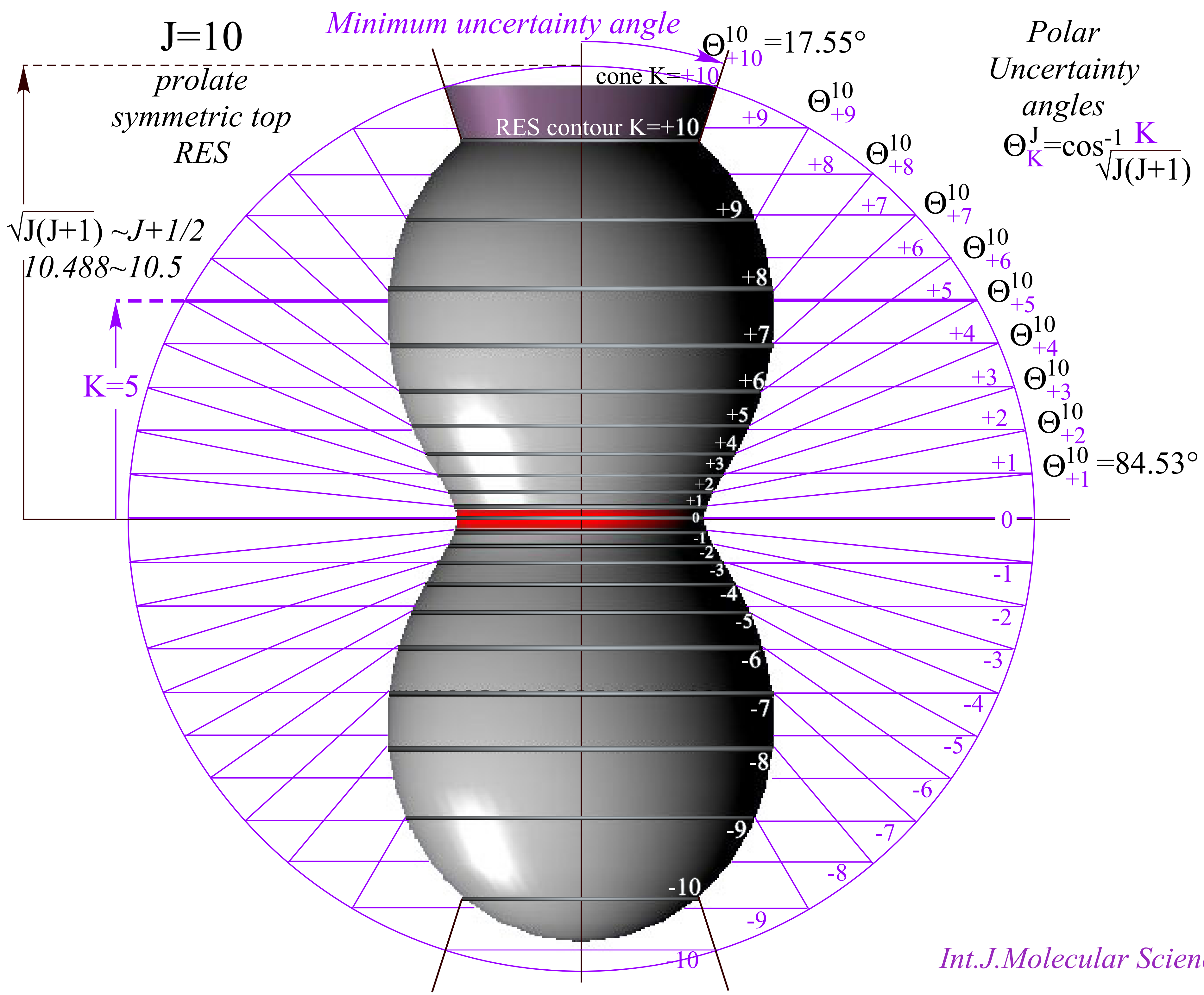
$H(\Theta^J_K) = BJ(J+1) + (C-B)J(J+1)\cos^2\Theta^J_K$

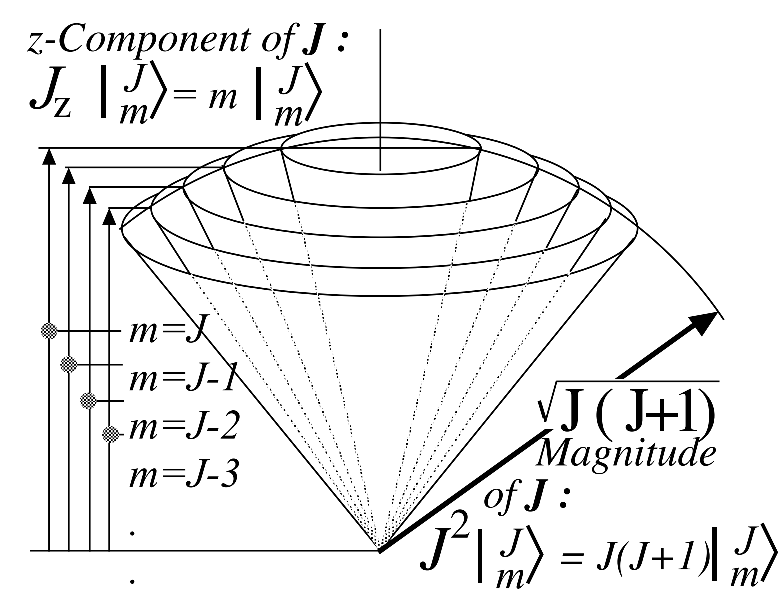
where: $\mathbf{J}_z = |\mathbf{J}|\cos\Theta = \sqrt{J(J+1)}\cos\Theta$

$\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle$

Conventional notation: $n=K$

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





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

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

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

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

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

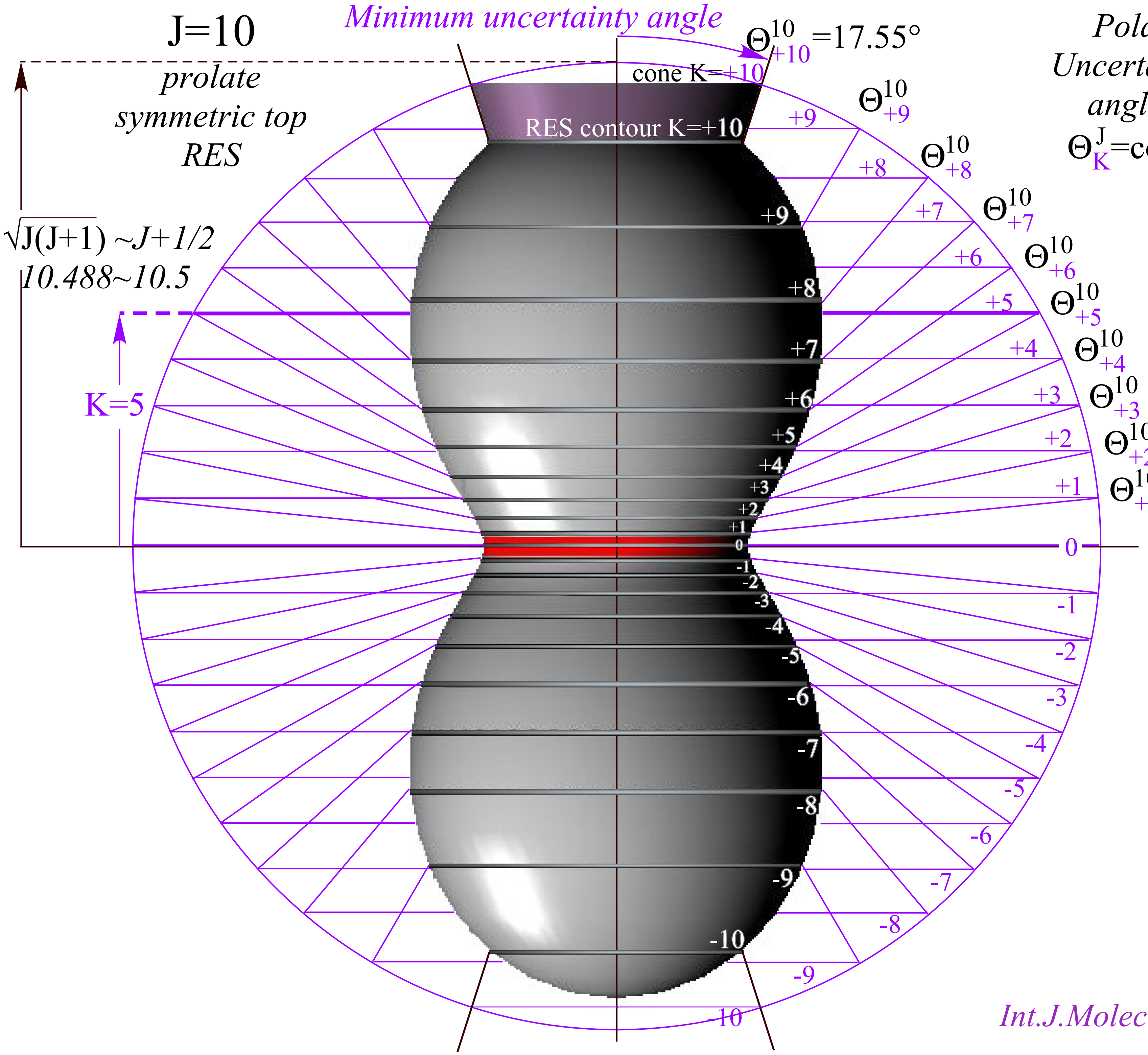
$$=BJ(J+1)+(C-B)K^2$$

where : $\mathbf{J}_z=|\mathbf{J}|\cos\Theta=\sqrt{J(J+1)}\cos\Theta$

$\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle$ Conventional notation: $n=K$

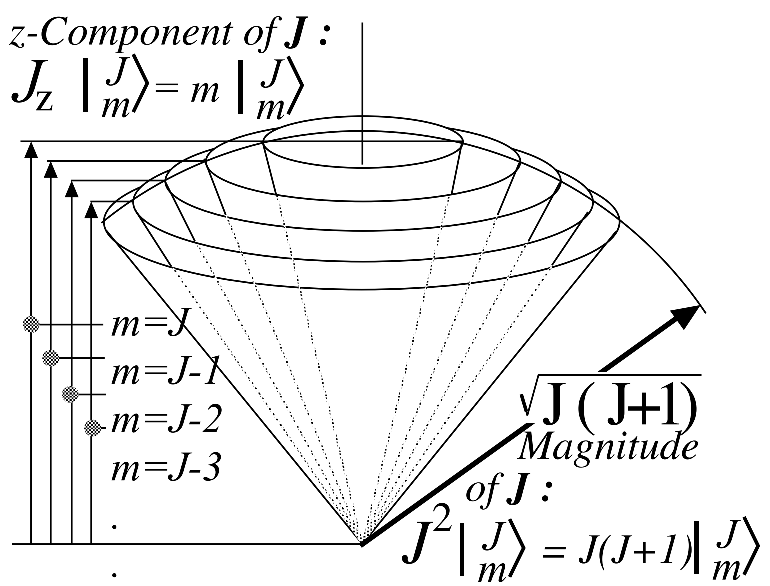
LAB $m=M$ BOD $n=K$

(Here this gives exact quantum eigenvalues!)



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

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



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

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|{}^J_{mn}\rangle = \mathbf{P}_{mn}{}^J|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma) \mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|{}^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|{}^J_{m'n}\rangle$

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Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

Asymmetric Top eigensolutions for J=1-2

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

Kinetic energy inertial coefficients:

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

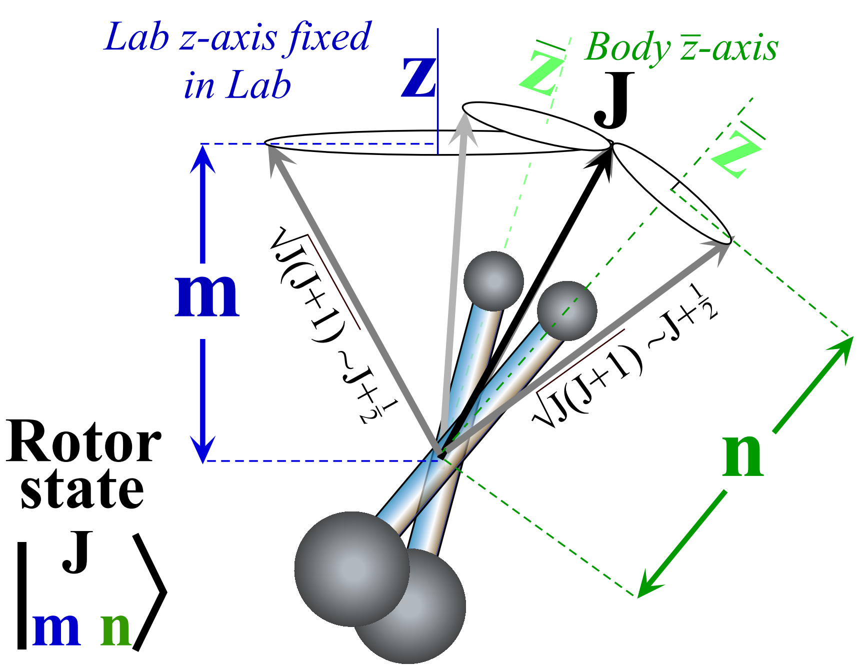
Eigensolution equations:

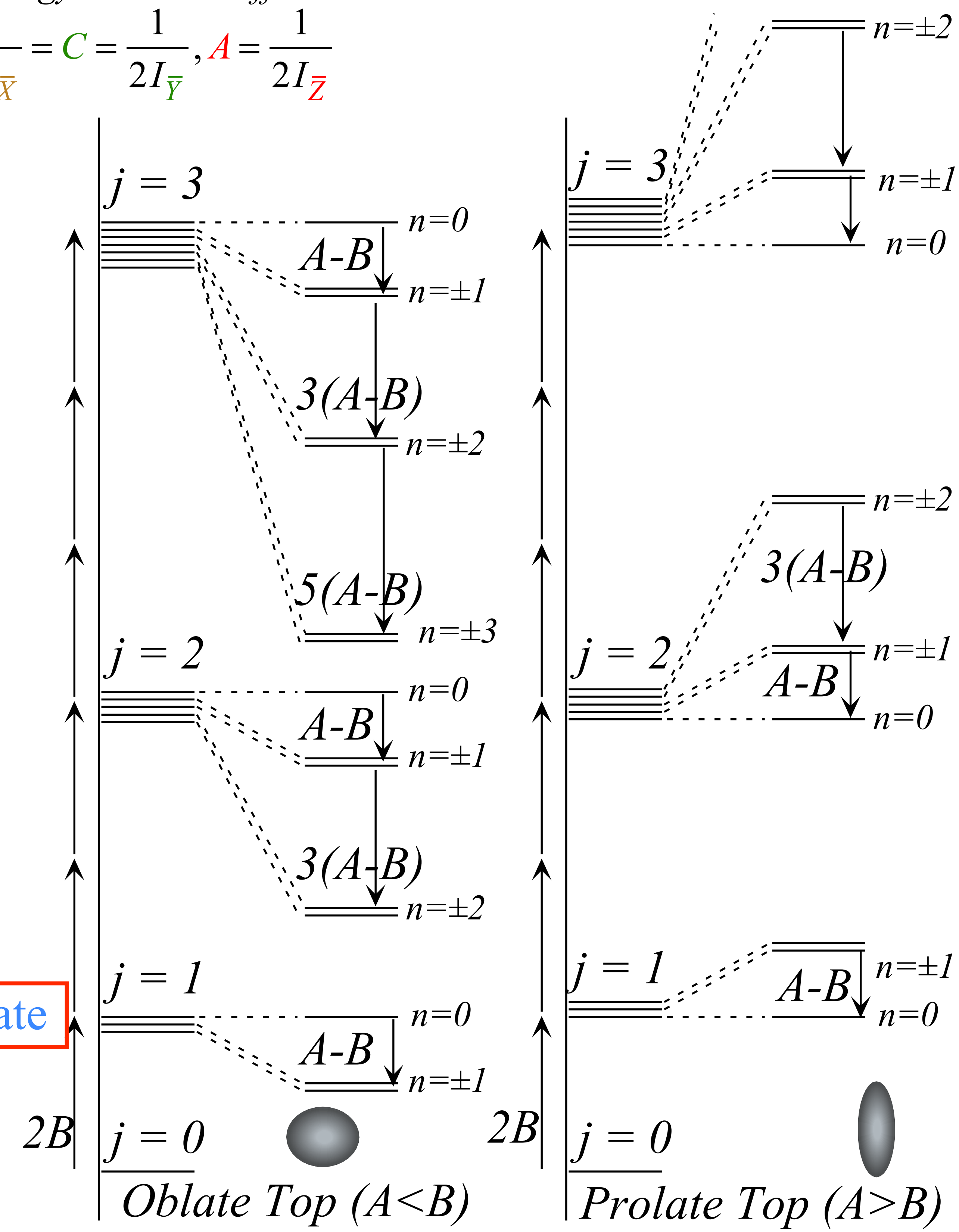
$$\mathbf{H}_{symmetric\ top}\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle$$

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

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

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





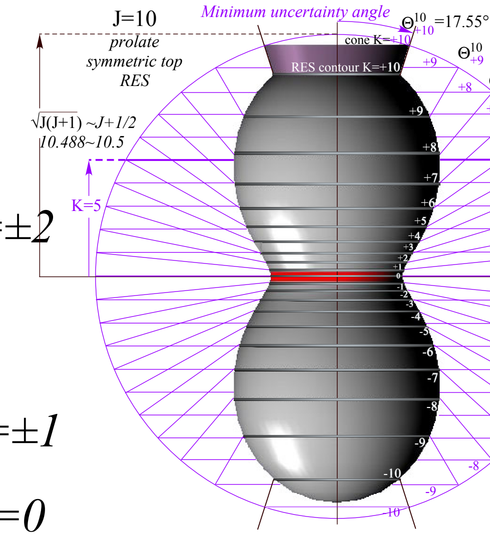
Even n=0 levels are $2j+1$-fold degenerate

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

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

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



Kinetic energy inertial coefficients:

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

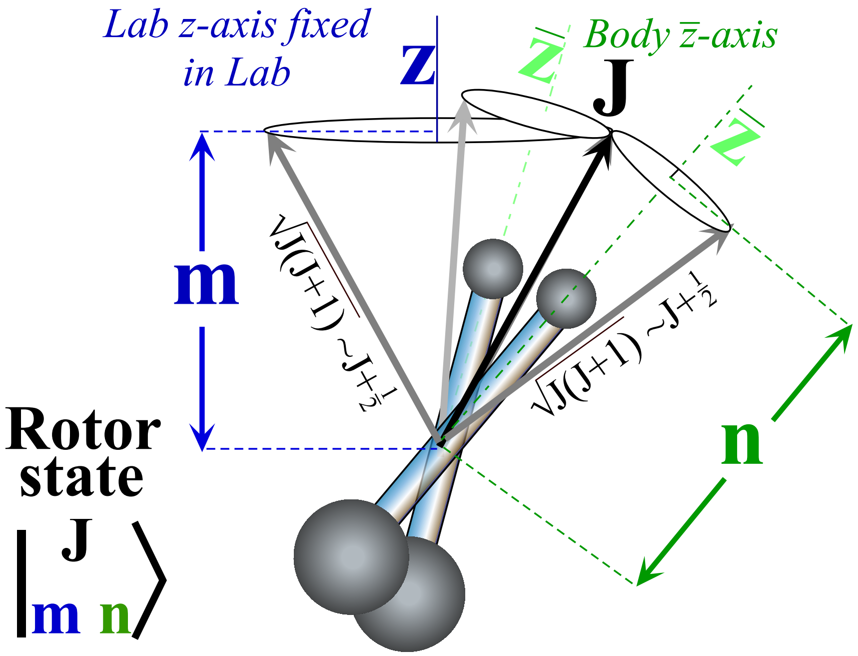
Eigensolution equations:

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

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

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

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



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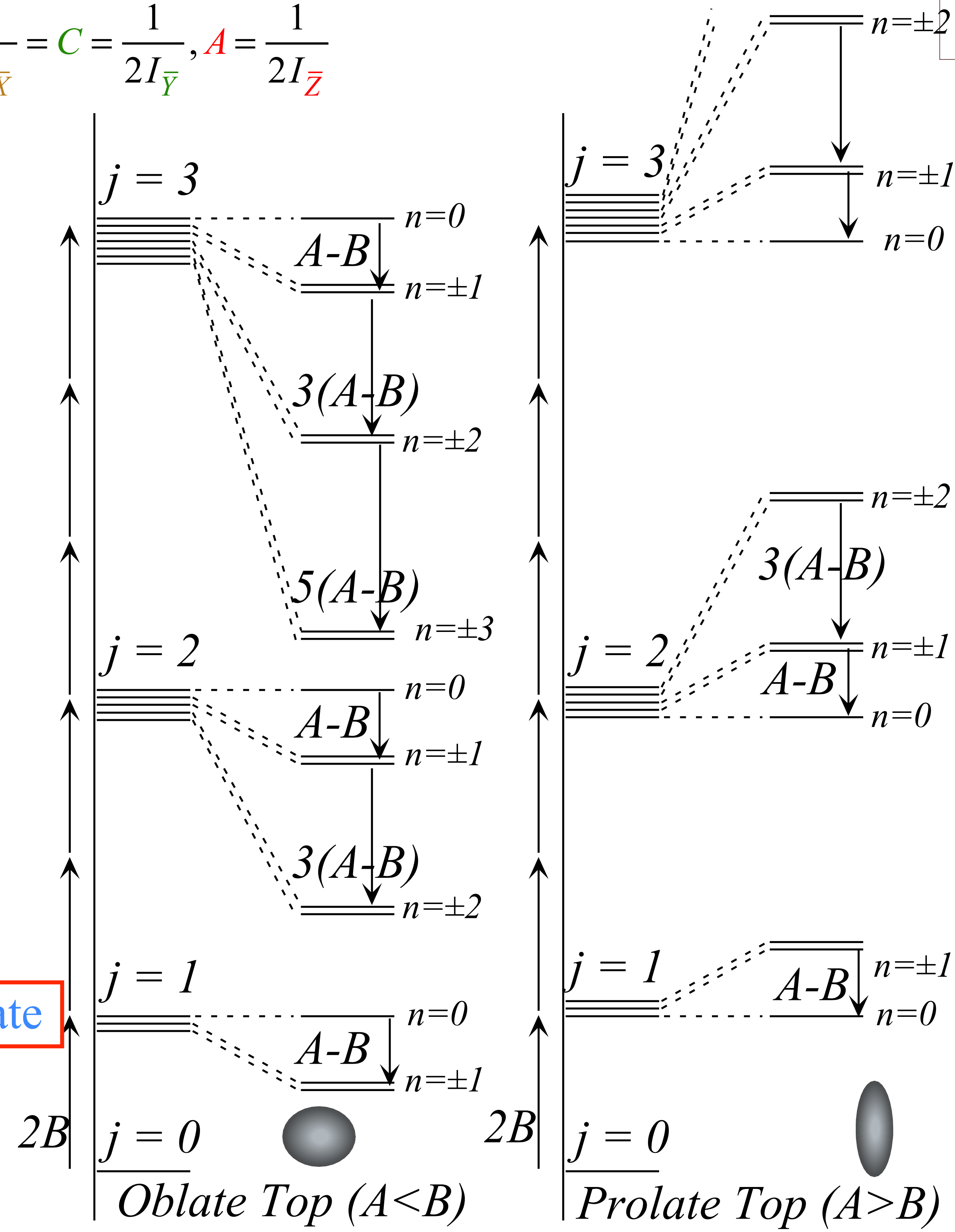

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

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

Kinetic energy inertial coefficients:

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

Eigensolution equations:

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

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

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

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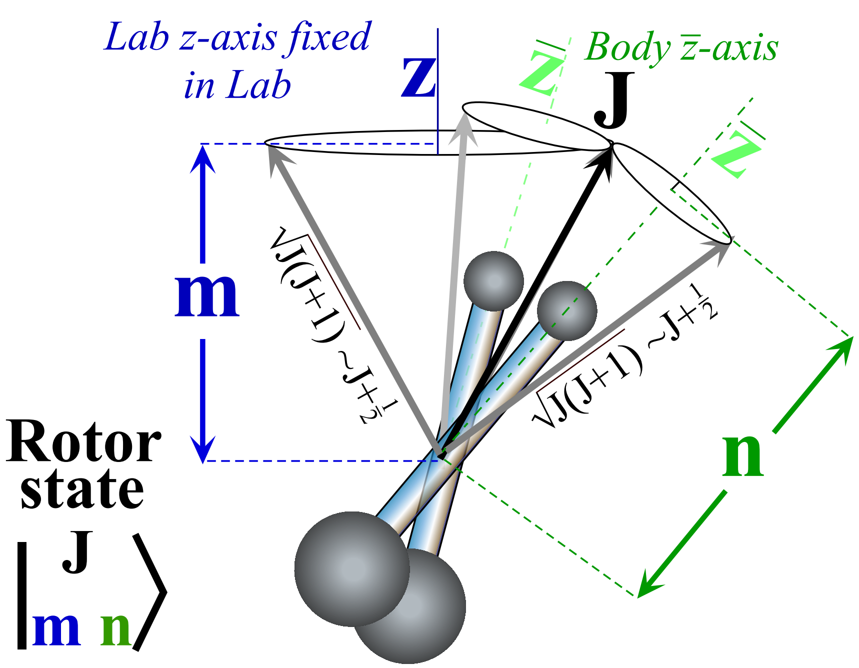

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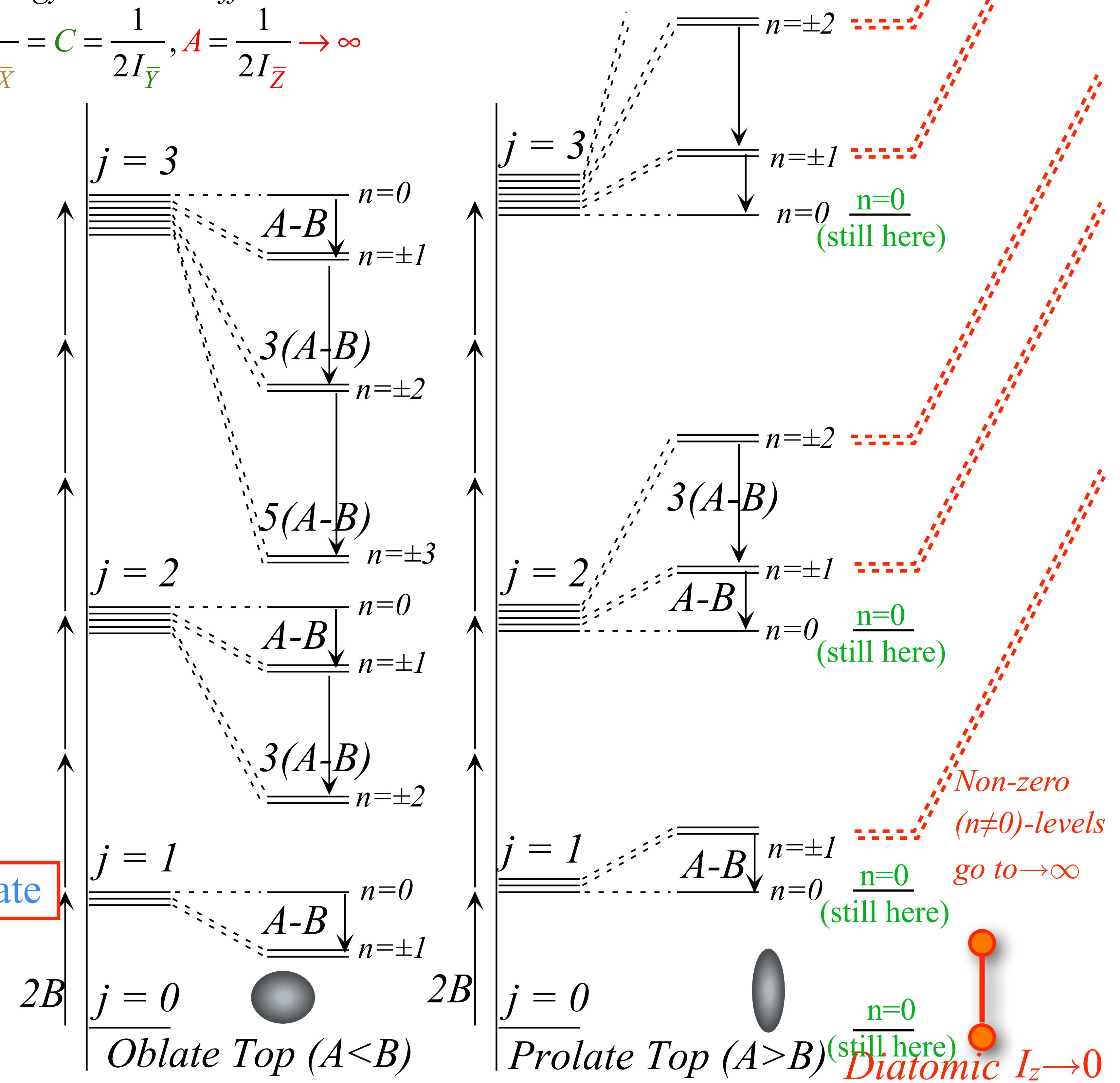

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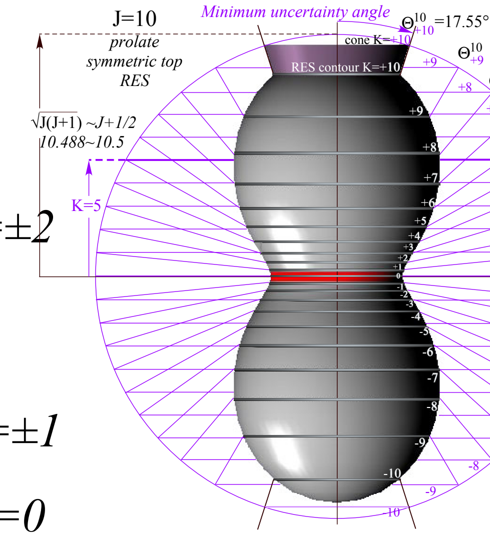

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$$\mathbf{H}_{symmetric\ top}\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle = B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle = \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

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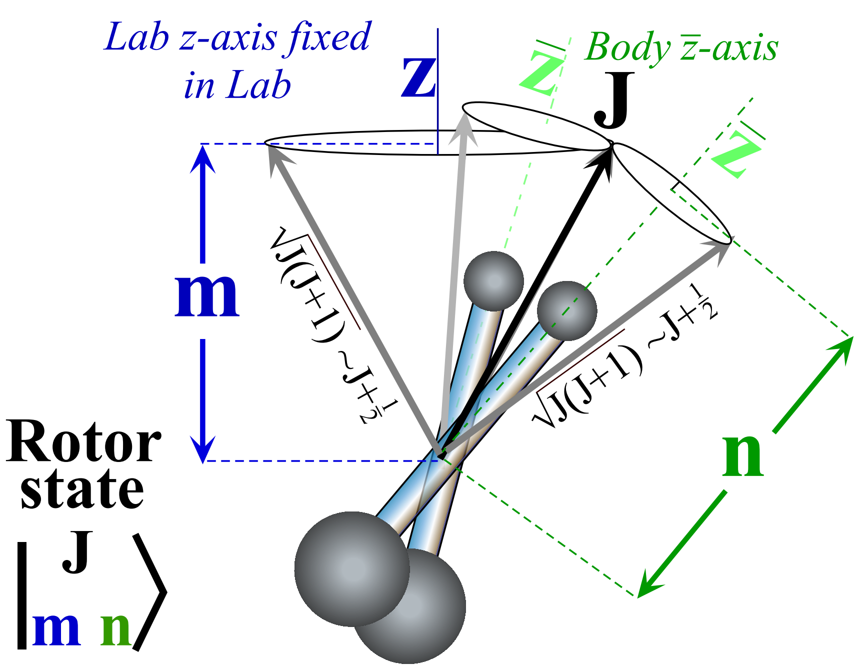

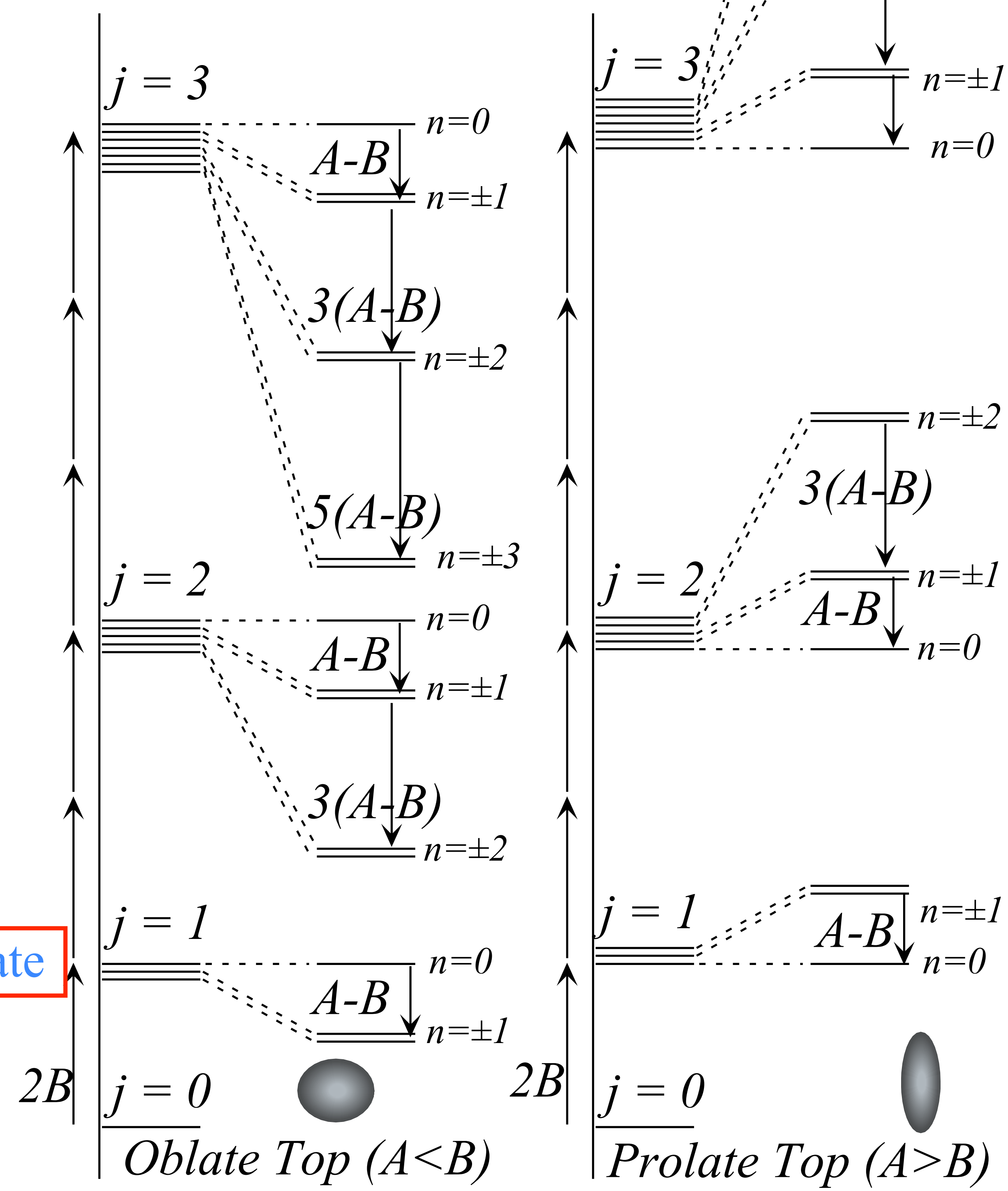

Even $n=0$ levels are $2j+1$-fold degenerate

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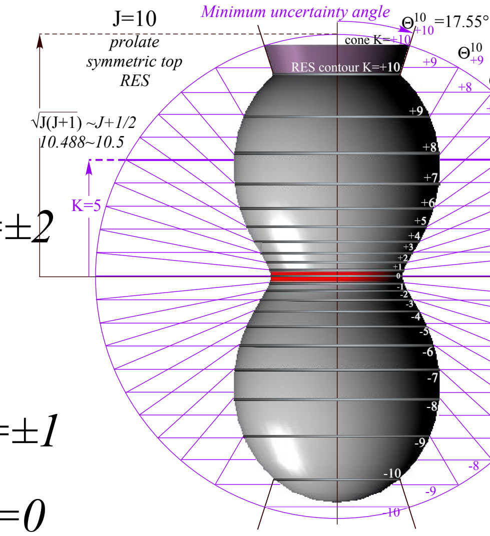
QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

Applications of R(3) rotation and U(2) representations — Molecular and nuclear eigenlevels

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



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Eigensolution equations:

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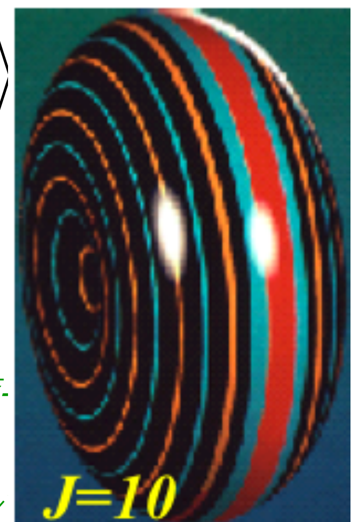
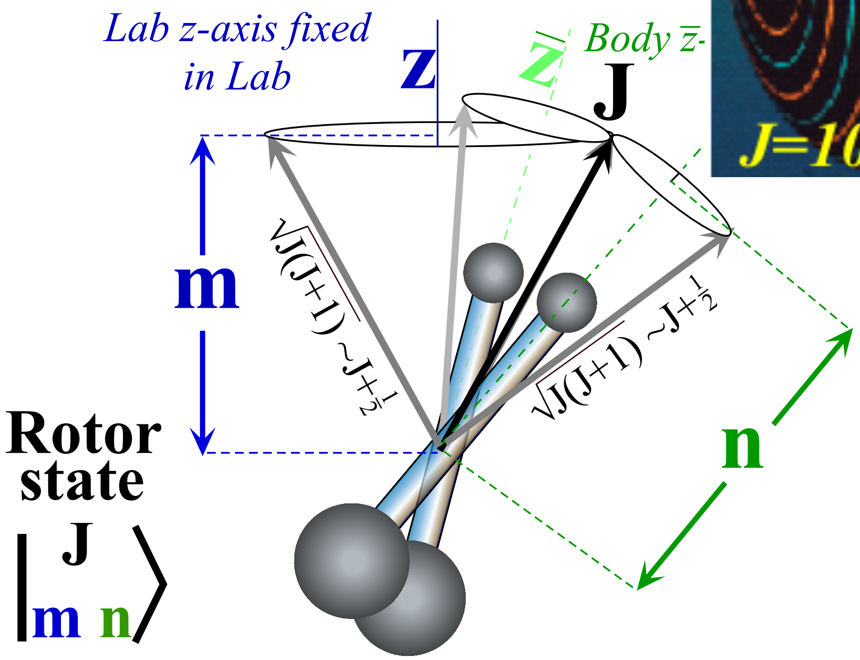
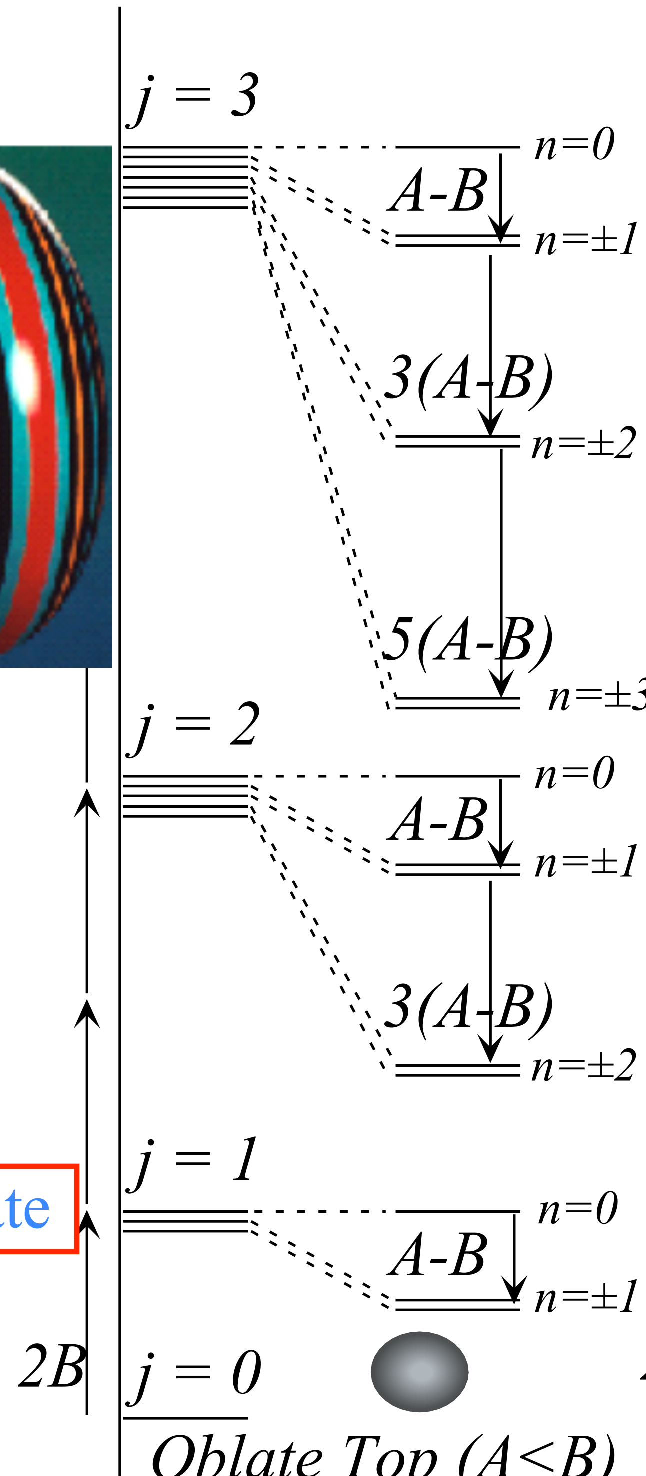
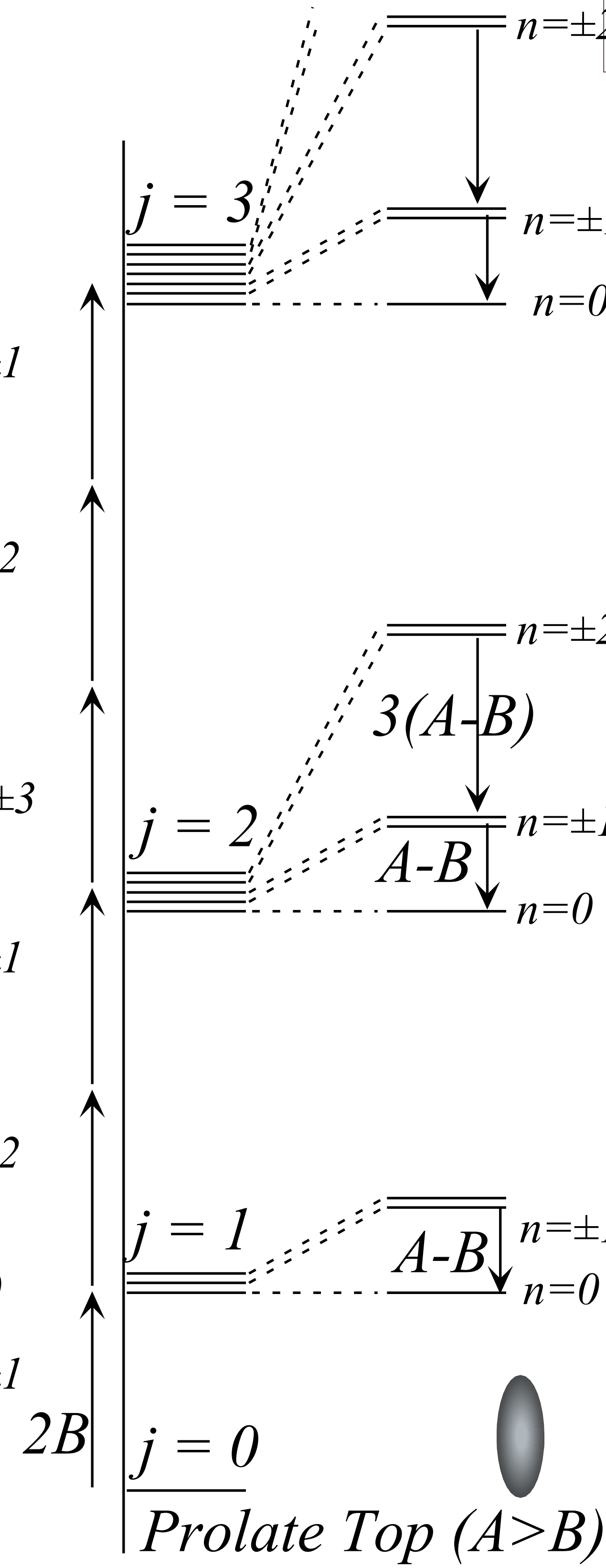
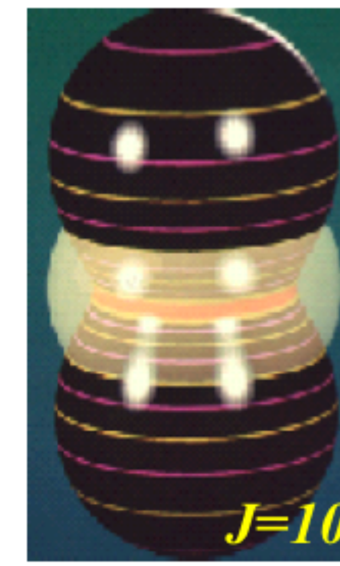
Mock-Mach-Multiplicity is $(2j+1)^2$ for each j











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

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

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J |_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma) \mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \sum_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

➡ *Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels* ⬅

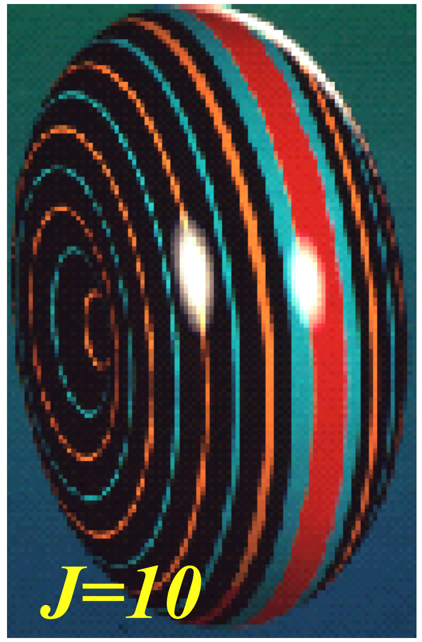
Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

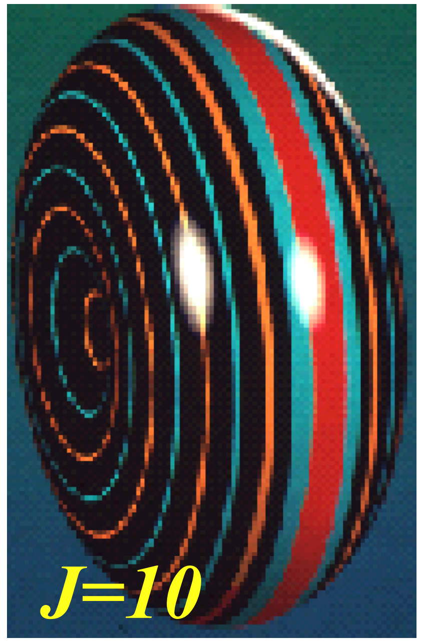
Asymmetric Top eigensolutions for J=1-2

RES of symmetric rotor (Prolate and Oblate)



after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

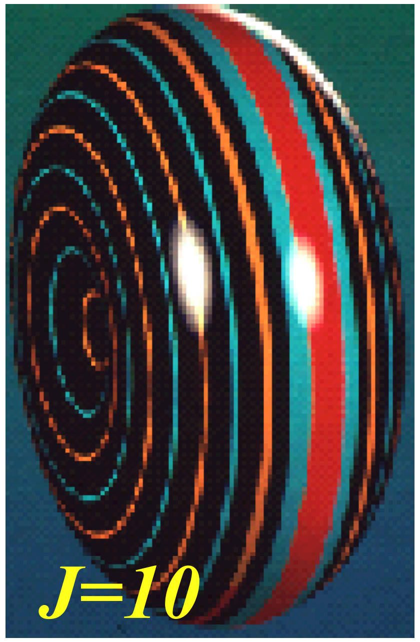
RES of symmetric rotor (Prolate and Oblate)



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

after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

RES of symmetric rotor (Prolate and Oblate)



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Related to RE Surface
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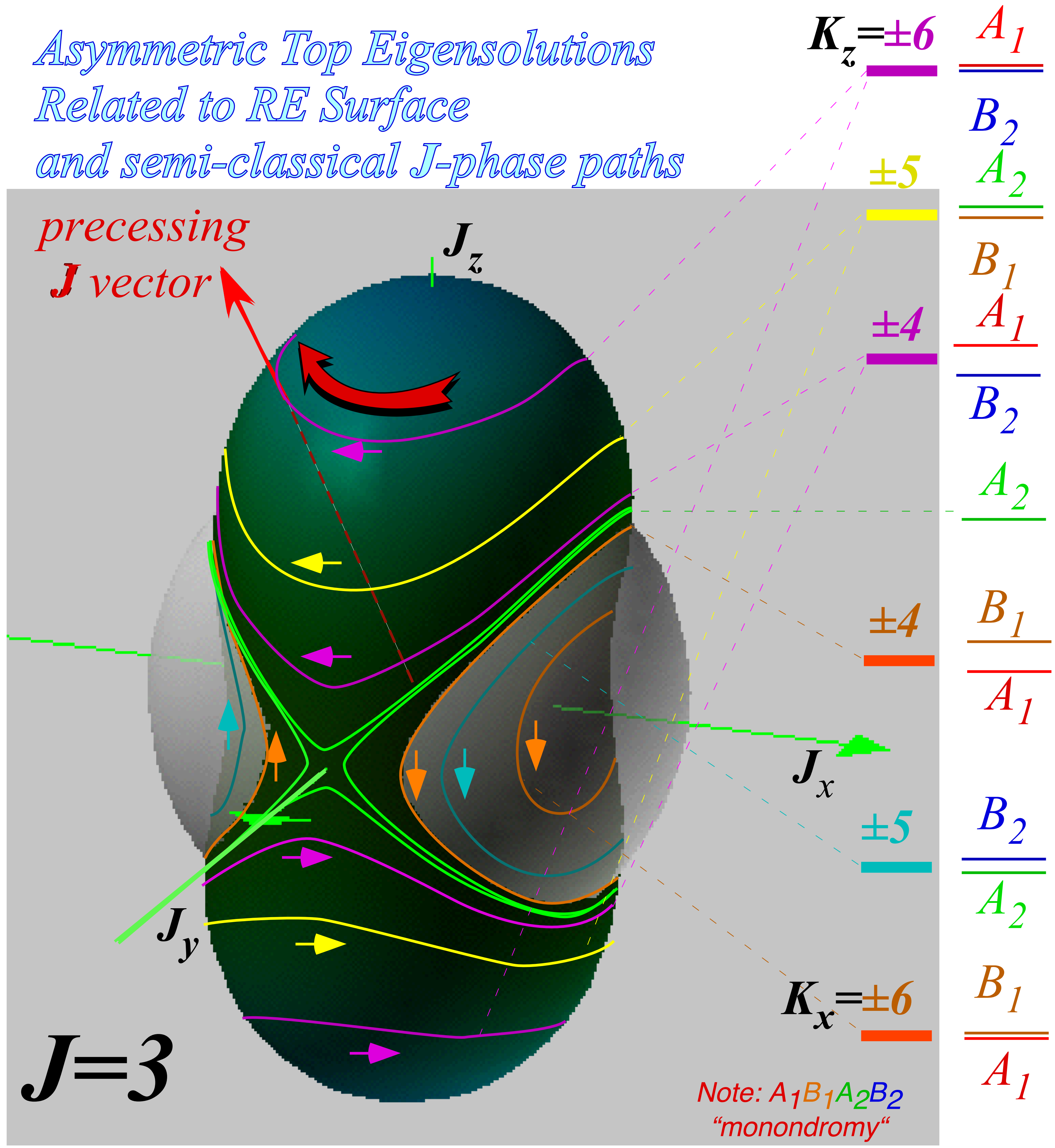
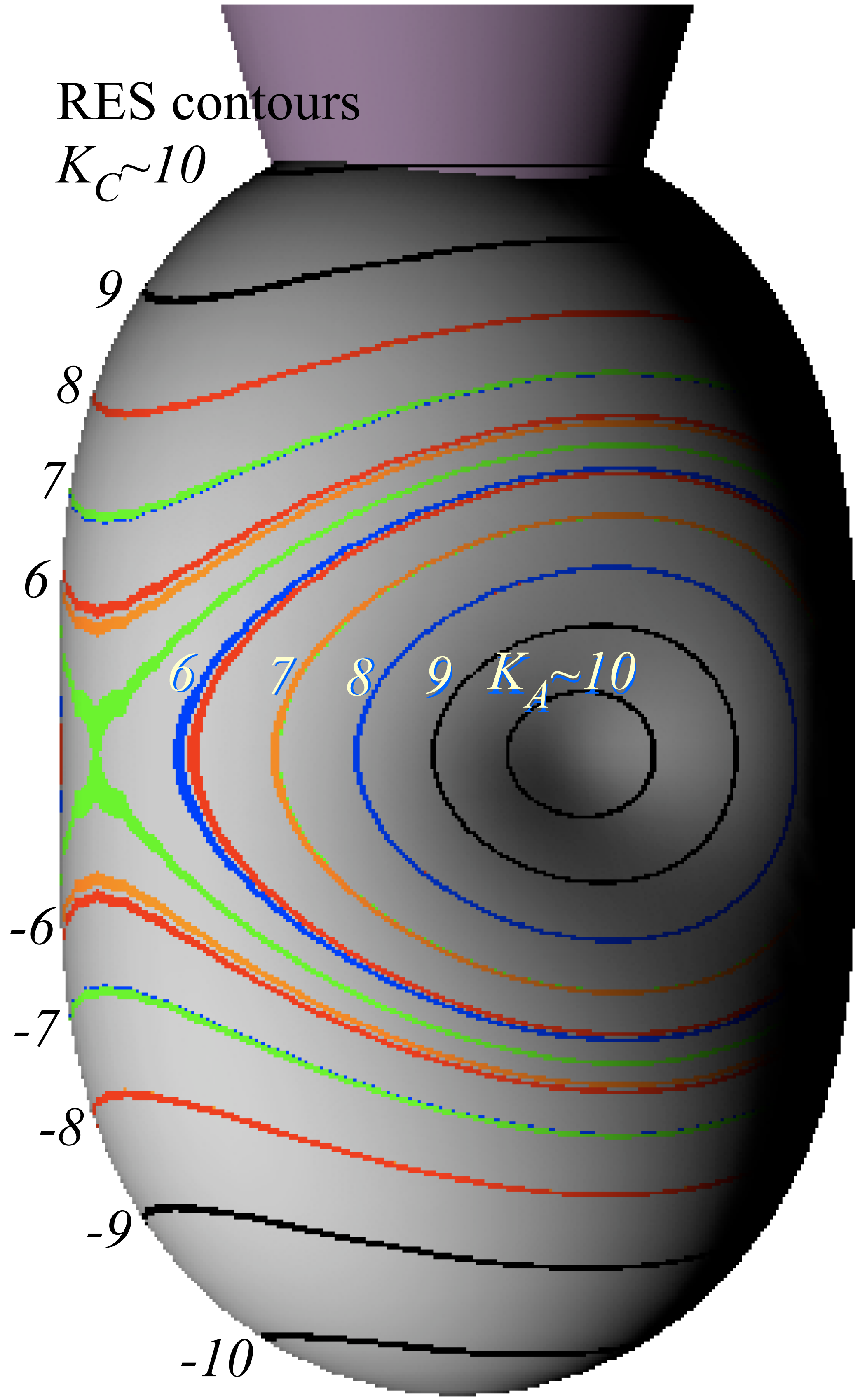


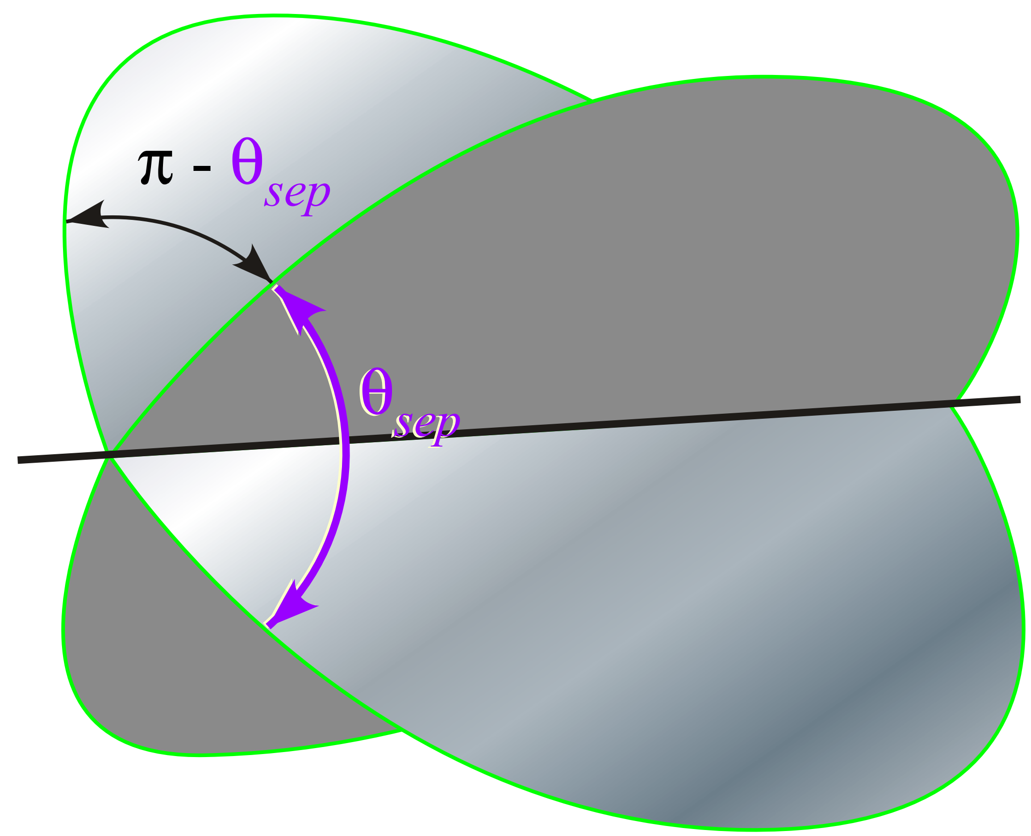
after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

RES contours
K_C~10



Separatrix circle pair
dihedral angle

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



Int.J.Molecular Science 14.(2013) Fig.3 p. 733

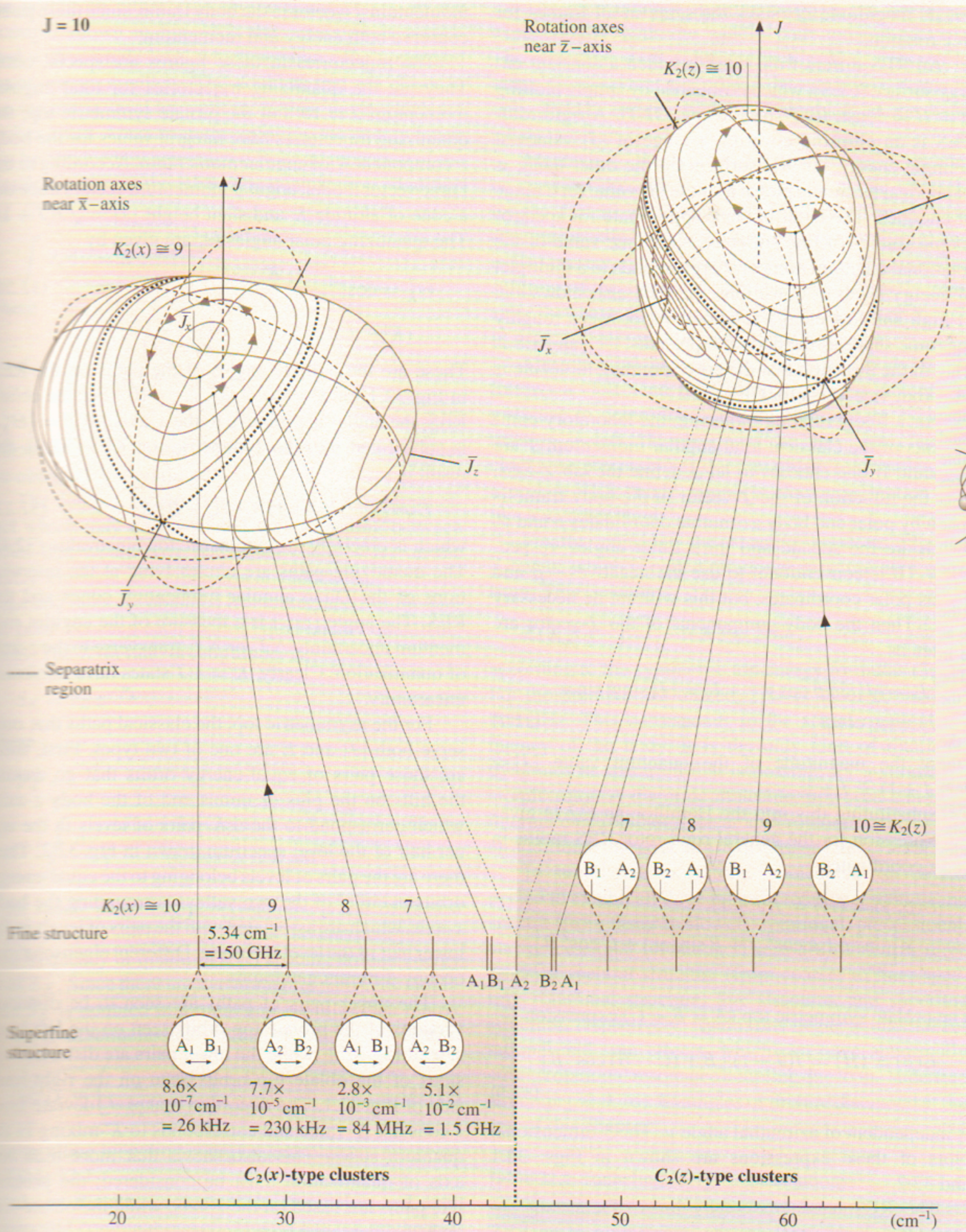
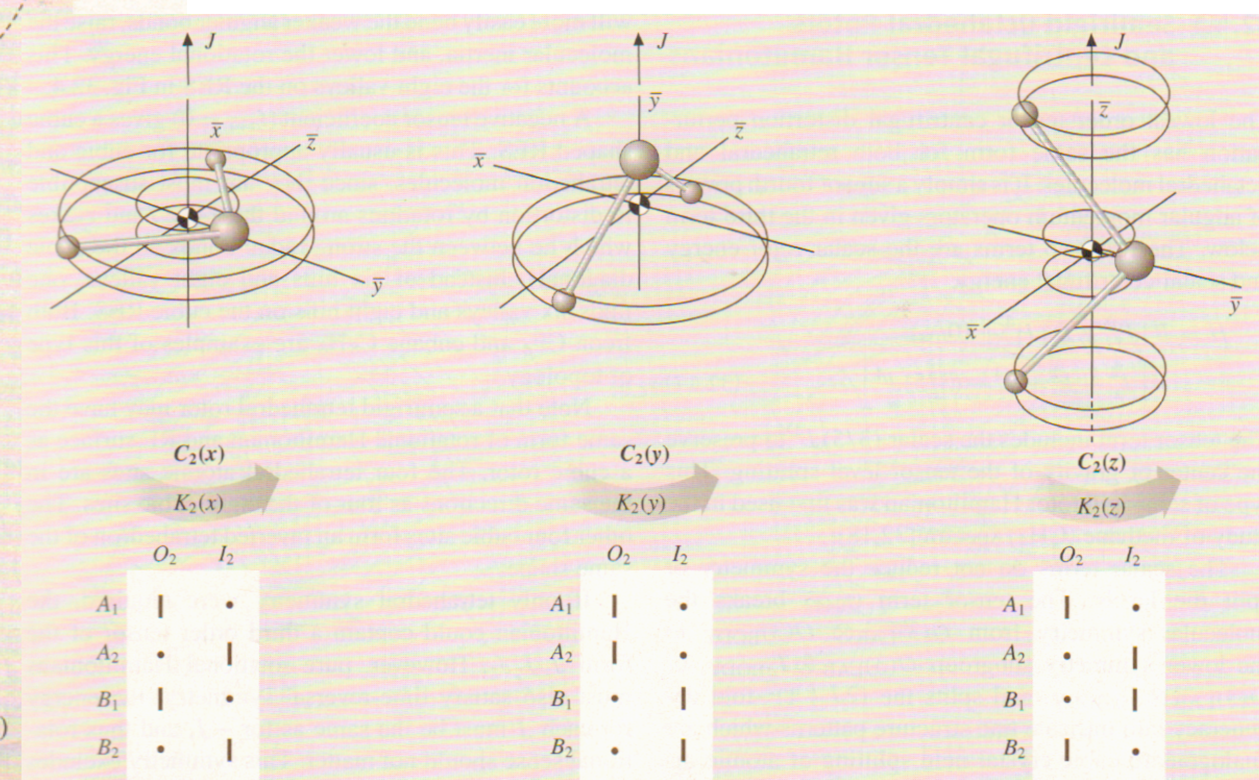


Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator ($A = 0.2$, $B = 0.4$, $C = 0.6\,cm^{-1}$)

Examples of Group⊃Sub-group correlation

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



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

after QTforCA Unit 8. Ch. 25 Fig. 25.4.2

Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$*-wavefunctions*

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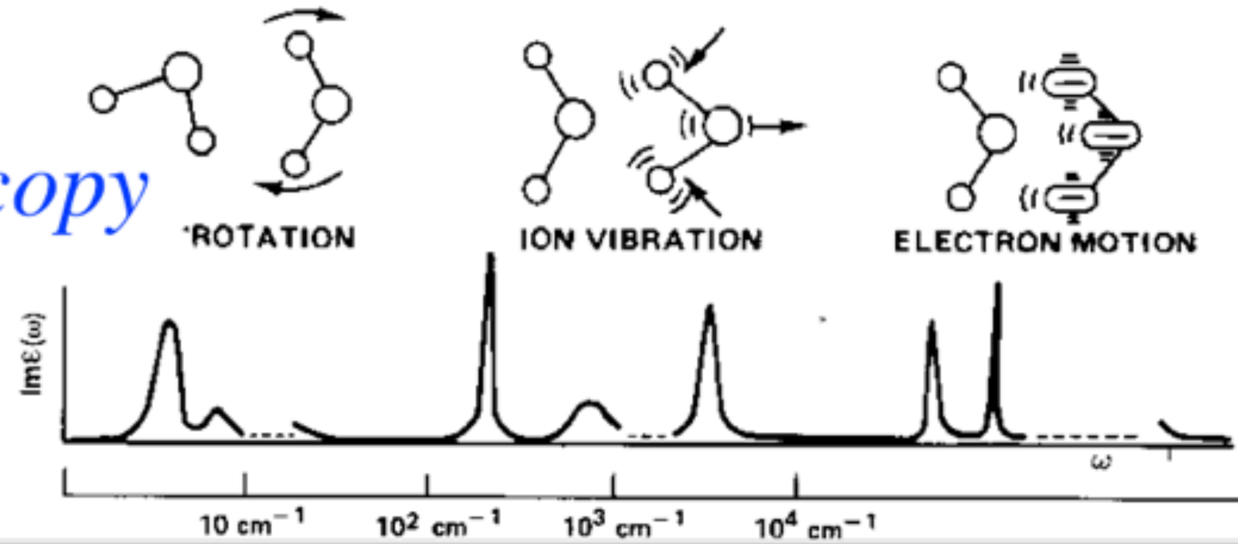
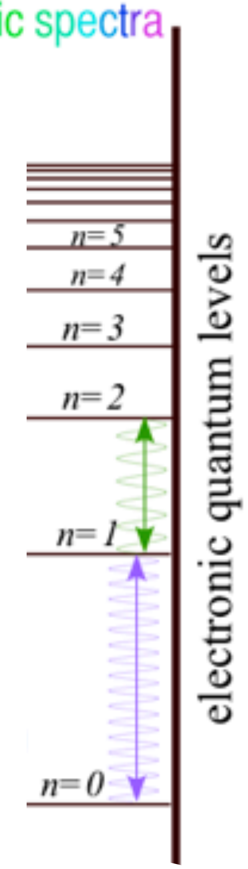


From Fig. 6.5.5.
Principles of Symmetry, Dynamics, and Spectroscopy
W. G. Harter, Wiley Interscience, NY (1993)

The frequency hierarchy

Radio-frequency | Microwave to far-infrared | Infrared | Near-infrared to visible to ultraviolet to X-ray

rotational | vibrational | electronic spectra



Typical VISIBLE
υ=600THz
$1/\lambda=2\cdot 10^6 m^{-1}$
$=2\cdot 10^4 cm^{-1}$
λ=0.5μm
=500nm
=5000A
$E_{eV}=2.48eV$

or

H-Lyman α ULTRAVIOLET
υ=2.4PHz
$E_{Ly\alpha}=10.2eV$
λ=125nm

Spectral Quantities

Frequency υ
Hertz(sec^{-1})
THz $10^{12}s^{-1}$
GHz $10^{9}s^{-1}$
MHz $10^{6}s^{-1}$
kHz $10^{3}s^{-1}$

Wavelength λ
meters(*m*)
fm $10^{-15}m$
pm $10^{-12}m$
nm $10^{-9}m$
μ*m* $10^{-6}m$
mm $10^{-3}m$
cm $10^{-2}m$
km $10^{3}m$

Wavenumber
per meter(m^{-1})
cm^{-1} $10^{2}m^{-1}$

Energy *ehυ*
electonVolts
(*eV*)

A sketch of modern molecular spectroscopy

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Principles of Symmetry, Dynamics, and Spectroscopy
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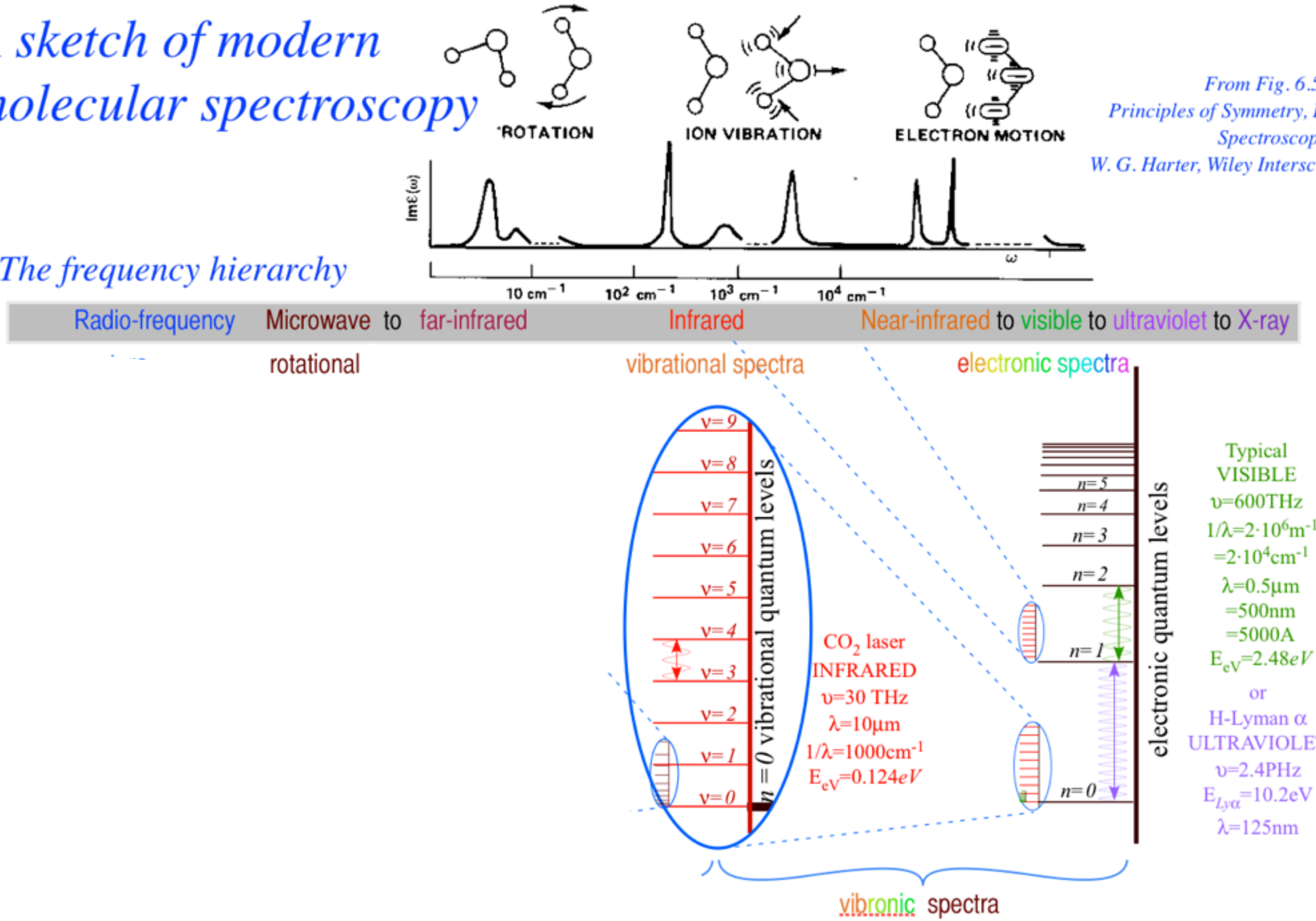


Spectral Quantities

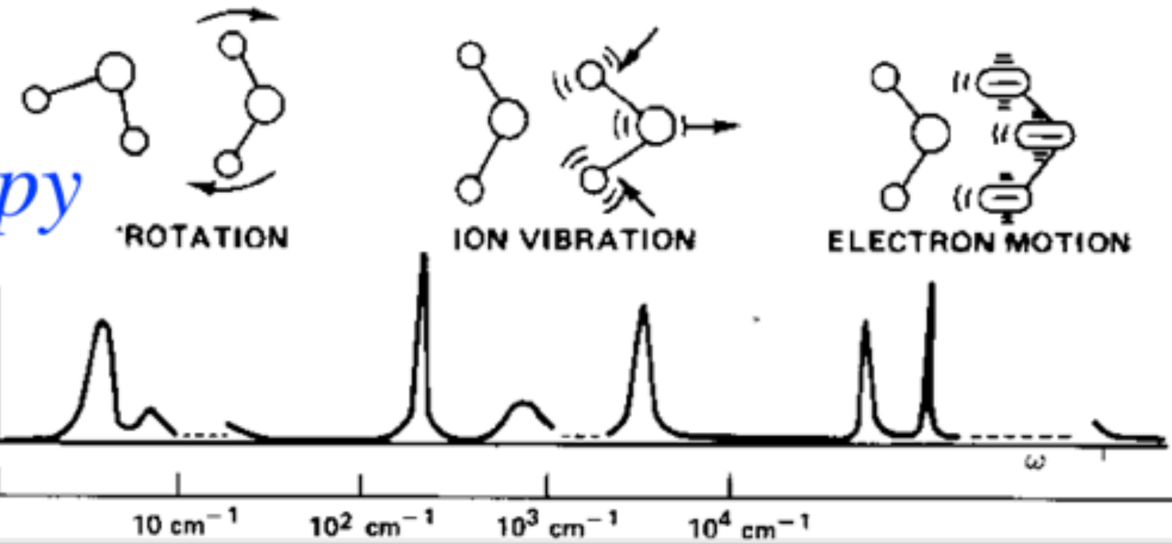
Frequency υ
Hertz(sec^{-1})
THz $10^{12}s^{-1}$
GHz $10^{9}s^{-1}$
MHz $10^{6}s^{-1}$
kHz $10^{3}s^{-1}$

Wavelength λ
meters(m)
fm $10^{-15}m$
pm $10^{-12}m$
nm $10^{-9}m$
μm $10^{-6}m$
mm $10^{-3}m$
cm $10^{-2}m$
km $10^{3}m$

Wavenumber
per meter(m^{-1})
cm^{-1} $10^{2}m^{-1}$

Energy $eh\upsilon$
electonVolts (eV)

A sketch of modern molecular spectroscopy



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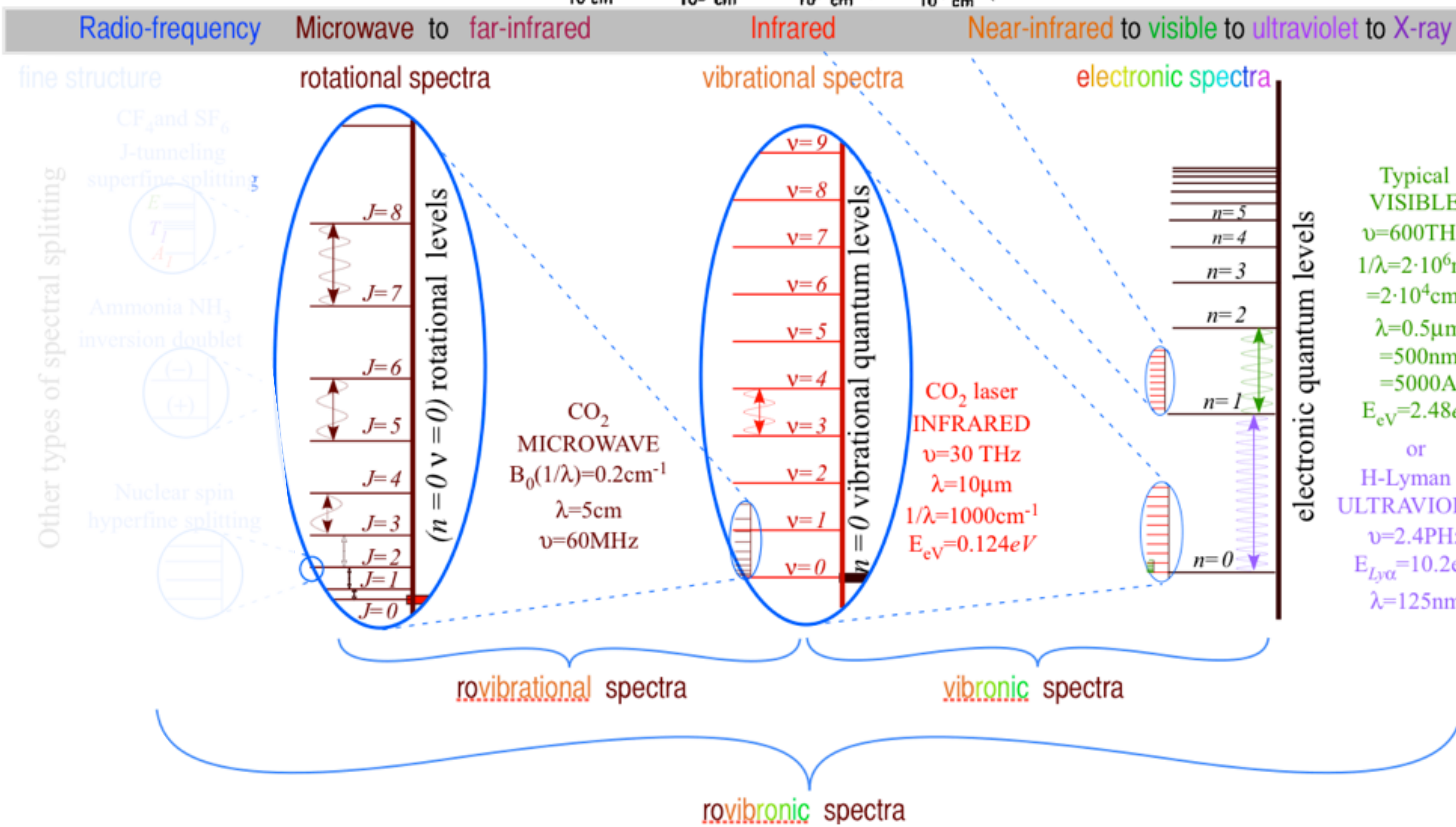
The frequency hierarchy



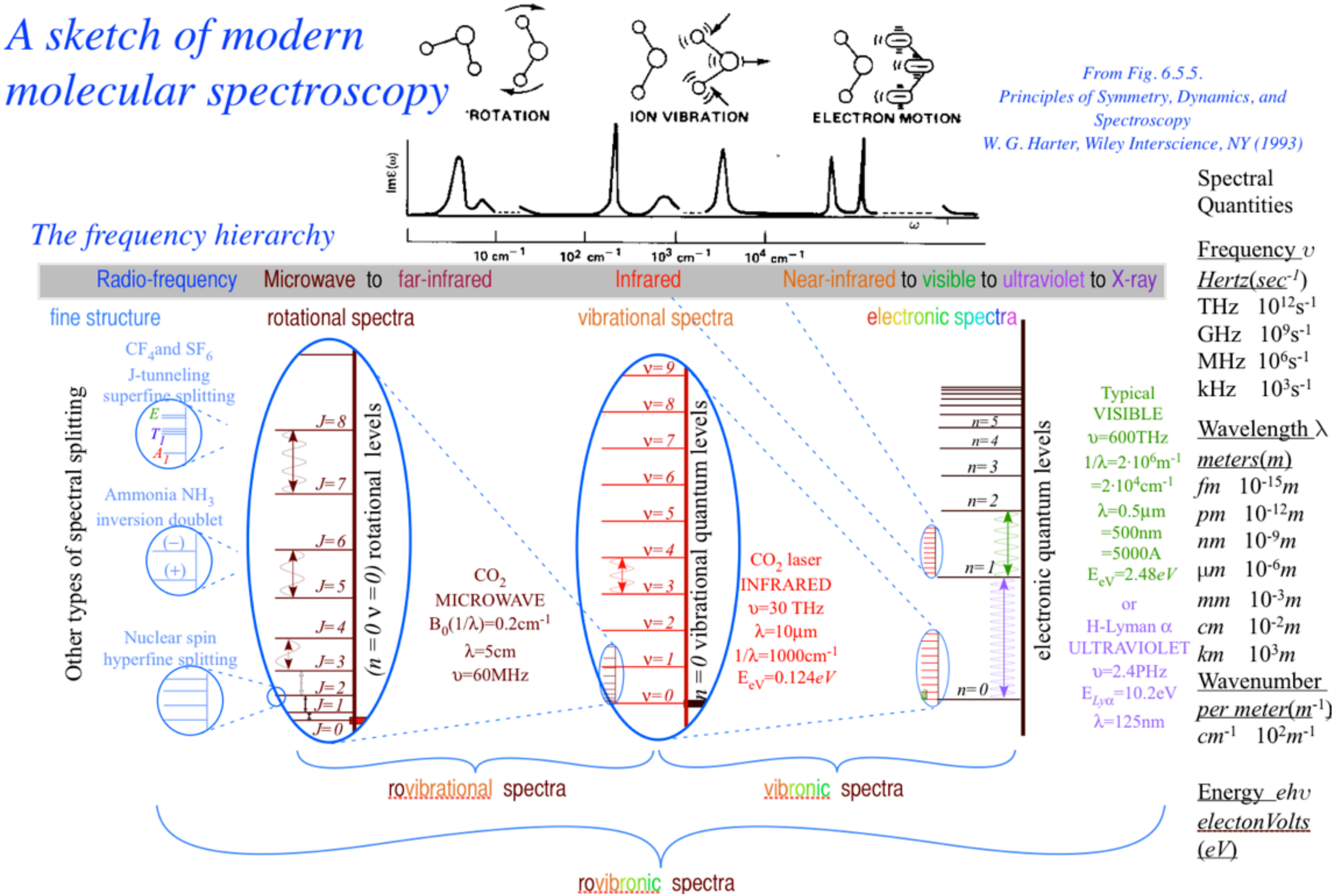
Spectral Quantities

Frequency υ
Hertz(sec^{-1})
THz $10^{12}s^{-1}$
GHz $10^{9}s^{-1}$
MHz $10^{6}s^{-1}$
kHz $10^{3}s^{-1}$

Wavelength λ
meters(m)
fm $10^{-15}m$
pm $10^{-12}m$
nm $10^{-9}m$
μm $10^{-6}m$
mm $10^{-3}m$
cm $10^{-2}m$
km $10^{3}m$

Wavenumber
per meter(m^{-1})
cm^{-1} $10^{2}m^{-1}$

Energy *ehυ*
electonVolts (eV)



A sketch of modern molecular spectroscopy
ROTATION
ION VIBRATION
ELECTRON MOTION
From Fig. 6.5.5.
Principles of Symmetry, Dynamics, and Spectroscopy
W. G. Harter, Wiley Interscience, NY (1993)
Imε(ω)
ω
10 cm⁻¹
10² cm⁻¹
10³ cm⁻¹
10⁴ cm⁻¹
The frequency hierarchy
Radio-frequency
Microwave to far-infrared
Infrared
Near-infrared to visible to ultraviolet to X-ray
fine structure
rotational spectra
vibrational spectra
electronic spectra
Other types of spectral splitting
CF₄ and SF₆
J-tunneling
superfine splitting
E
T₁
A₁
Ammonia NH₃
inversion doublet
(−)
(+)
Nuclear spin
hyperfine splitting
J=8
J=7
J=6
J=5
J=4
J=3
J=2
J=1
J=0
(n = 0 v = 0) rotational levels
CO₂
MICROWAVE
B₀(1/λ)=0.2cm⁻¹
λ=5cm
υ=60MHz
v=9
v=8
v=7
v=6
v=5
v=4
v=3
v=2
v=1
v=0
n = 0 vibrational quantum levels
CO₂ laser
INFRARED
υ=30 THz
λ=10μm
1/λ=1000cm⁻¹
E_eV=0.124eV
n=5
n=4
n=3
n=2
n=1
n=0
electronic quantum levels
Typical
VISIBLE
υ=600THz
1/λ=2·10⁶m⁻¹
=2·10⁴cm⁻¹
λ=0.5μm
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H-Lyman α
ULTRAVIOLET
υ=2.4PHz
E_Lyα=10.2eV
λ=125nm
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Frequency υ
Hertz(sec⁻¹)
THz 10¹²s⁻¹
GHz 10⁹s⁻¹
MHz 10⁶s⁻¹
kHz 10³s⁻¹
Wavelength λ
meters(m)
fm 10⁻¹⁵m
pm 10⁻¹²m
nm 10⁻⁹m
μm 10⁻⁶m
mm 10⁻³m
cm 10⁻²m
km 10³m
Wavenumber
per meter(m⁻¹)
cm⁻¹ 10²m⁻¹
Energy ehυ
electonVolts
(eV)
rovibrational spectra
vibronic spectra
rovibronic spectra

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Rotational Energy Surfaces (RE or RES) of asymmetric rotor and energy levels

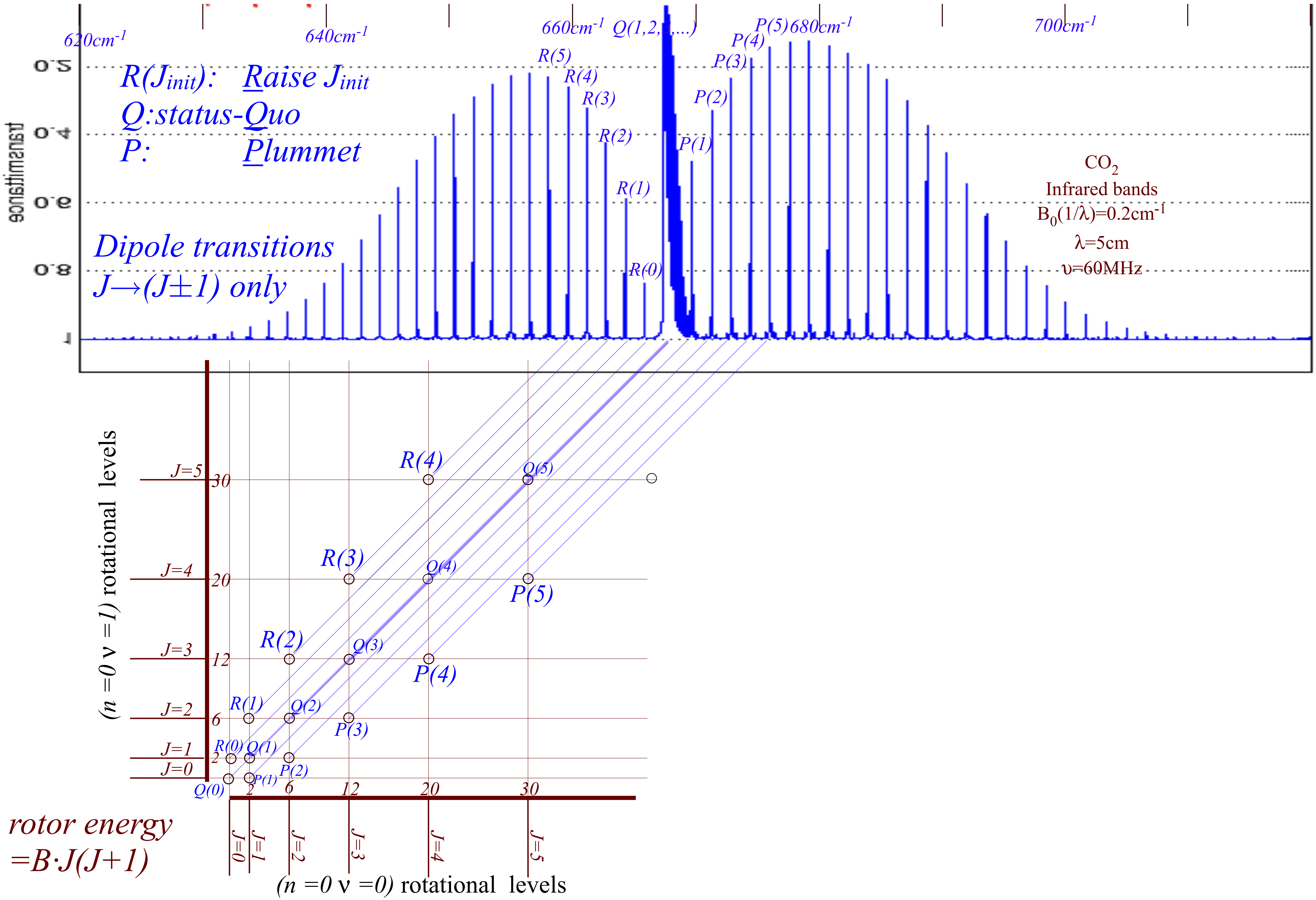
Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

Example of CO_2 rovibration $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

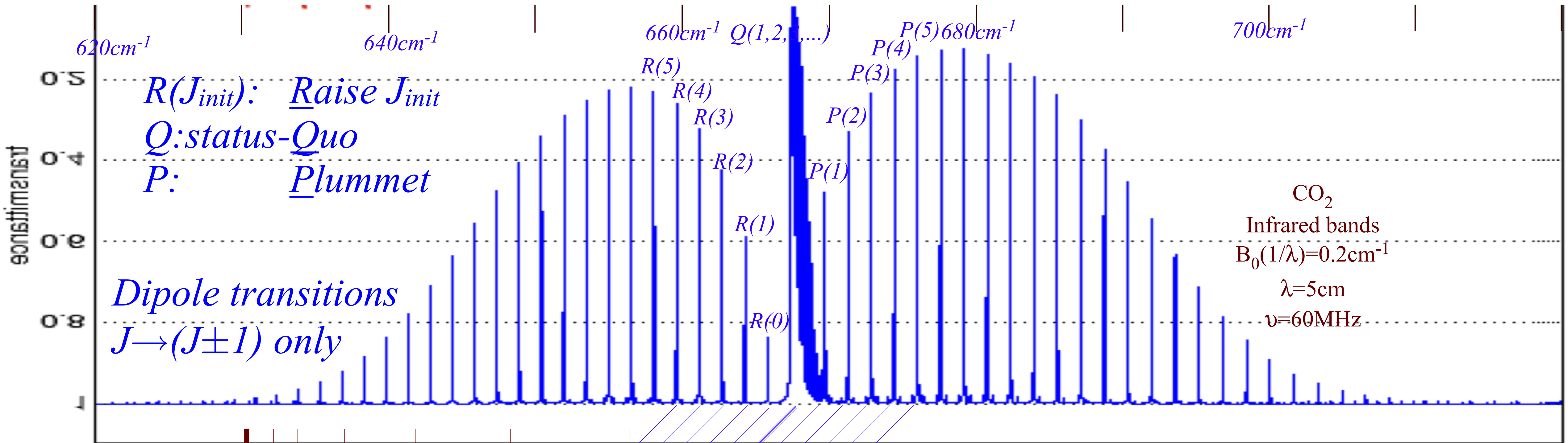
Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

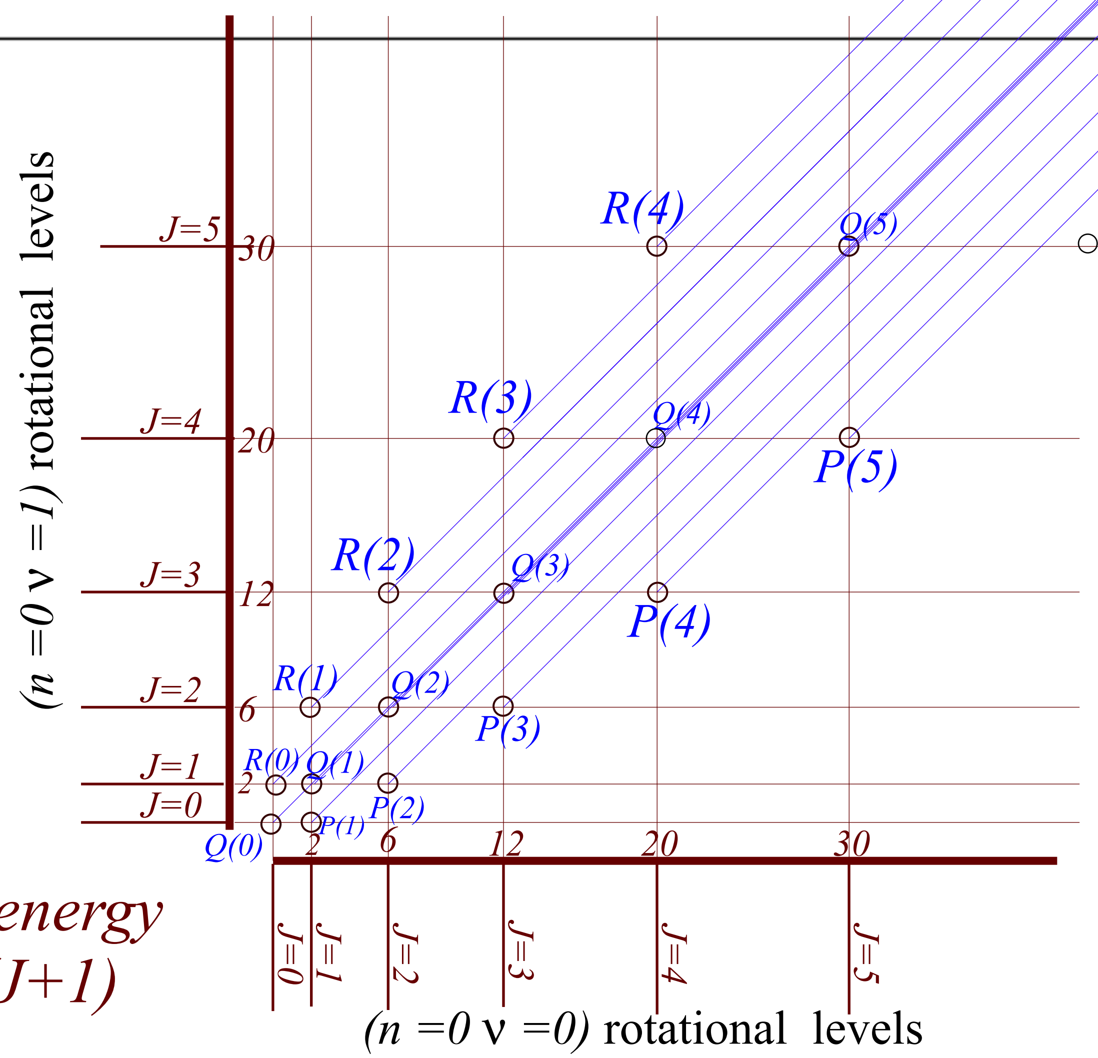
Asymmetric Top eigensolutions for J=1-2

Example of CO_2 rotational $(\upsilon=0)\Leftrightarrow(\upsilon=1)$ bands

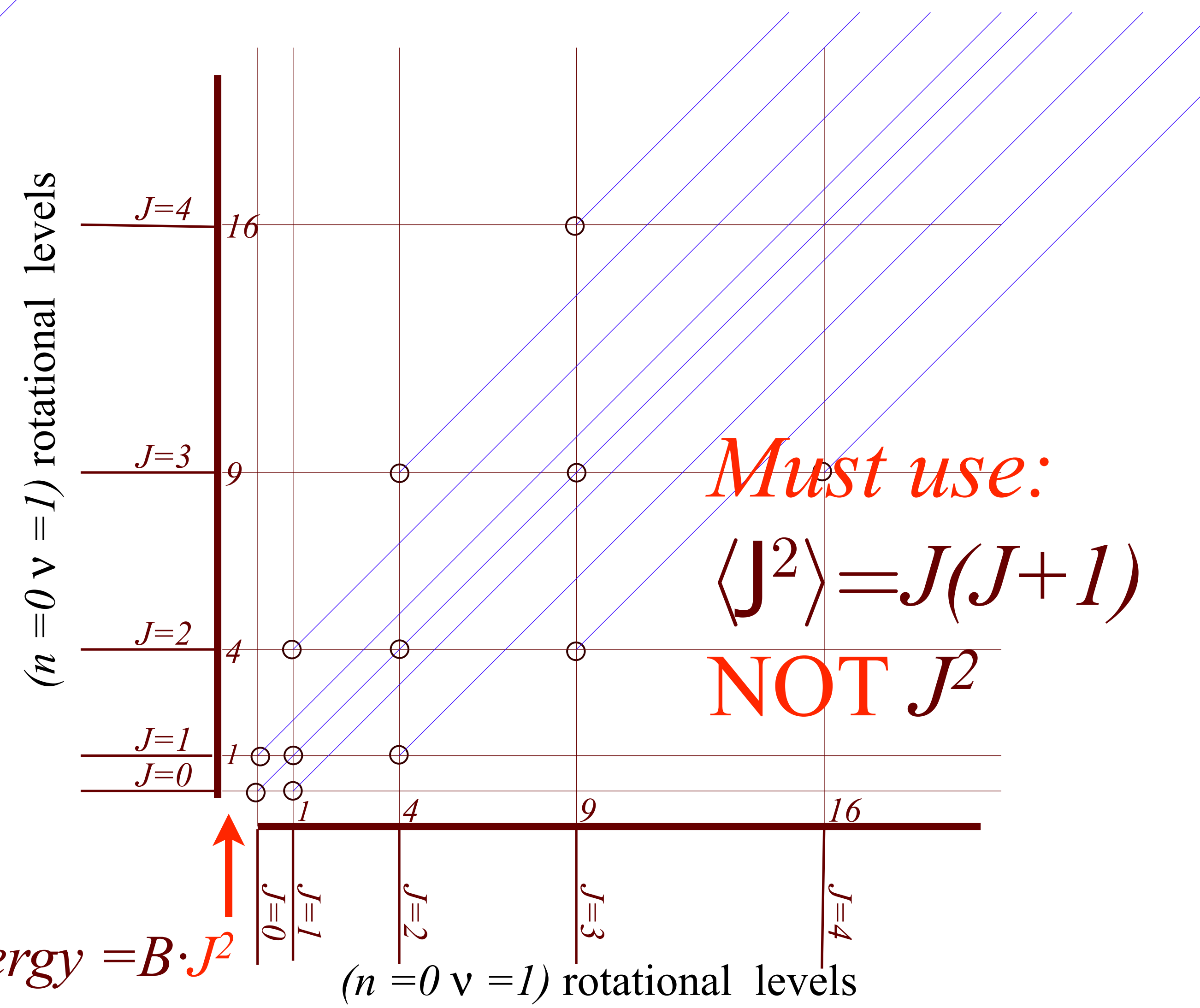


Example of CO_2 rotational $(\upsilon=0)\Leftrightarrow(\upsilon=1)$ bands





rotor energy
$=B\cdot J(J+1)$

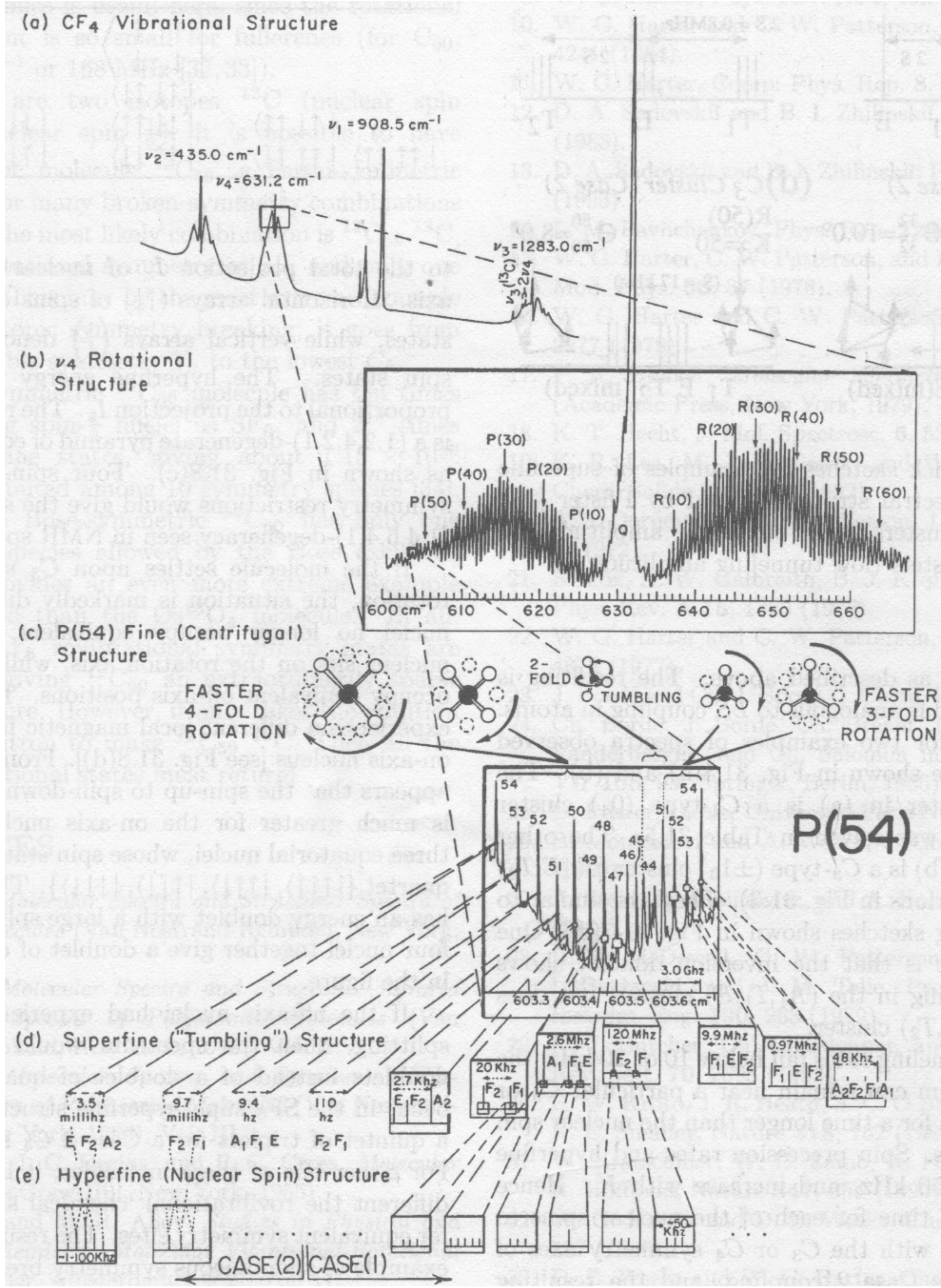


Must use:
$\langle J^2\rangle = J(J+1)$
NOT J^2

What does NOT work: rotor energy $=B\cdot J^2$

Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

W.G.Harter
Ch. 31
Atomic, Molecular, & Optical Physics Handbook
Am. Int. of Physics
Gordon Drake Editor
(1996)



Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

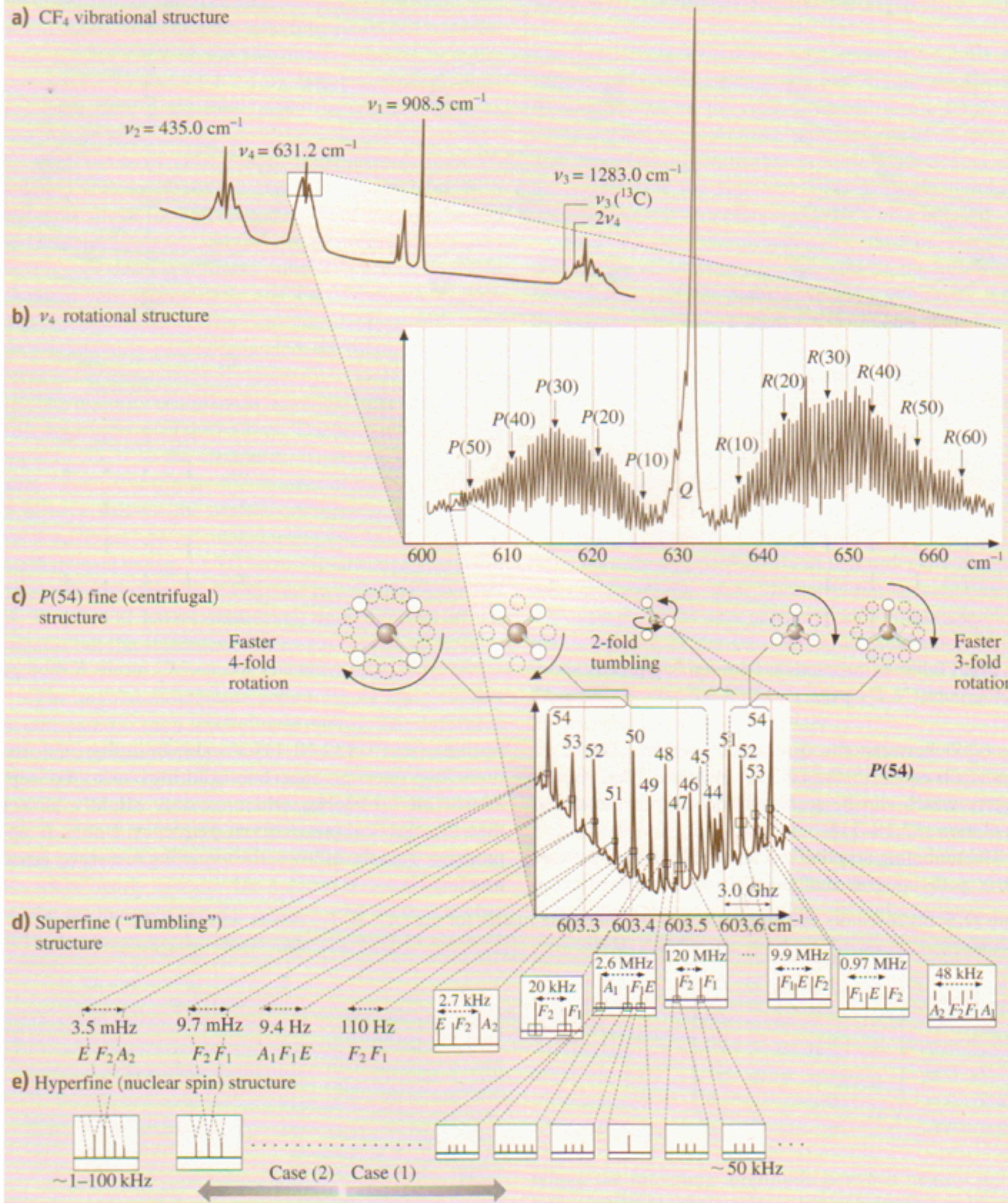
W.G.Harter

Fig. 32.7

Springer Handbook of Atomic, Molecular, & Optical Physics

Gordon Drake Editor

(2005)



Three (3) applications of R(3) rotation and U(2) unitary representations $D^J_{mn}(\alpha,\beta,\gamma)$

1. Atomic and molecular $D^{J*}_{mn}(\alpha,\beta,\gamma)$-wavefunctions

"Mock-Mach" lab-vs-body-defined states $|^J_{mn}\rangle = \mathbf{P}_{mn}{}^J |_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma) \mathbf{R}(\alpha,\beta,\gamma) |_{(0,0,0)}\rangle$

2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

General Stern-Gerlach and polarization transformations $\mathbf{R}(\alpha,\beta,\gamma)|^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|^J_{m'n}\rangle$

Angular momentum cones and high J properties

3. Atomic and molecular multipole Hamiltonian tensor operators $\mathbf{T}_q^k$ and eigenvalues

Multipole $\mathbf{T}_q^k$ expansion of asymmetric-rotor Hamiltonians $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

Multipole $\mathbf{T}_q^k$ expansion of symmetric-rotor Hamiltonians $\mathbf{H} = B\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$

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

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➤ *Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians* ◀

Asymmetric Top eigensolutions for J=1-2

Go to Lecture 26 p. 15 to 25 to…

(For more detailed and clearer discussion)

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

(Go to Lecture 26 p. 15 to 25 to…)

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

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

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

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

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

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

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

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

LAB matrix elements use the usual atomic formula:

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

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

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

BOD matrix elements are the same after switching *m's* into *n's* and changing sign of $\mathbf{J}_Y$ matrix (*-conjugation)

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

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

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

Hamiltonian matrices for asymmetric rotor Hamiltonian

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

First are matrix formulas for BOD J^2 components.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

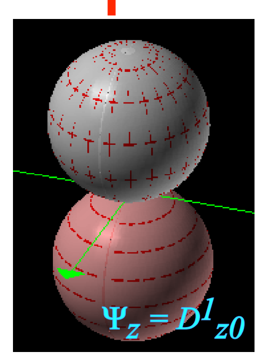
eigen-values: $(B+C=5,\quad A+B=3,\quad A+C=4)$

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

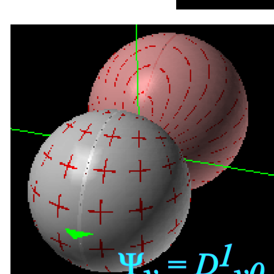
$$\left|B+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle - 1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle \quad \text{y-like}$$

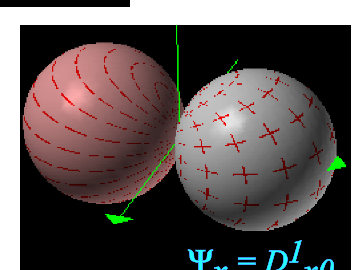
$$\left|A+B\right\rangle = +\left|{}^{1}_{m,0}\right\rangle \quad \text{z-like}$$

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



j = 1
Standing
p-Waves

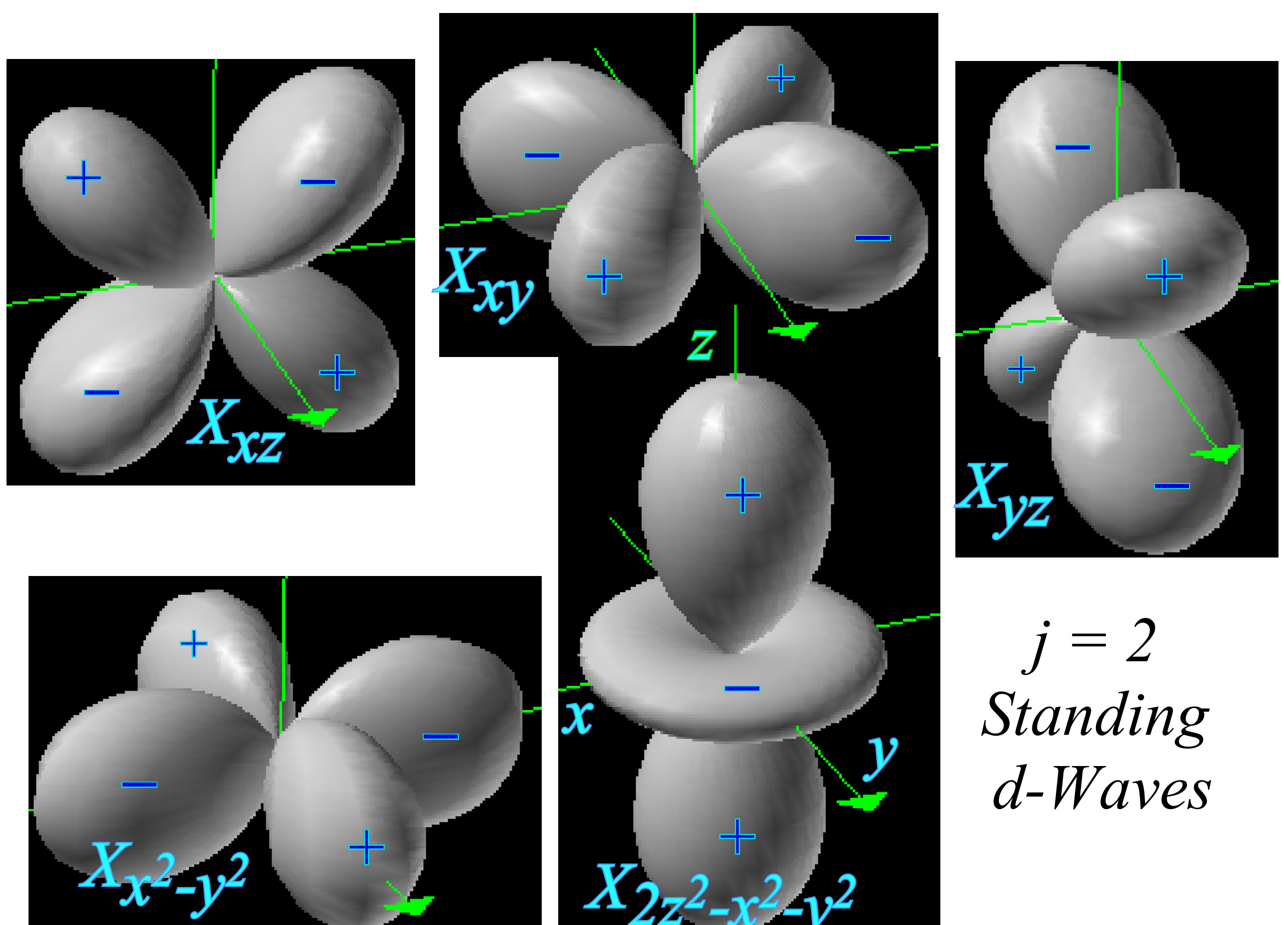




Body-based J=1
vector-like eigenfunctions

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

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



j = 2
Standing
d-Waves

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

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

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

$$\left|A_1 2^+\right\rangle=\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle+\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle,\qquad \left|B_1 1^+\right\rangle=\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle+\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle,\qquad \left|A_1 0\right\rangle=\left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle=\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle-\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle,\qquad \left|A_2 1^-\right\rangle=\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle-\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

The following basis transformation "almost diagonalizes" $\langle\mathbf{H}\rangle^{J=2}$ by reducing it to block form.
Let: $\Sigma = A+B$ and $\Delta = A-B$ to shorten expressions.

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

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

New D_2 basis:

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

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

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

$$\left|A_2 1^-\right\rangle=\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle-\tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

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

Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$
$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$
$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

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

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

×

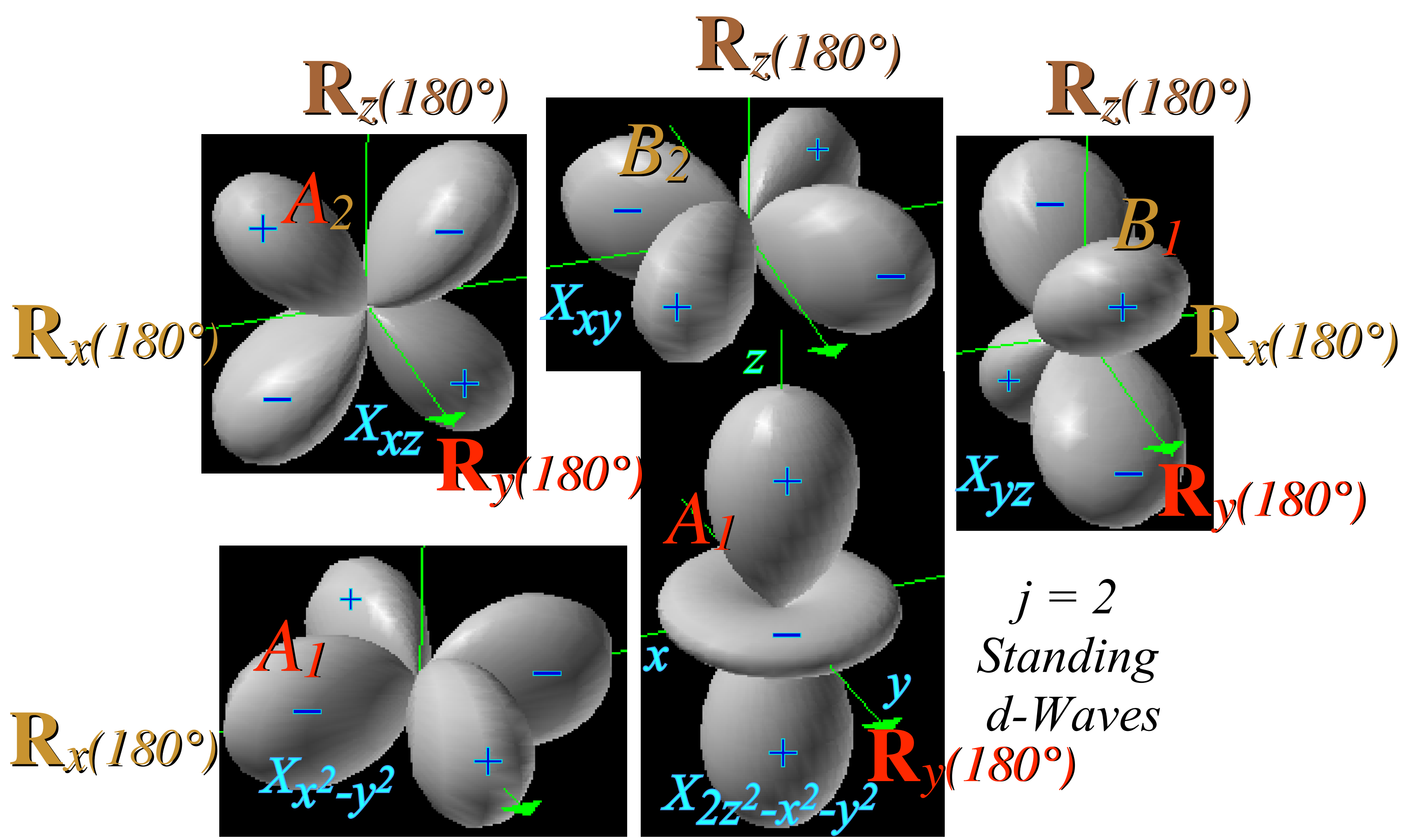
C_2^y	**1**	$\mathbf{R}_y$
+	1	1
−	1	−1

=

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

=

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



Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$

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

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

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$

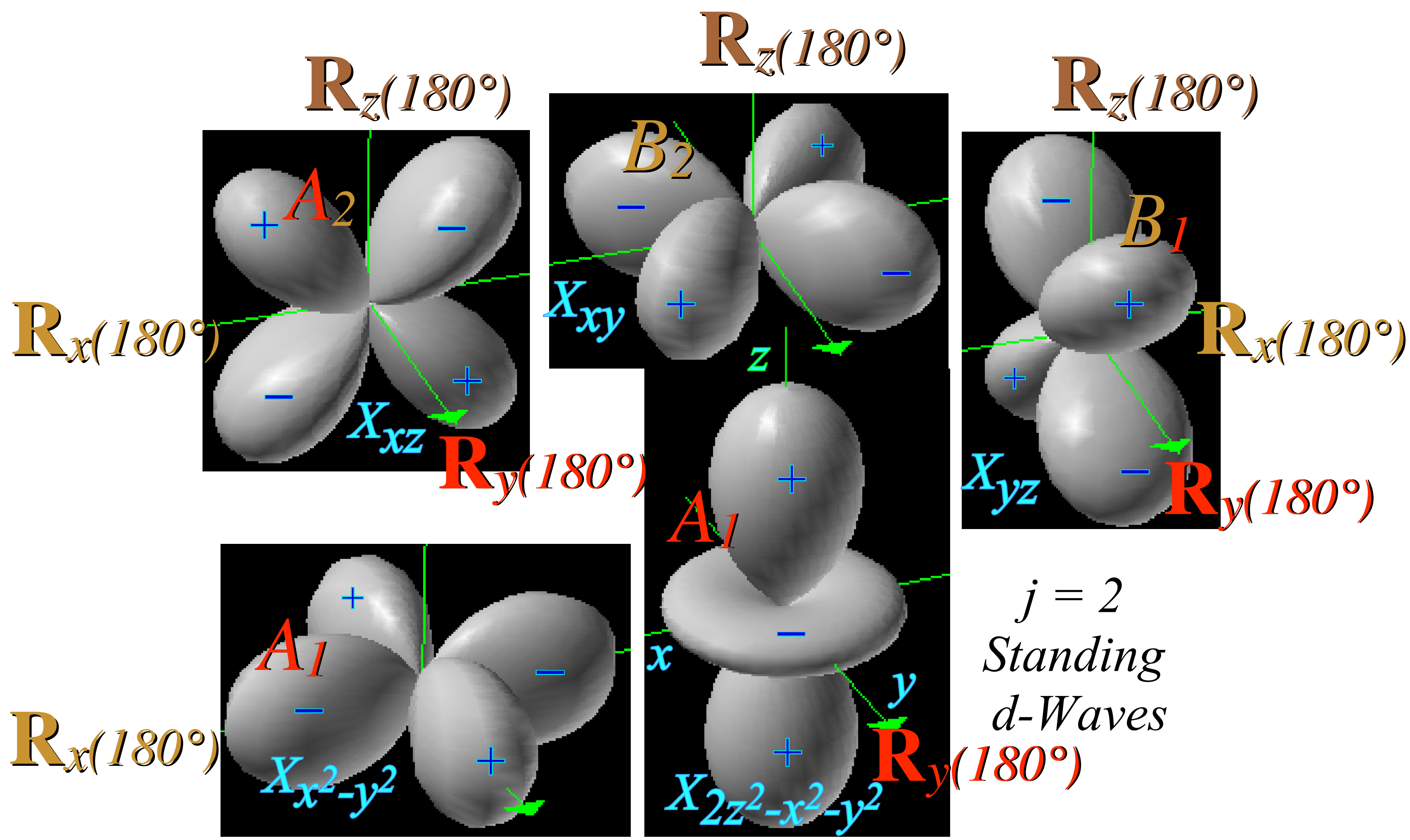
$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

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

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



Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$
$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$
$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

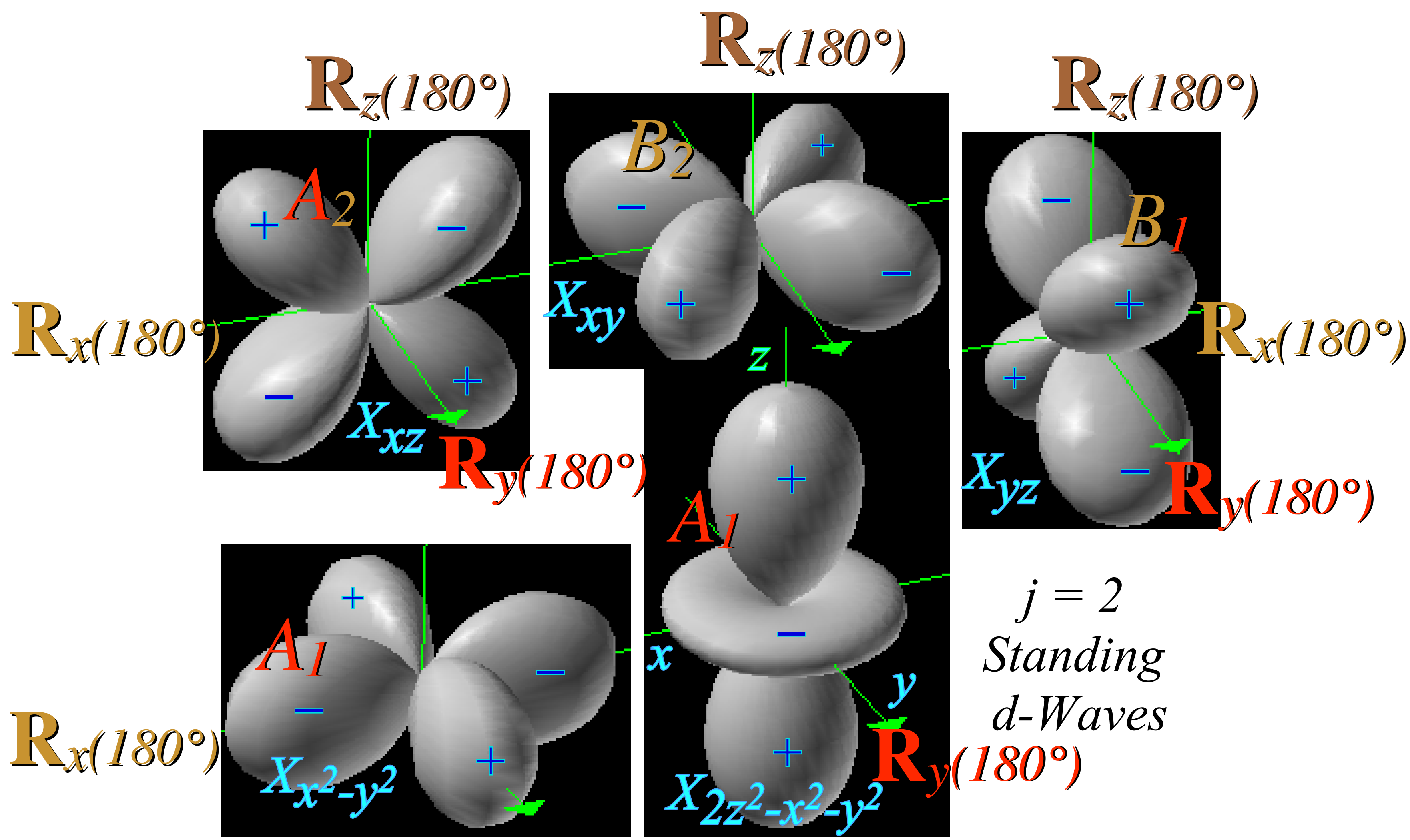
Need only diagonalize the two A_1's:

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

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

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

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



j = 2
Standing
d-Waves

Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$
$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$
$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

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

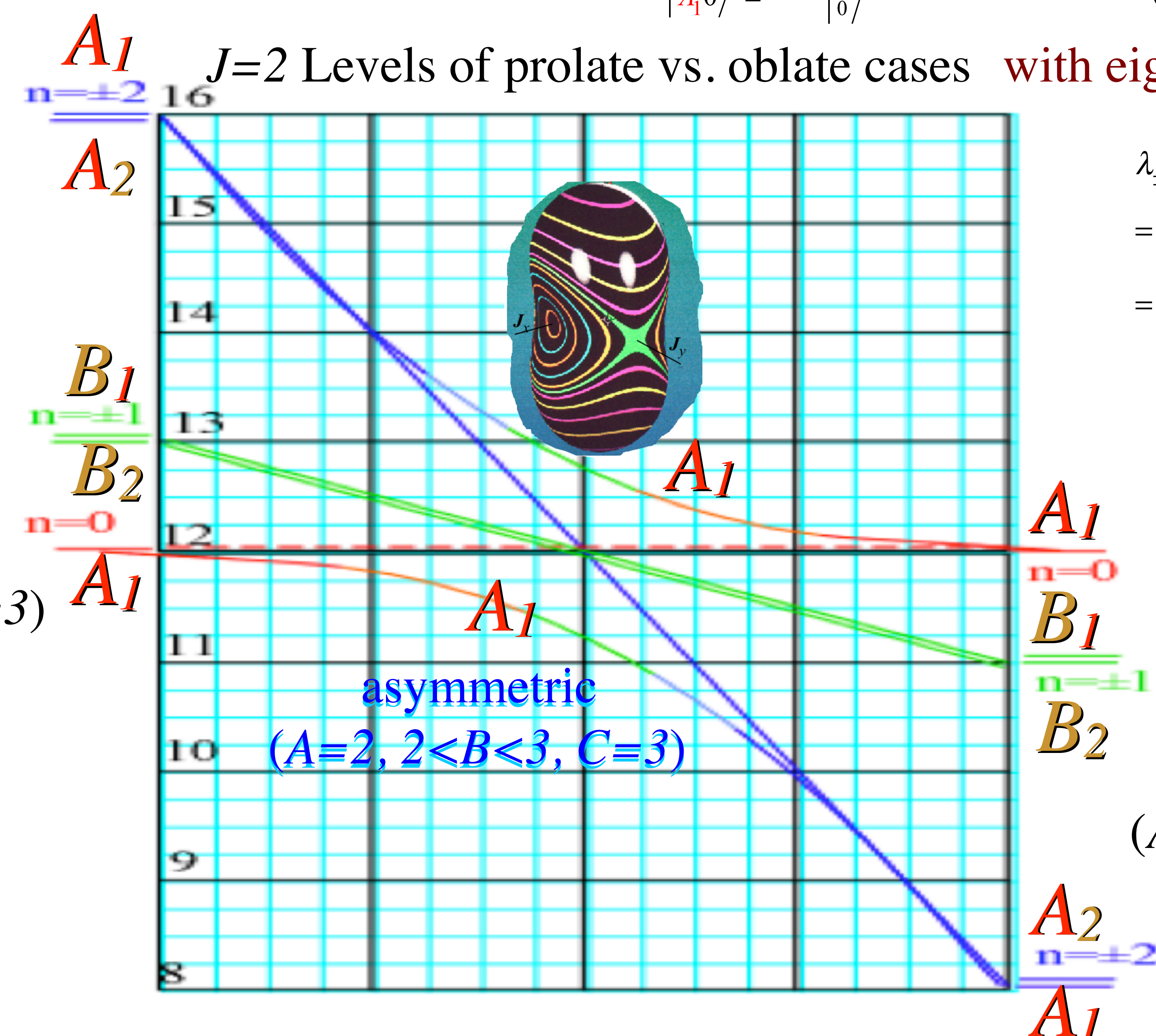
$$= (2C+2A+2B)\cdot \mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

with eigenvalues:

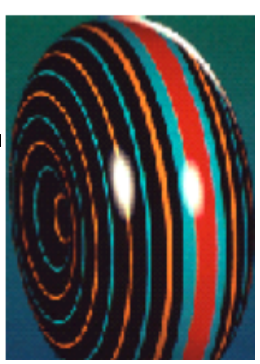
$$\lambda_{\pm} = 2C+2A+2B \pm \sqrt{(2C-A-B)^2 + 3(A-B)^2}$$
$$= 2(A+B+C) \pm 2\sqrt{C^2 - (A+B)C + A^2 - AB + B^2}$$
$$= 2C+4B \pm 2(C-B) = \begin{cases} 4C+2B \\ 6B \end{cases} \quad \text{if: } A=B$$

J=2 Levels of prolate vs. oblate cases

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



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



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

$B(J(J+1) + (C-B)n^2 = 2B+4C = 4+12 = 16$ ($n=\pm 2$)

$5B+C = 10+3 = 13$ ($n=\pm 1$) , $6B = 12$ ($n=0$)

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

$B(J(J+1) + (A-B)n^2 = 2B+4A = 4+4 = 8$ ($n=\pm 2$)

$5B+A = 10+1 = 11$ ($n=\pm 1$) , $6B = 12$ ($n=0$)

Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$

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

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

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$

$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

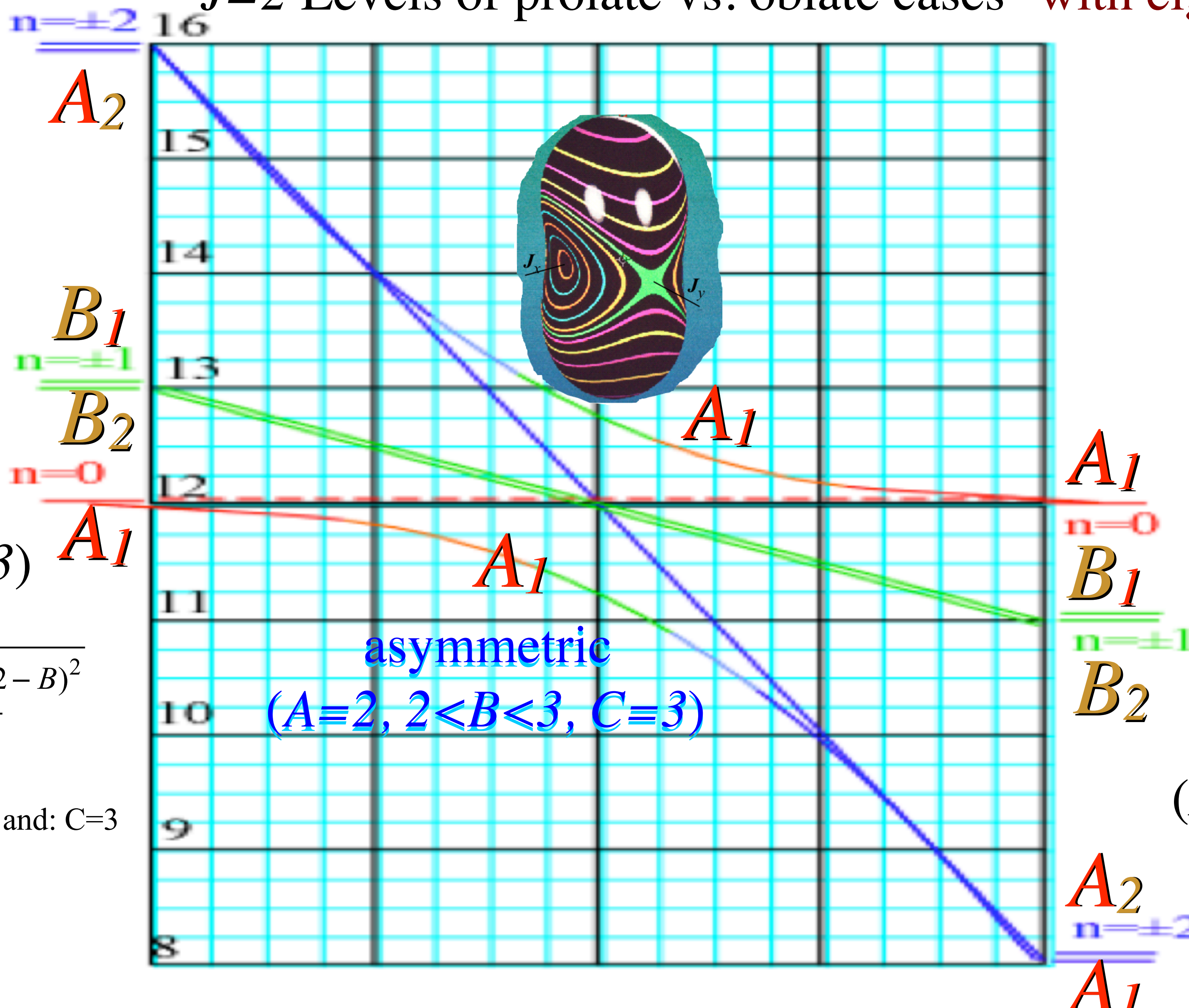
Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

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

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

$J=2$ Levels of prolate vs. oblate cases



with eigenvalues:

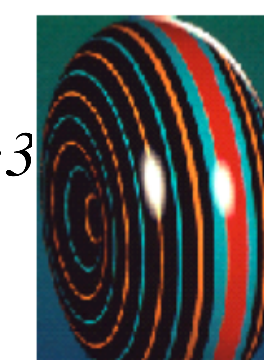
$$\begin{pmatrix} 14+B & \sqrt{3}(2-B) \\ \sqrt{3}(2-B) & 6+3B \end{pmatrix} =$$

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

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

$$\lambda_\pm = 10+2B \pm \sqrt{(4-B)^2+3(2-B)^2}$$
$$= 2(5+B) \pm 2\sqrt{7-5B+B^2}$$
$$= 14 \pm 2 = \begin{cases} 16 \\ 12 \end{cases} \text{ if: } A=B=2 \text{ and: } C=3$$

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



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

$B(J(J+1)+(C-B)n^2 = 2B+4C = 4+12 = 16$ ($n=\pm 2$)

$5B+C = 10+3 = 13$ ($n=\pm 1$) , $6B = 12$ ($n=0$)

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

$B(J(J+1)+(A-B)n^2 = 2B+4A = 4+4 = 8$ ($n=\pm 2$)

$5B+A = 10+1 = 11$ ($n=\pm 1$) , $6B = 12$ ($n=0$)

Review of freshman Chemistry and Physics (contd)

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

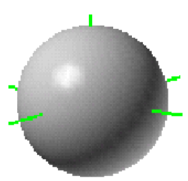
Energy 101 $E = \frac{1}{2} m\,v^2 = p^2/2m$ $E = \frac{1}{2} I\,\omega^2 = J^2/2I$ $BUCK$

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

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

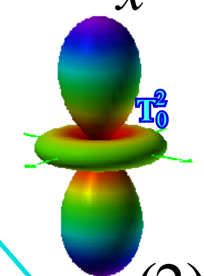
...and its multi-pole expansion...

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



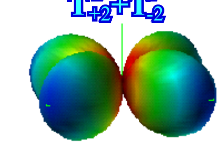
Spherical Top
(A=B=C)
$\mathbf{H} = B\,\mathbf{J}^2$

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



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

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



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

Asymmetric Top
(A≠B≠C)

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

(Derivation follows next lecture…)

Partial listing of the Harter-Soft/Heyoka LearnIt Web Apps as of April 24, 2017
(Apps are being upgraded as time permits)

Production Links - ***For the students & general public***

BohrIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BohrItWeb.html"
BounceIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BounceItWeb.html"
BoxIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BoxItWeb.html"
CoulIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/CoulItWeb.html"
Cycloidulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/CycloidulumWeb.html"
LearnIt - Production; URL is "**http://www.uark.edu/ua/modphys**" or "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
Pendulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/PendulumWeb.html"
QuantIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/QuantItWeb.html"
Relativity - Pirelli Entrant: URL is "http://www.uark.edu/ua/pirelli" or "http://www.uark.edu/ua/pirelli/html/default.html"
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"

Testing Links - ***For internal use and testing by Harter & Heyoka***

BohrIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BohrItWeb.html"
BounceIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BounceItWeb.html"
BounceIt Title Page - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BounceItTitlePage.html"
BoxIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BoxItWeb.html"
CoulIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/CoulItWeb.html"
Cycloidulum - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/CycloidulumWeb.html"
Harter-Soft Web Apps - Quick Reference - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
JerkIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
ModernPhysics - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/IntroCover.html"
Pendulum - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/PendulumWeb.html"
QuantIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/QuantItWeb.html"
Trebuchet Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/TrebuchetWeb.html"

Link to the complete listing of Harter-Soft LearnIt Web Apps and resources for Physics