Group Theory in Quantum Mechanics

Lecture 25 *(4.24.14)*

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 $|^J_{mn}\rangle = \mathbf{P}^J_{mn}|(0,0,0)\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|(0,0,0)\rangle$

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 rovibrational $(\upsilon=0)\Leftrightarrow(\upsilon=1)$bands

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

Asymmetric Top eigensolutions for J=1-2

As of April 3, 2014

Links to the current Harter-Soft LearnIt web apps for Physics

Bold links have default redirect pages. *Italics* are not yet meant for production.Red: the final stages of testing.

List of *production* Harter-Soft Web Apps & Textbooks (For public)

Classical Mechanics with a Bang! - URL is "http://www.uark.edu/ua/modphys/markup/CMwBangWeb.html"
Quantum Theory for the Computer Age - URL is "http://www.uark.edu/ua/modphys/markup/QTCAWeb.html"
LearnIt Web Applications - URL is "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"

Individual web-apps for current classes:

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"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
MolVibes - Production; URL is "http://www.uark.edu/ua/modphys/markup/MolVibesWeb.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"

The old relativity website (2005):
Relativity - Pirelli Entrant - Production; URL is "**http://www.uark.edu/ua/pirelli**" or "http://www.uark.edu/ua/pirelli/html/default.html"

Newer relativity web-apps currently being developed (2013-)
RelativIt Production; URL is "http://www.uark.edu/ua/modphys/markup/RelativItWeb.html"
RelaWavity Production; URL is "http://www.uark.edu/ua/modphys/markup/RelaWavityWeb.html"

Additional classical wep-apps:
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"
WaveIt Production; URL is "http://www.uark.edu/ua/modphys/markup/WaveItWeb.html"

Link to master list of all Harter-Soft Web Apps & Textbooks (Prod, Testing, & Developement)

http://www.uark.edu/ua/modphys/testing/markup/Harter-SoftWebApps.html

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:
$\alpha \to \phi$
polar angle:
$\beta \to \theta$

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

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

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

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

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

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

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. $\cos^2\frac{\beta}{2} = \frac{1+\cos\beta}{2}$, $\sin^2\frac{\beta}{2} = \frac{1-\cos\beta}{2}$, $\sin\frac{\beta}{2}\cos\frac{\beta}{2} = \frac{\sin\beta}{2}$,

$$Y^{1*}_1(\phi,\theta) = \sqrt{\tfrac{3}{4\pi}}\, e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}} = D^1_{1,0}(\phi,\theta)$$

$$Y^{1*}_0(\phi,\theta) = \sqrt{\tfrac{3}{4\pi}}\, \cos\beta = D^1_{0,0}(\phi,\theta)$$

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

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 $(j=\ell=1)$ 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

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

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

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

$$Y^{1*}_1(\phi,\theta) = \sqrt{\tfrac{3}{4\pi}}\,e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}} = D^1_{1,0}(\phi,\theta)$$

$$Y^{1*}_0(\phi,\theta) = \sqrt{\tfrac{3}{4\pi}}\,\cos\beta = D^1_{0,0}(\phi,\theta)$$

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

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 ($j=\ell=1$) wavefunctions

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

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

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

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

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

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: $\alpha \to \phi$
polar angle: $\beta \to \theta$

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

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

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

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

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 ($j=\ell=1$) wavefunctions

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

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

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

3-D linear-circular polarization T-matrix:

$$\begin{pmatrix} \left\langle {}^1_1 \middle| {}^1_x \right\rangle & \left\langle {}^1_1 \middle| {}^1_y \right\rangle & \left\langle {}^1_1 \middle| {}^1_z \right\rangle \\ \left\langle {}^1_0 \middle| {}^1_x \right\rangle & \left\langle {}^1_0 \middle| {}^1_y \right\rangle & \left\langle {}^1_0 \middle| {}^1_z \right\rangle \\ \left\langle {}^{1}_{-1} \middle| {}^1_x \right\rangle & \left\langle {}^{1}_{-1} \middle| {}^1_y \right\rangle & \left\langle {}^{1}_{-1} \middle| {}^1_z \right\rangle \end{pmatrix} = \begin{pmatrix} \frac{-1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 \end{pmatrix}$$

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

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

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

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

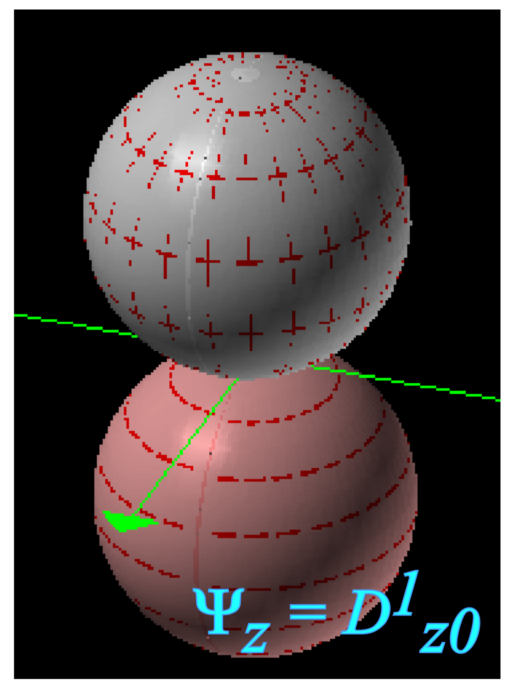
$$Y^{1*}_1(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}e^{-i\phi}\frac{-\sin\theta}{\sqrt{2}}=D^1_{1,0}(\phi,\theta)$$
$$Y^{1*}_0(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}\cos\beta=D^1_{0,0}(\phi,\theta)$$
$$Y^{1*}_{-1}(\phi,\theta)=\sqrt{\tfrac{3}{4\pi}}e^{+i\phi}\frac{\sin\theta}{\sqrt{2}}=D^1_{-1,0}(\phi,\theta)$$

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

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

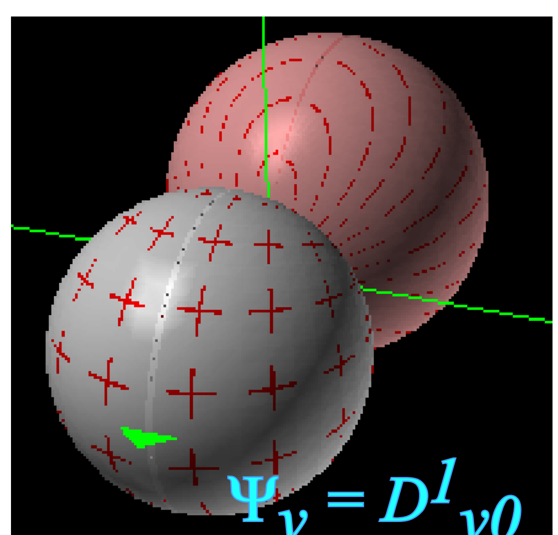
Dipole ($j=\ell=1$) waves

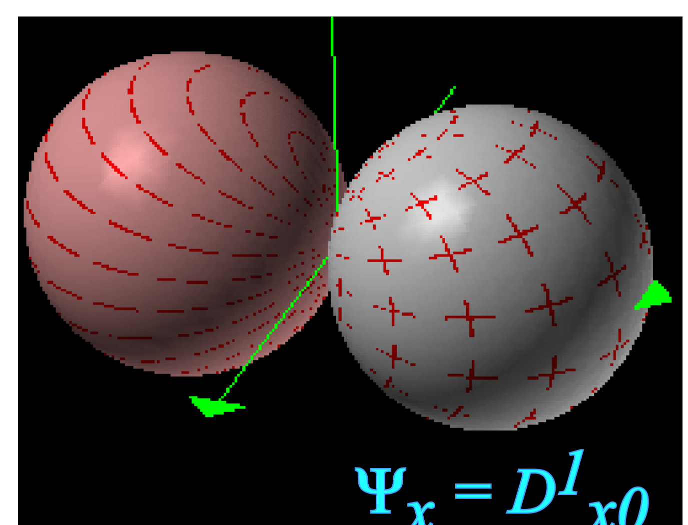
$$D^{1*}_{1,0}(\phi\theta 0)=-e^{i\phi}\frac{\sin\theta}{\sqrt{2}}=-\frac{\cos\phi\sin\theta+i\cos\phi\sin\theta}{\sqrt{2}}=-\frac{x+iy}{r\sqrt{2}}$$
$$D^{1*}_{0,0}(\phi\theta 0)=\cos\theta=\cos\theta=z/r$$
$$D^{1*}_{-1,0}(\phi\theta 0)=e^{-i\phi}\frac{\sin\theta}{\sqrt{2}}=\frac{\cos\phi\sin\theta-i\cos\phi\sin\theta}{\sqrt{2}}=\frac{x-iy}{r\sqrt{2}}$$

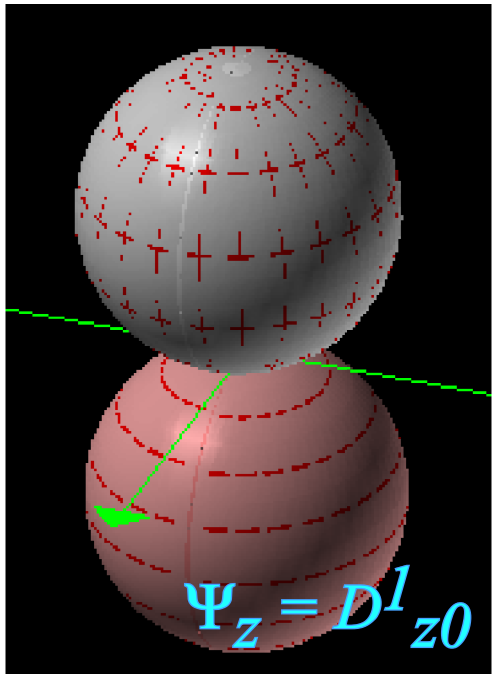


j = 1
Standing
p-Waves

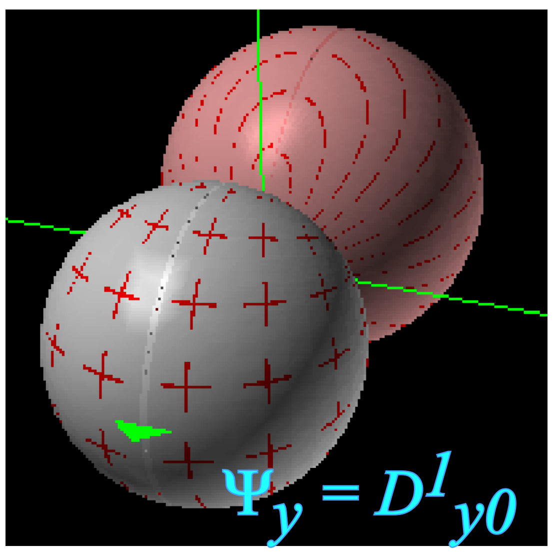
$$\Psi^1_x(\phi,\theta)=D^1_{x,z}(\phi,\theta,0)=\cos\phi\sin\theta$$
$$\Psi^1_y(\phi,\theta)=D^1_{y,z}(\phi,\theta,0)=\sin\phi\sin\theta$$
$$\Psi^1_z(\phi,\theta)=D^1_{z,z}(\phi,\theta,0)=\cos\theta$$

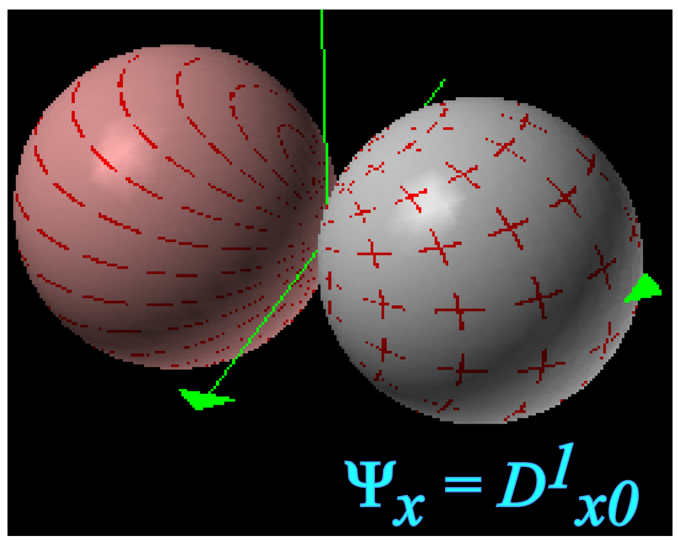






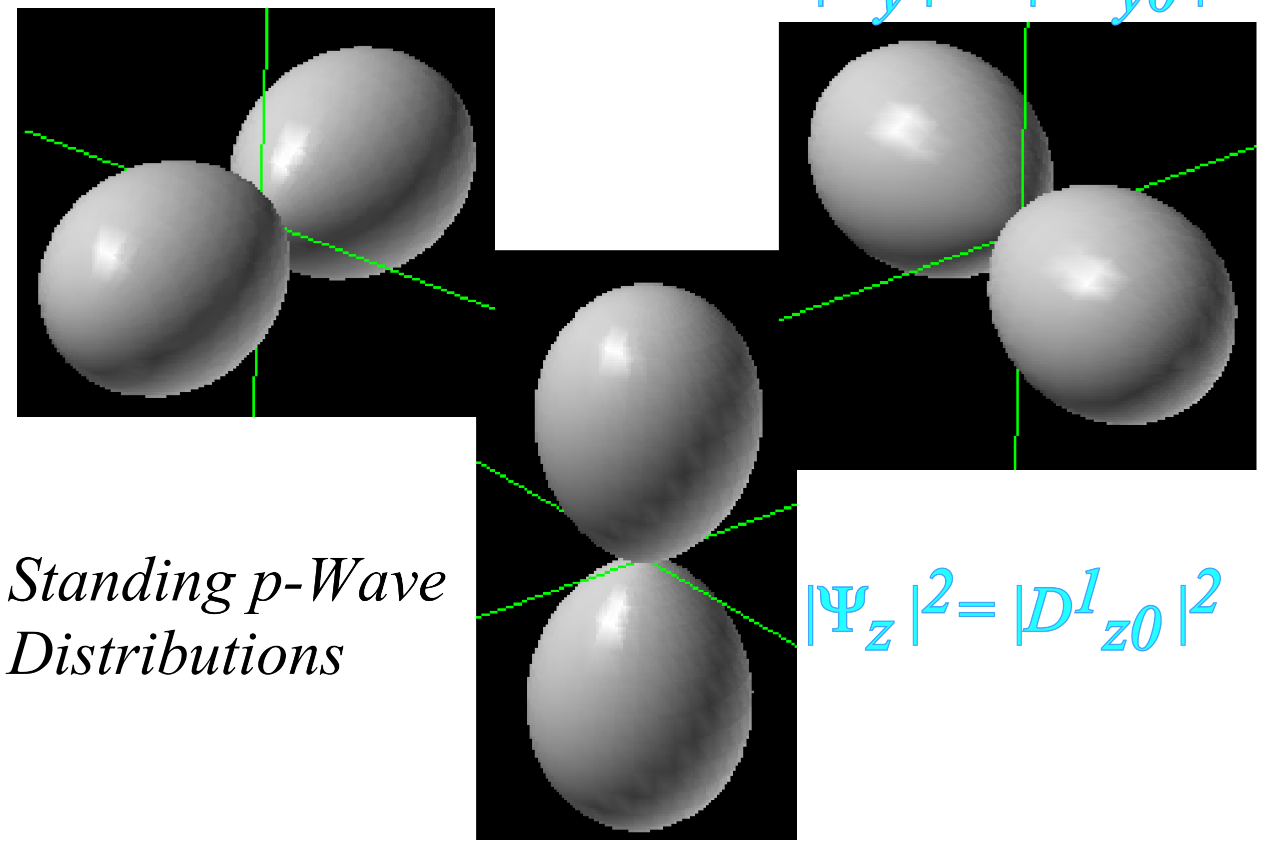
j = 1
Standing
p-Waves





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

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

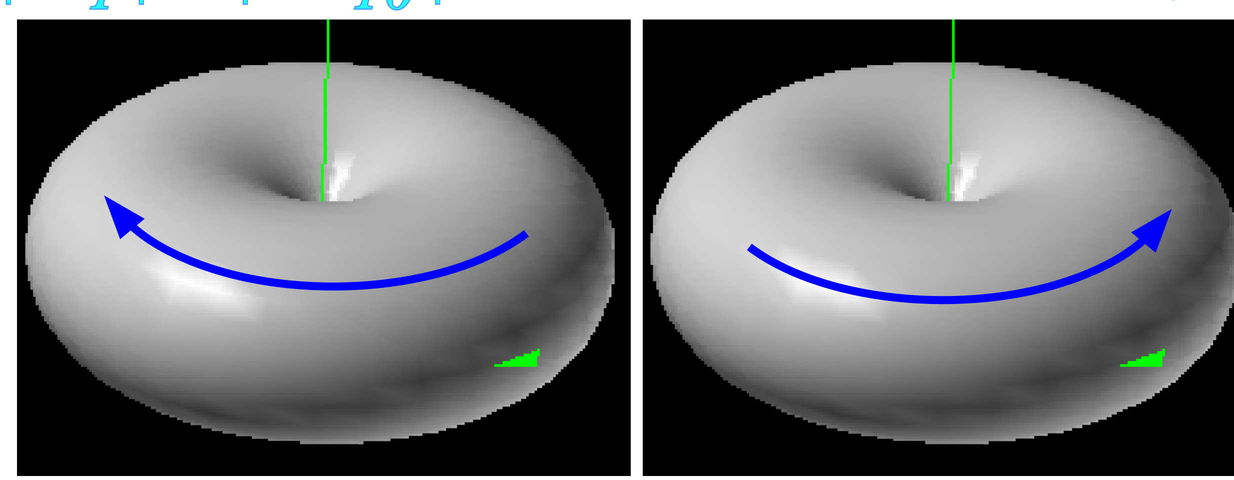


Standing p-Wave Distributions

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

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

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

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

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

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

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

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

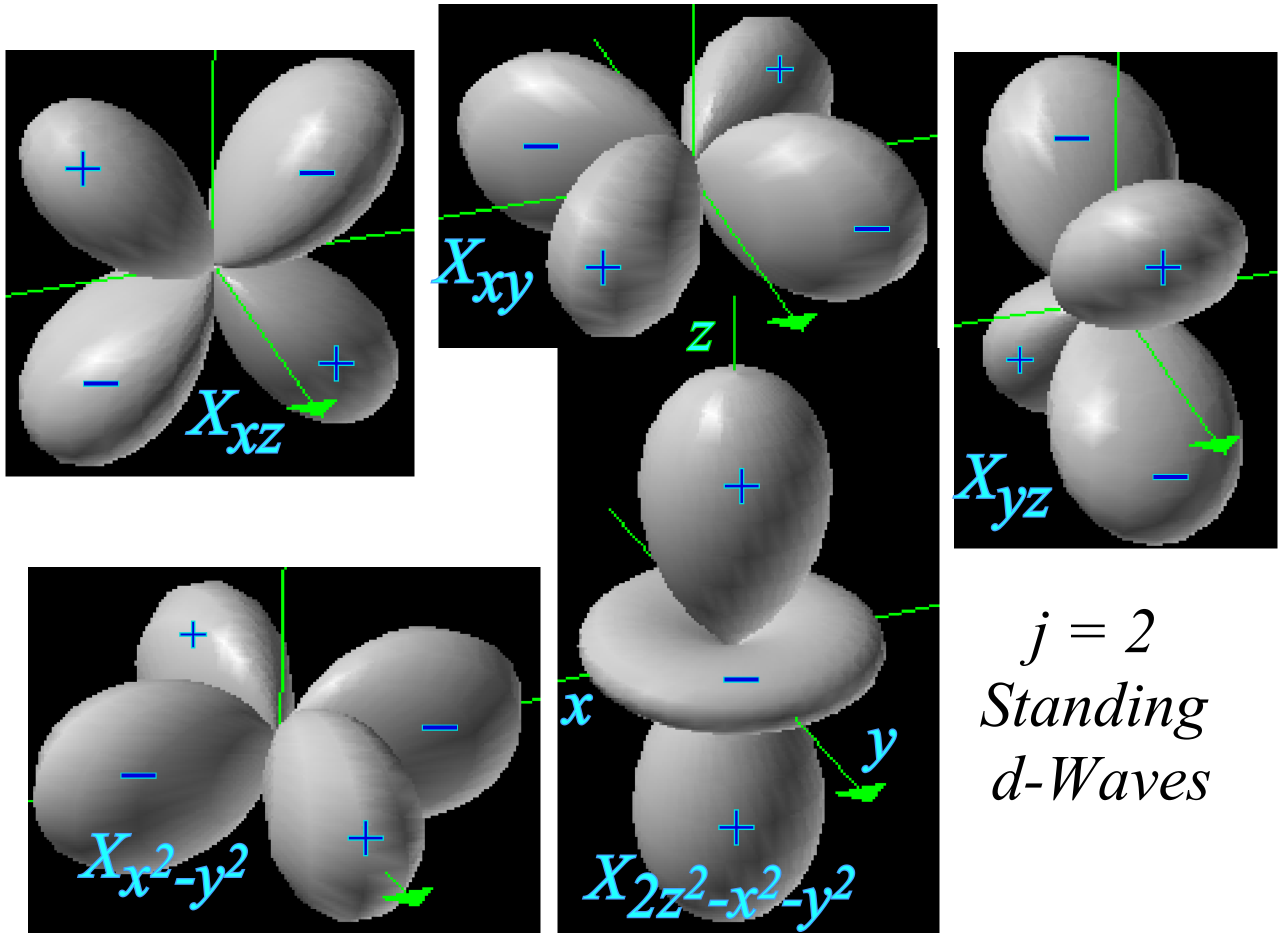
$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=1}(\phi\theta) = D^{2*}_{1,0}(\phi\theta 0) = -\sqrt{\frac{3}{2}}e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

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

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

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

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



j = 2
Standing
d-Waves

<u>*Notation Switch*</u>:
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).

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

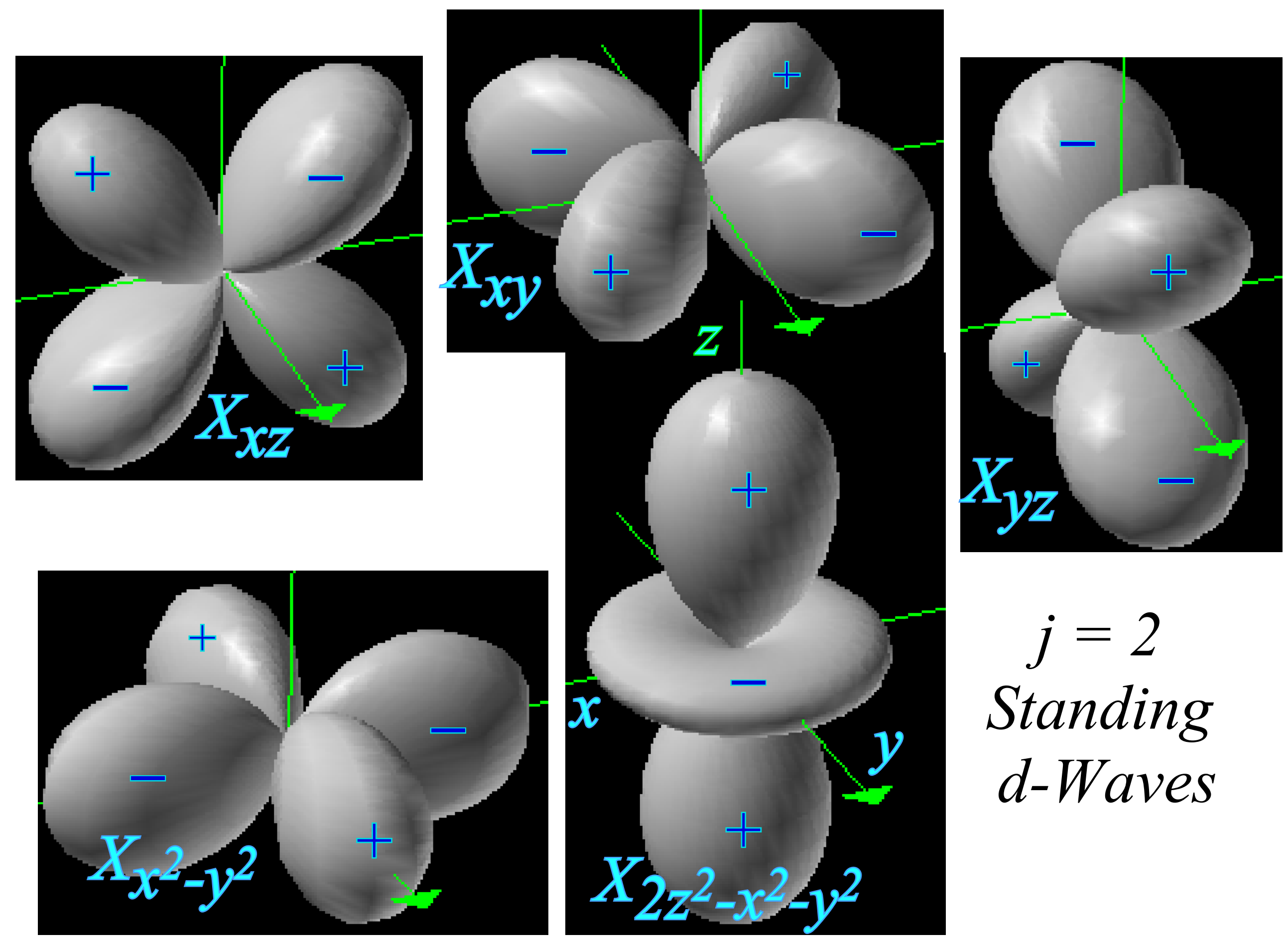
$$\sqrt{4\pi/5}\;Y^{\ell=2}_{m=2}(\phi\theta) = D^{2*}_{2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}}e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x+iy)^2}{r^2}$$

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

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

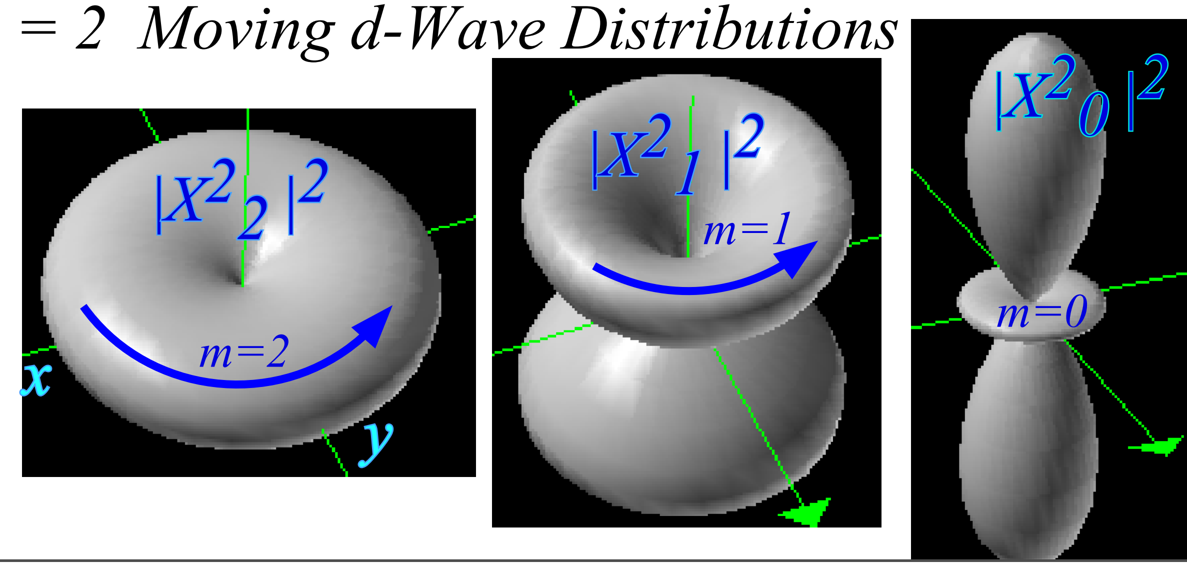
$$\sqrt{4\pi/5}\;Y^{\ell=2}_{m=-1}(\phi\theta) = D^{2*}_{-1,0}(\phi\theta 0) = \sqrt{\frac{3}{2}}e^{-i\phi}\sin\theta\cos\theta = \sqrt{\frac{3}{2}}\frac{(x-iy)z}{r^2}$$

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



j = 2
Standing d-Waves

j = 2 Moving d-Wave Distributions



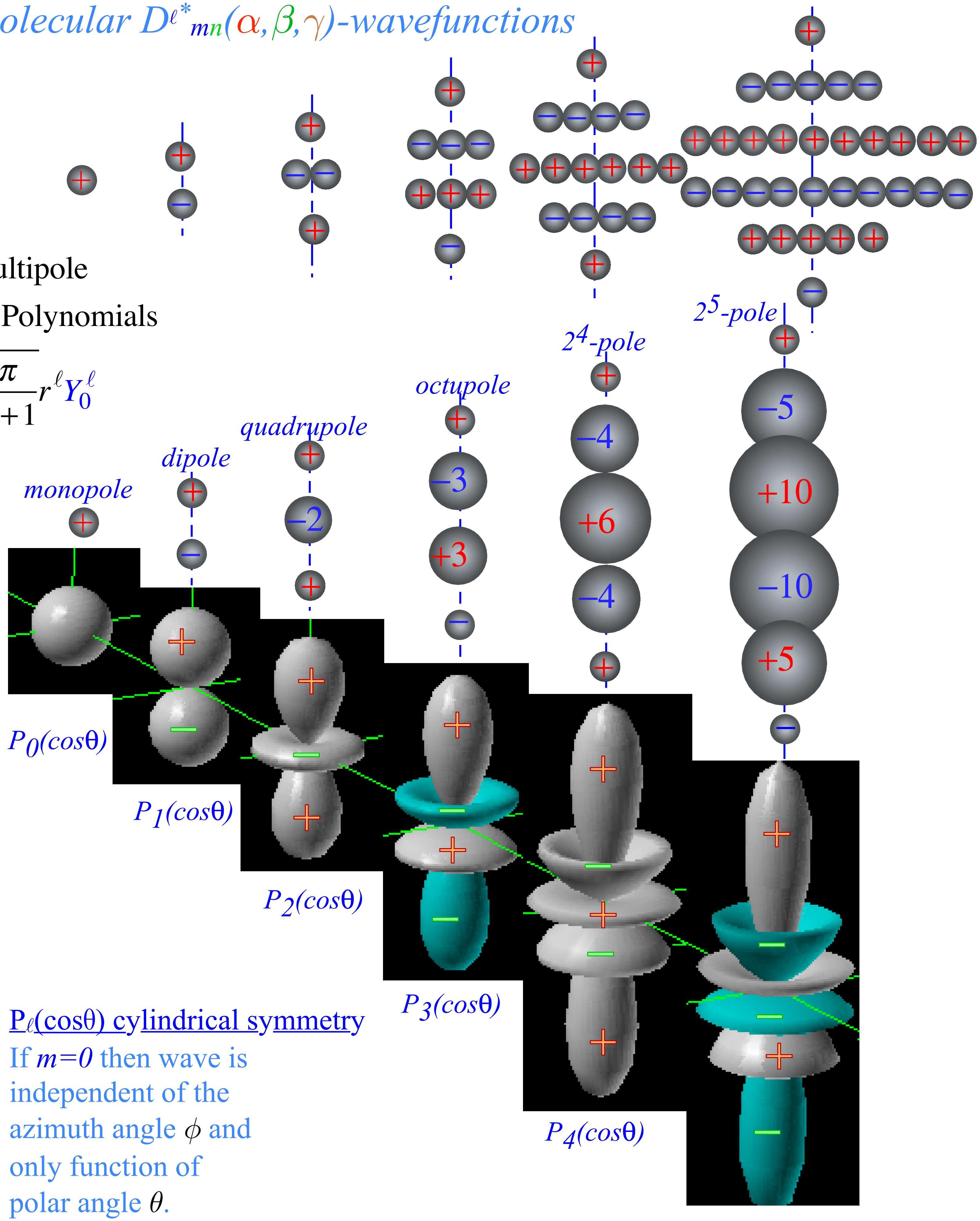
Notation Switch:
azimuth angle:
$\alpha \to \phi$
polar angle:
$\beta \to \theta$

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:
$\alpha \rightarrow \phi$
polar angle:
$\beta \rightarrow \theta$

$P_\ell(\cos\theta)$ 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 $|^J_{mn}\rangle = \mathbf{P}^J_{mn}|_{(0,0,0)}\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|_{(0,0,0)}\rangle$

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

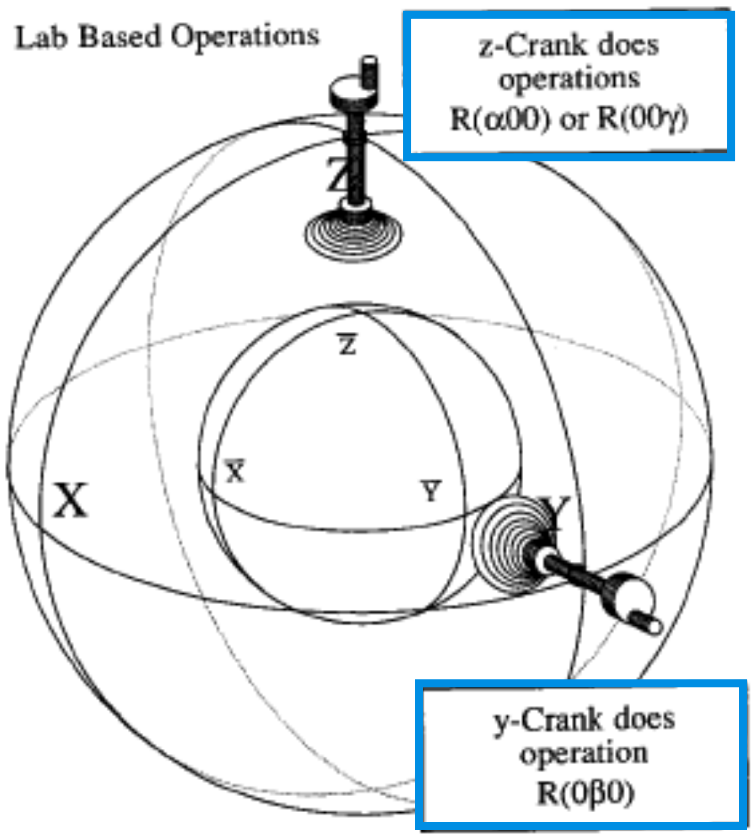
"Mock-Mach" lab-vs-body-defined states $\left|{}^{J}_{mn}\right\rangle = \mathbf{P}^{J}_{mn}\left|(0,0,0)\right\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)\left|(0,0,0)\right\rangle$

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!*

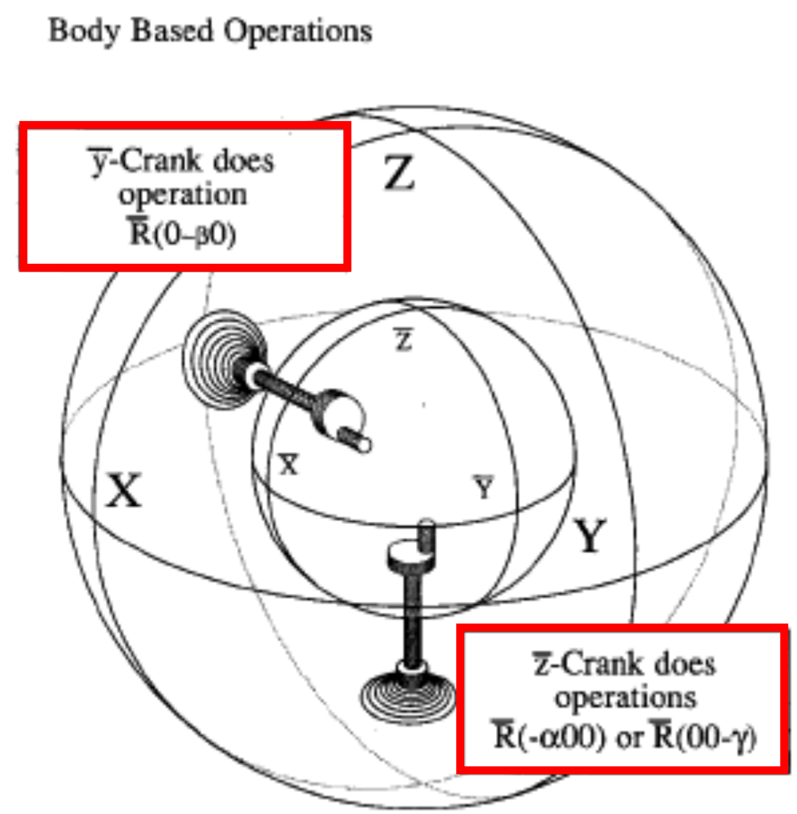


Figure from Ch. 5 of PSDS (Originally in Rev. Mod. Phys. 50, 1, p. 37-83 (1978) Fig. 2)

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

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

For $SU(2)$ and $R(3)$, sum over rotations is an integral over Euler angles $(\alpha\beta\gamma)$.

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

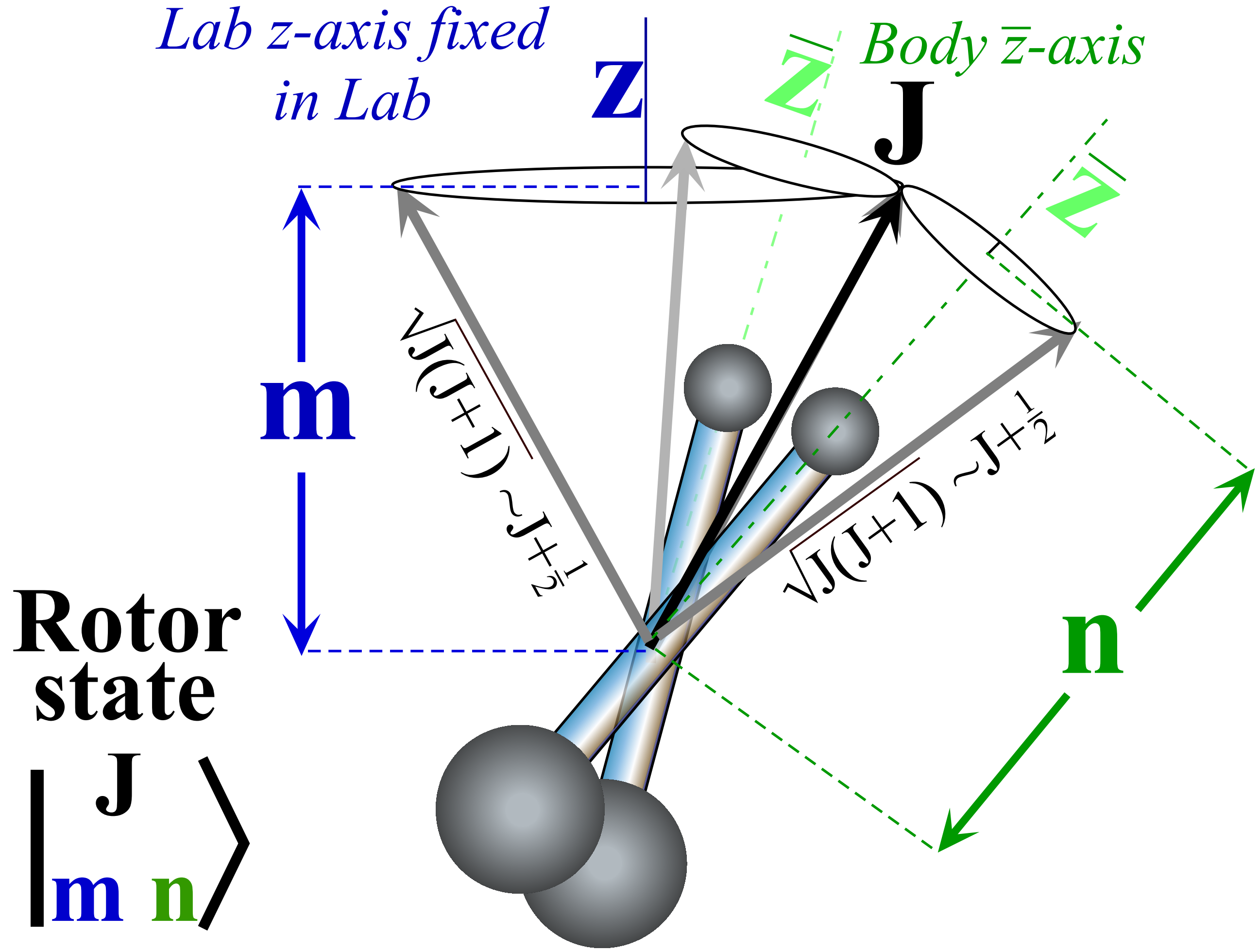
$$\text{for } R(3): \frac{\ell^j}{N}\int d(\alpha\beta\gamma) = \frac{2j+1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma = 2j+1 = \ell^j$$

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⟩.

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



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

"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〉.

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

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

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

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

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

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.

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

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

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

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

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

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

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

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⟩.

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

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.

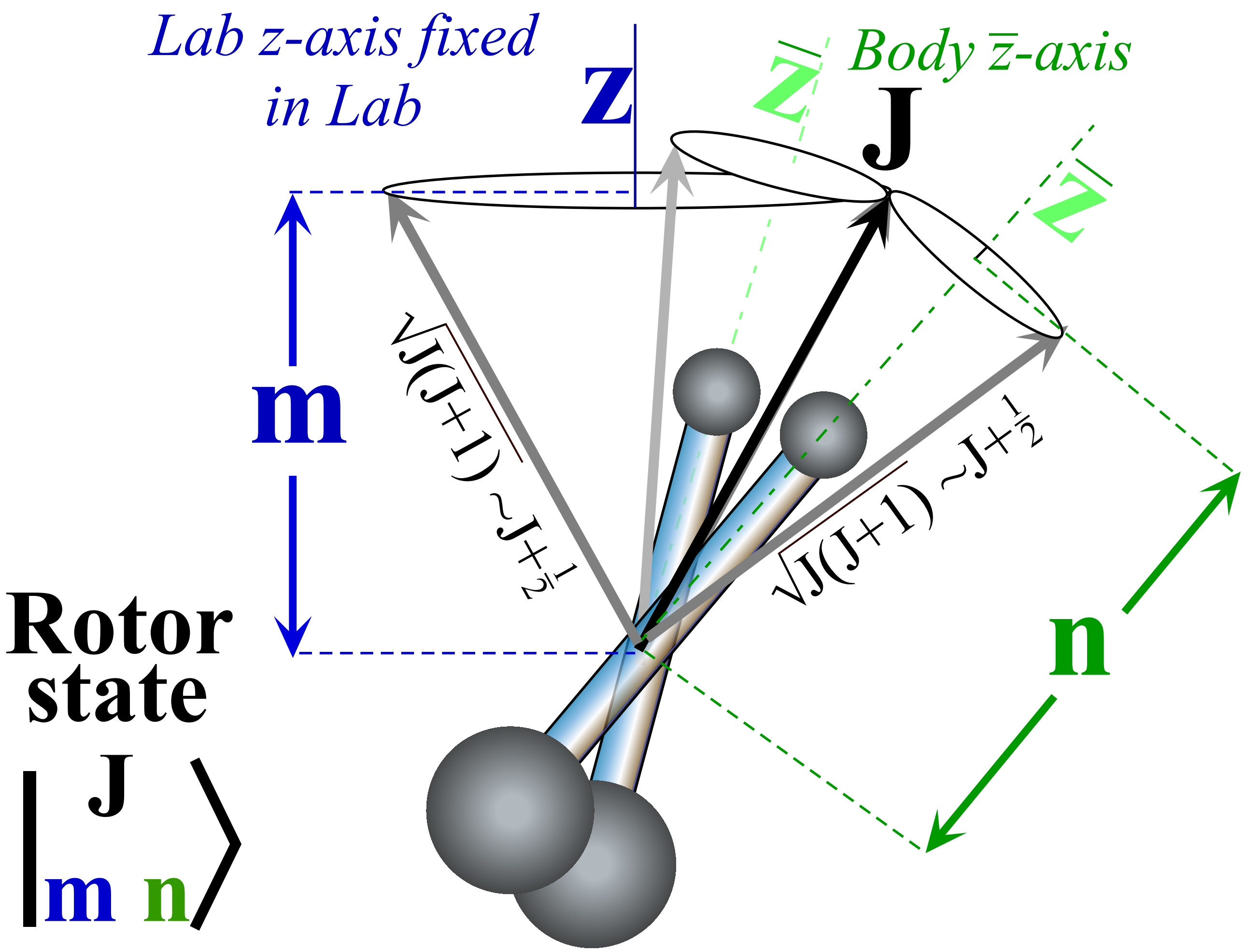
LAB $m \leftrightarrow m'$ *transform*
$$\mathbf{R}(\alpha\beta\gamma)\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle = \sum_{m'=-j}^{j} D^{j}_{m',n}(\alpha\beta\gamma)\left|\begin{smallmatrix} j \\ m',n \end{smallmatrix}\right\rangle$$

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

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

LAB *m* *eigenvalues*
$$\mathbf{s}_Z\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle = m\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle$$

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



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

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

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

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

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*

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

BOD $n \leftrightarrow n'$ *transform*

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

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

LAB *m* *eigenvalues*

$$\mathbf{s}_Z\left|{j \atop m,n}\right\rangle = m\left|{j \atop m,n}\right\rangle$$

BOD *n* *eigenvalues*

$$\bar{\mathbf{s}}_{\bar{Z}}\left|{j \atop m,n}\right\rangle = -n\left|{j \atop m,n}\right\rangle$$

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 $\mathbf{T}^k_q$ 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

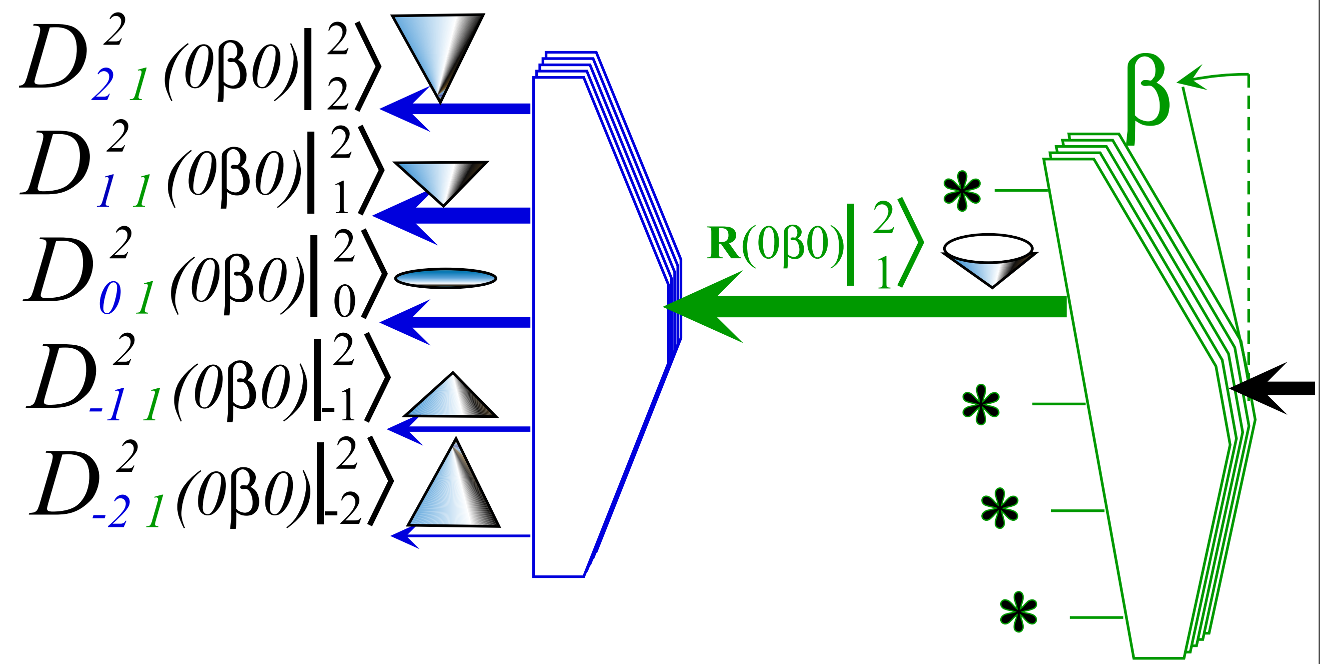
2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

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

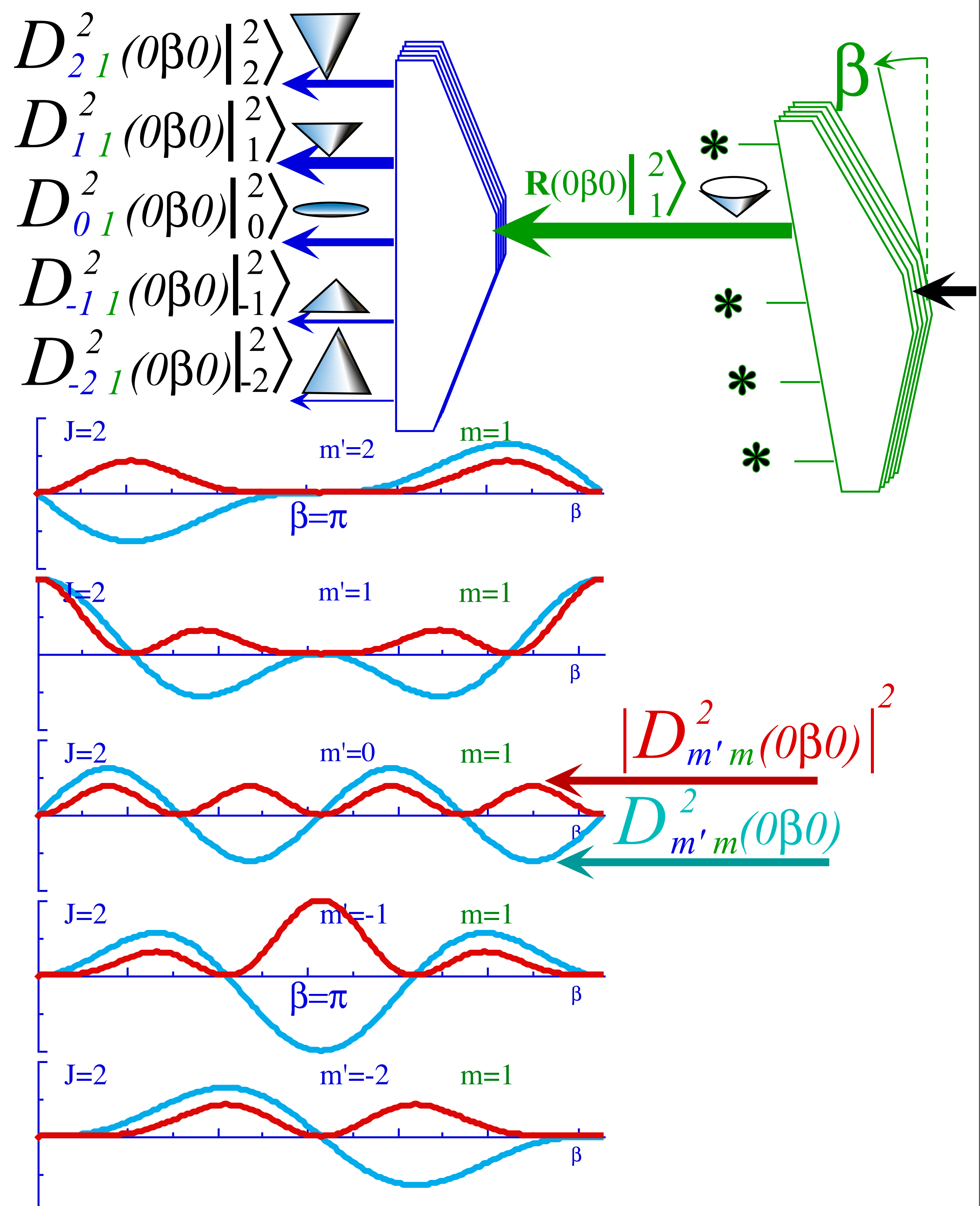
2. R(3) rotation and U(2) unitary $D^J_{mn}(\alpha,\beta,\gamma)$-transformation matrices

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

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

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



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

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

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

QTforCA Unit 8. Ch. 23 Fig. 23.2.1

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

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

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

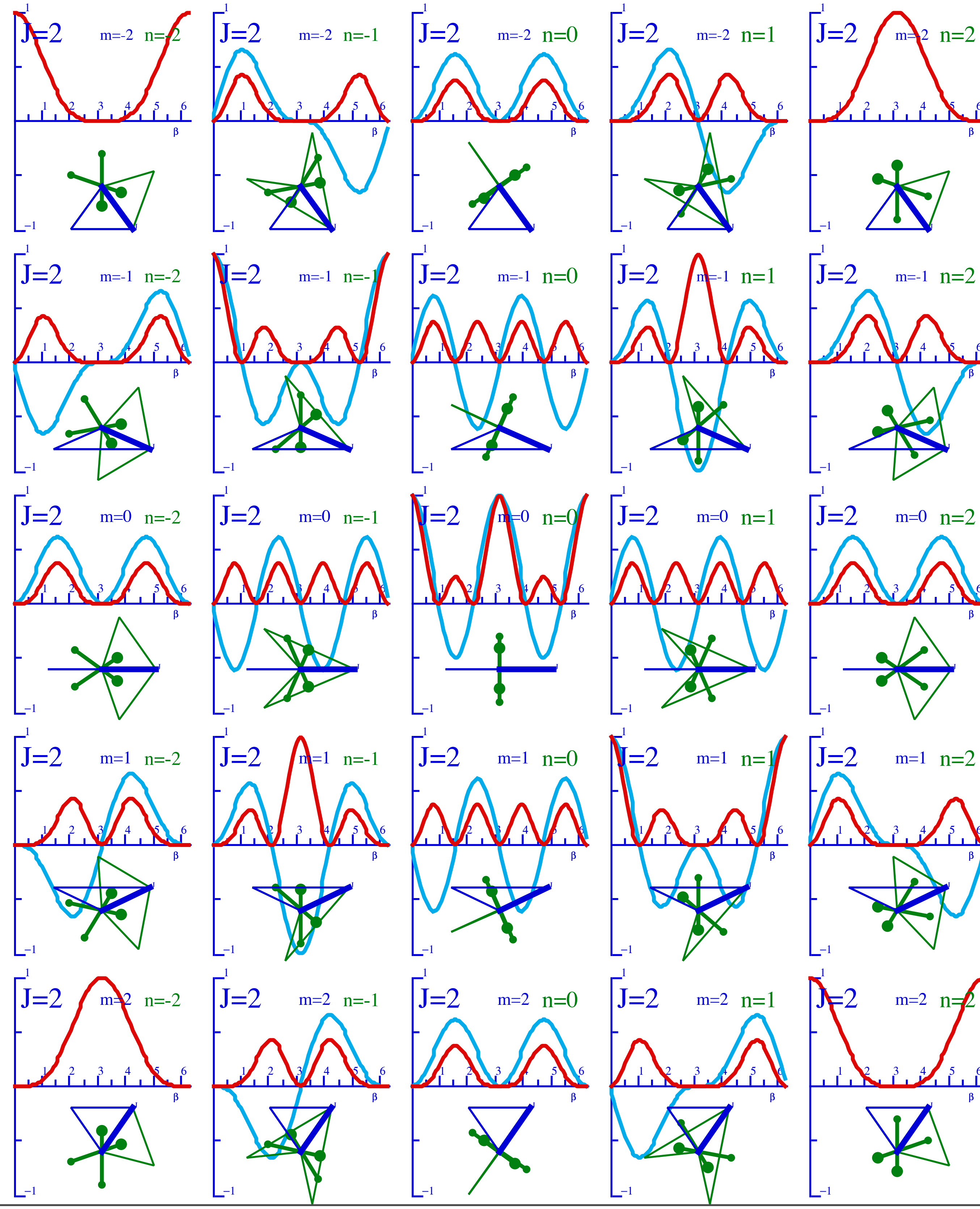
$$\mathbf{R}(0\beta 0)\left|{}^j_n\right\rangle = \sum_{m'=-j}^{j}\left|{}^j_{m'}\right\rangle\left\langle{}^j_{m'}\right|\mathbf{R}(0\beta 0)\left|{}^j_n\right\rangle$$

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

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.

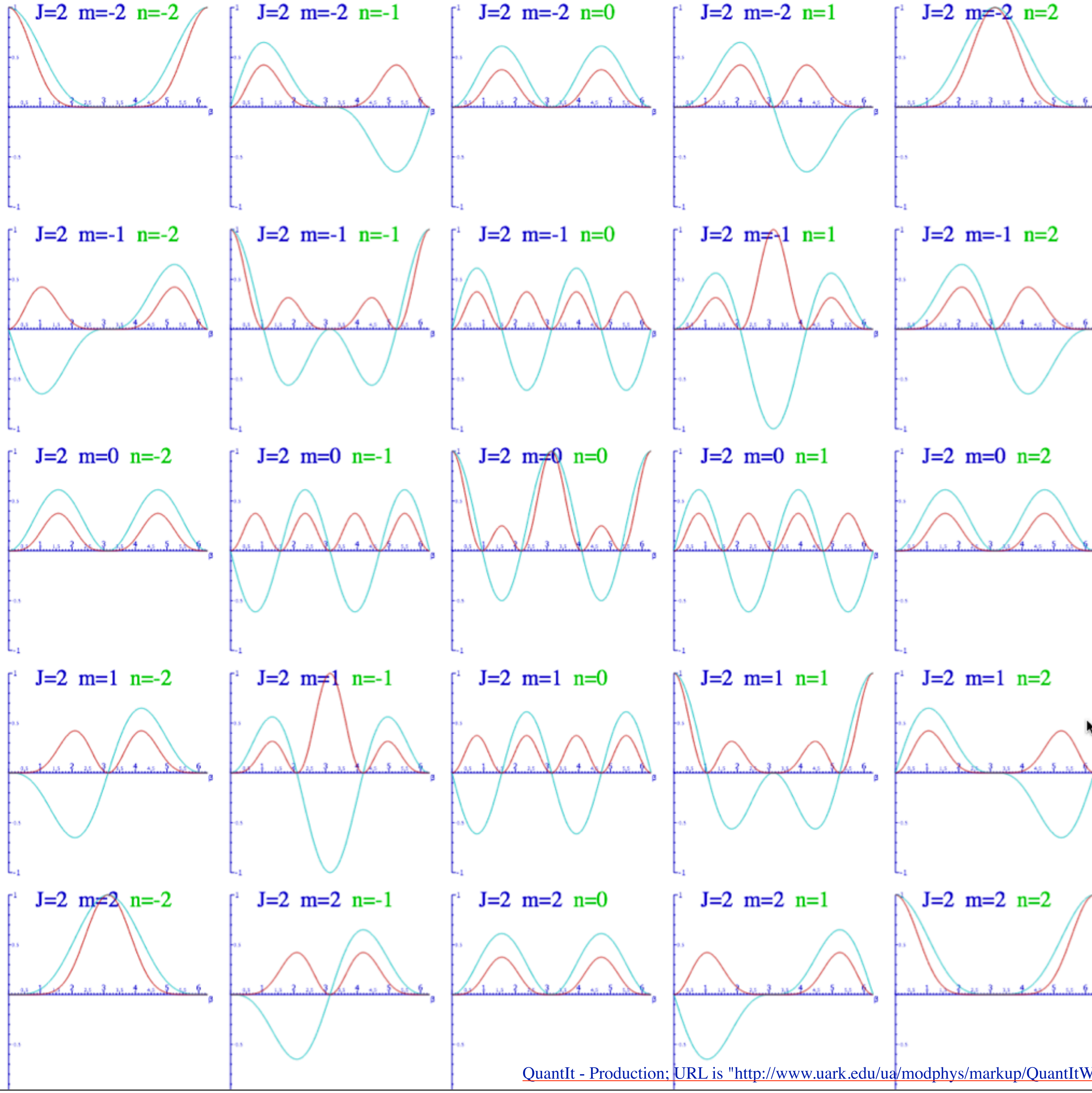
$$\left\langle{}^{j'}_{m'}\right|\mathbf{R}(\alpha\beta\gamma)\left|{}^2_1\right\rangle = \delta^{j'2}D^2_{m'1}(\alpha\beta\gamma) = \left\langle{}^{j'}_{m'}\middle|{}^2_1\right\rangle_R$$

$D^j_{m'n}(0\beta 0)$ 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 - Production; URL is "http://www.uark.edu/ua/modphys/markup/QuantItWeb.html"

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 $\mathbf{T}^k_q$ 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

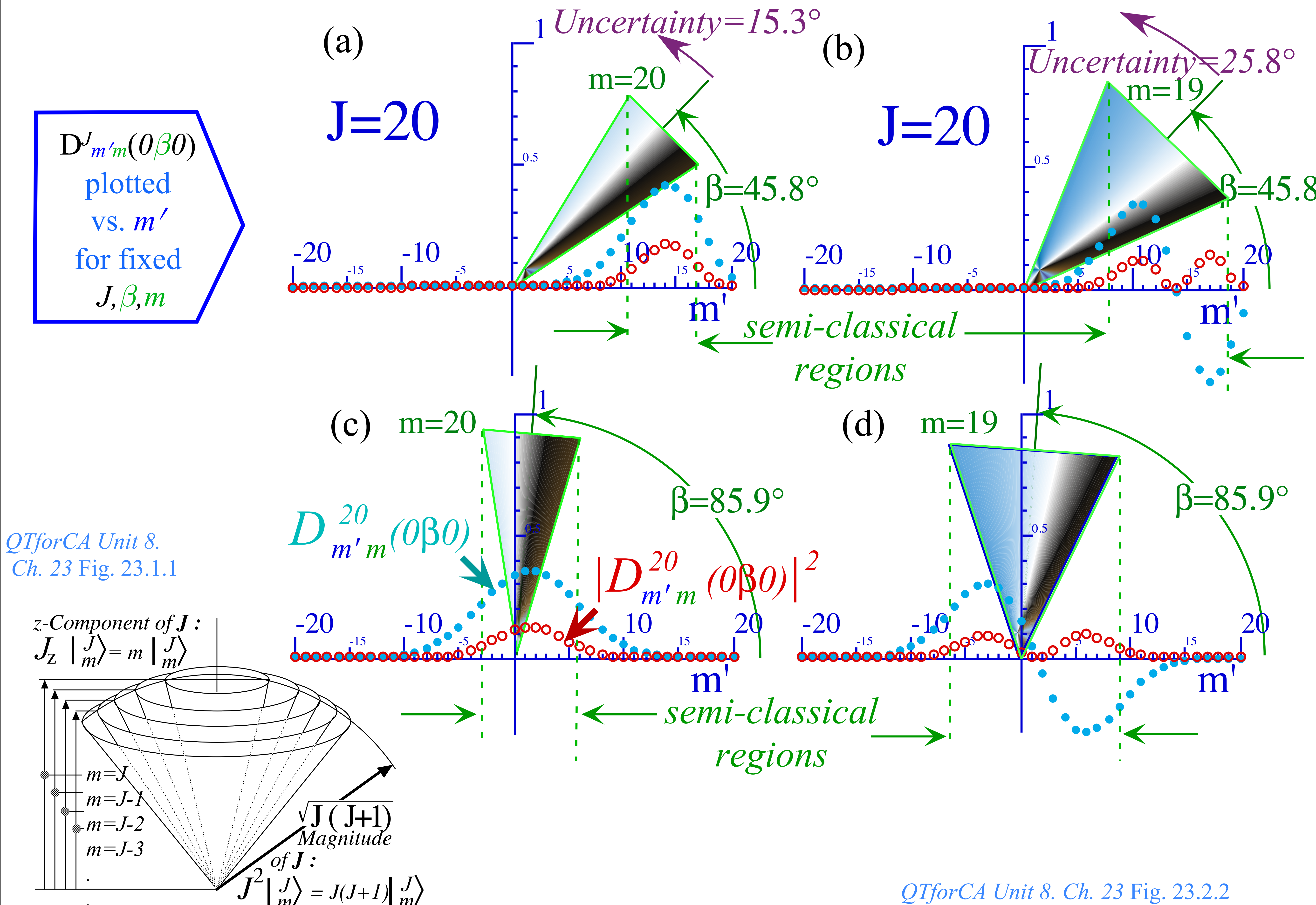
Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

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

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

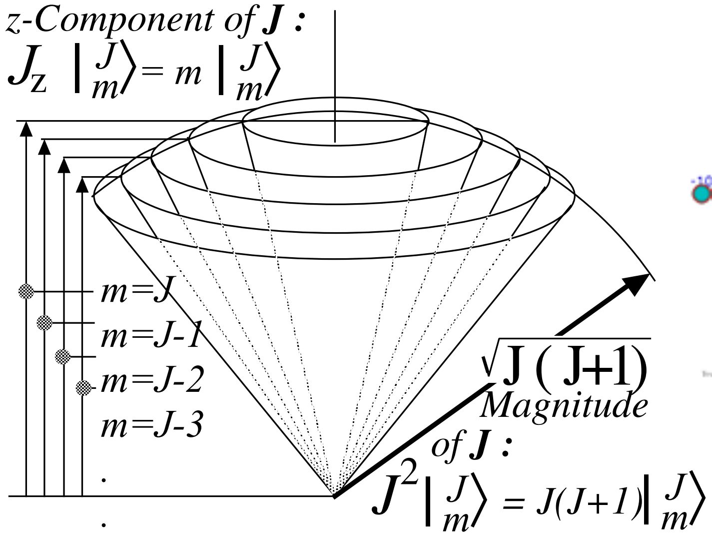
Asymmetric Top eigensolutions for J=1-2

Angular momentum cones and high J properties



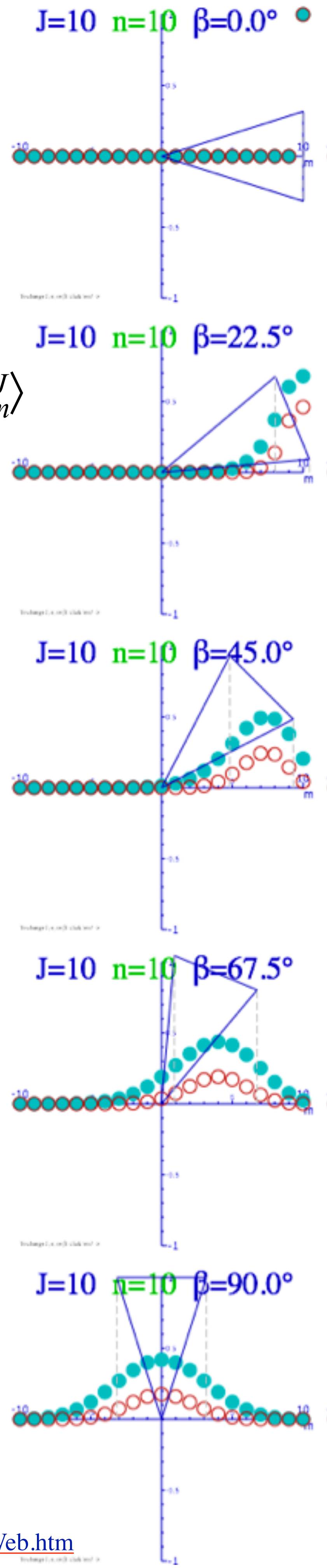
QTforCA Unit 8. Ch. 23 Fig. 23.1.1

QTforCA Unit 8. Ch. 23 Fig. 23.2.2

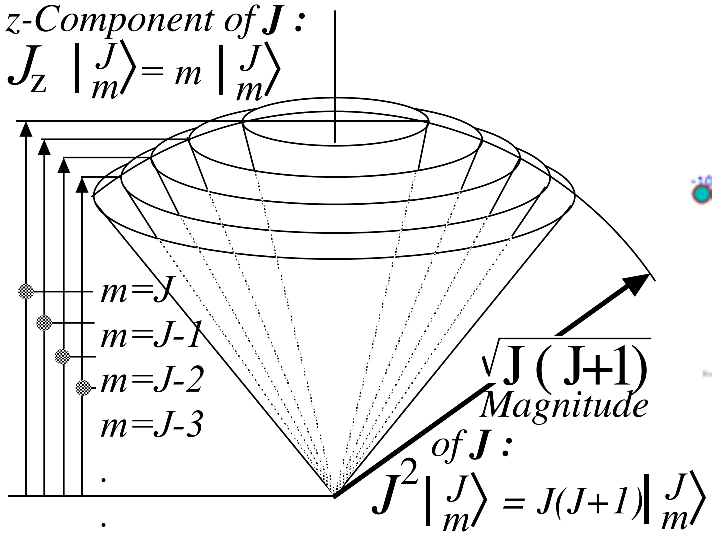


$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

$n=10$

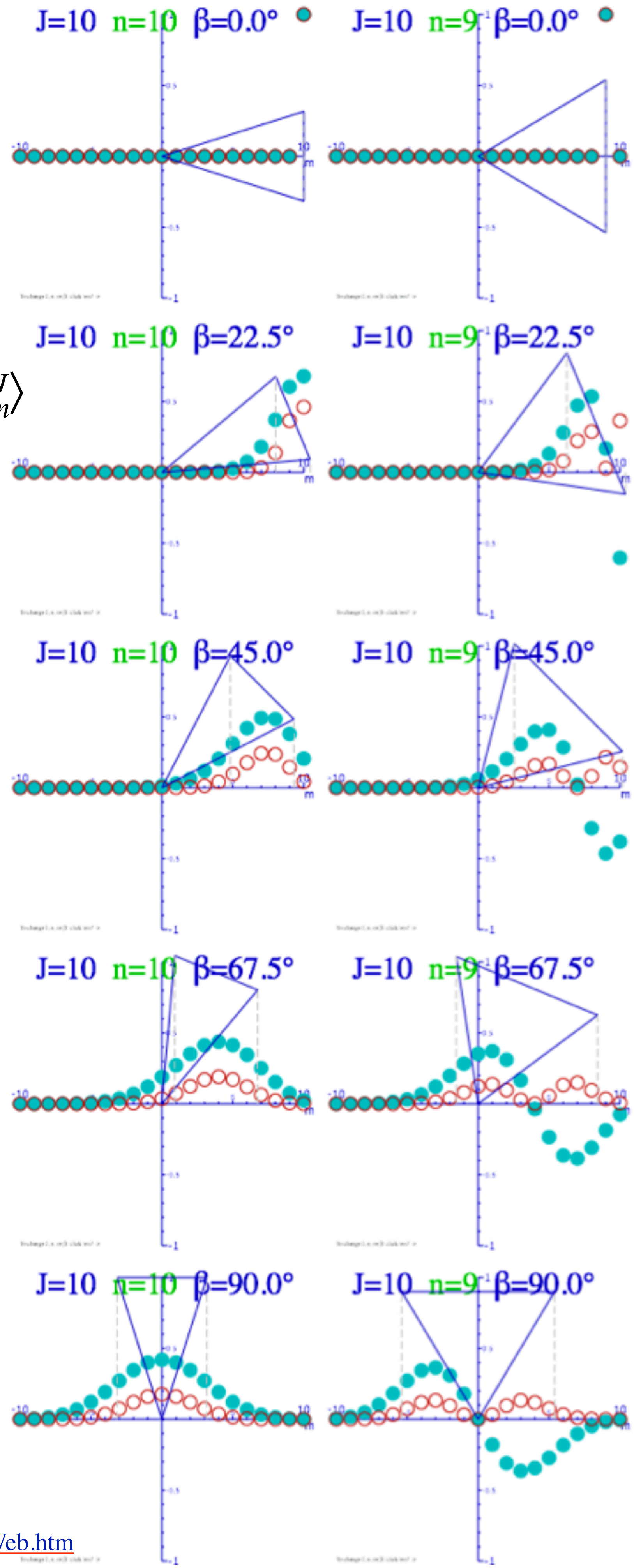


http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

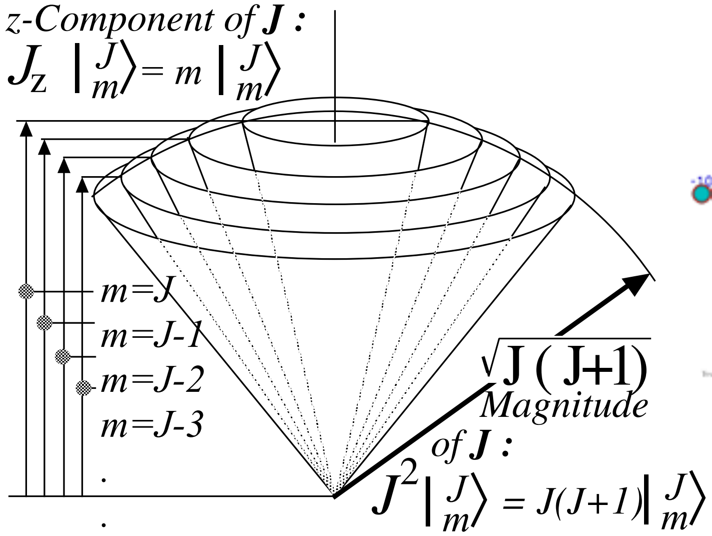


$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

$n=9$

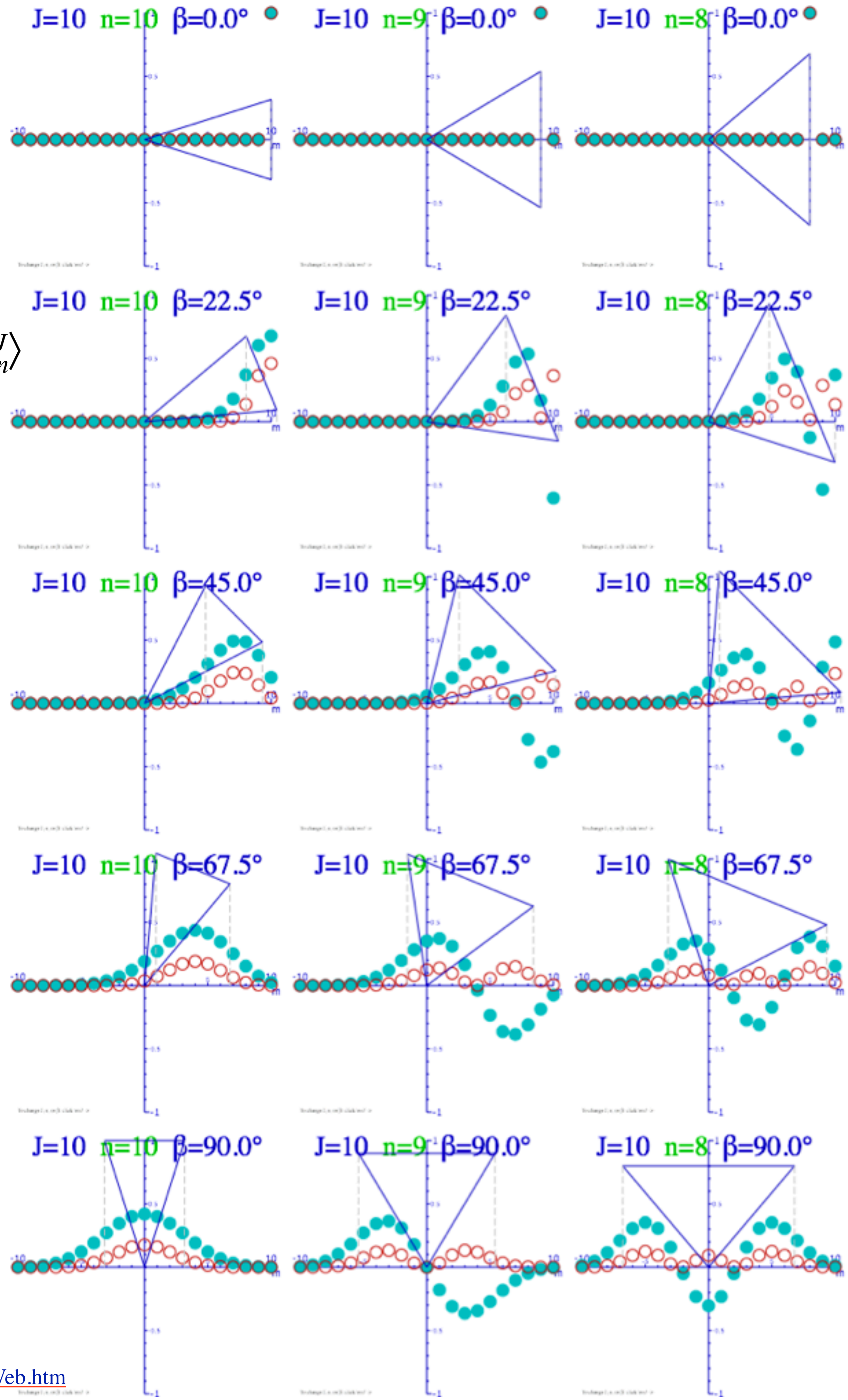


http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

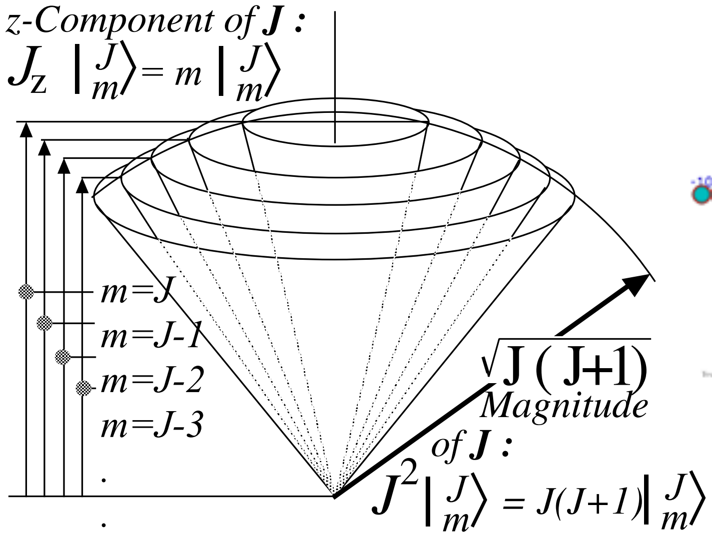


$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

$n=8$

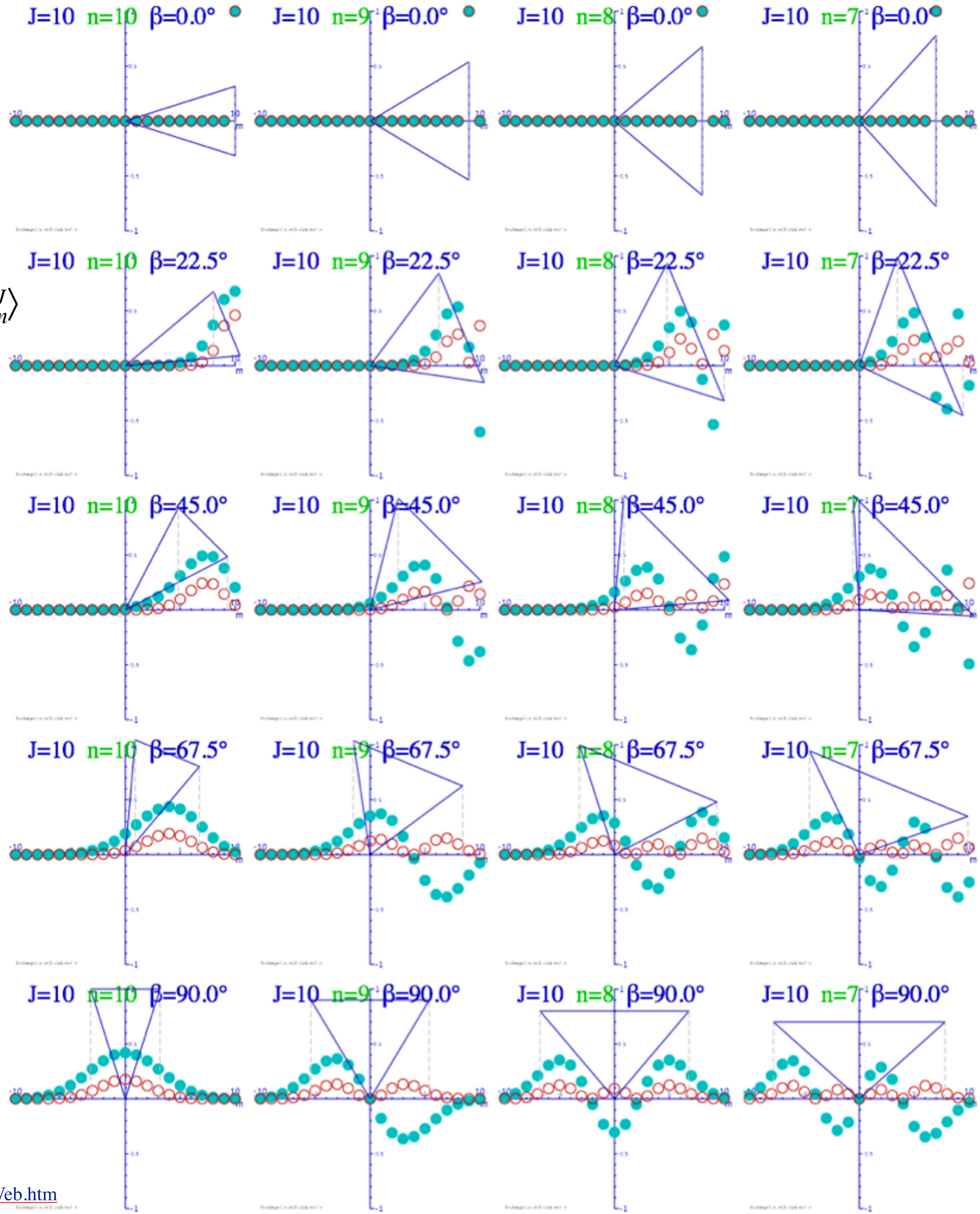


http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

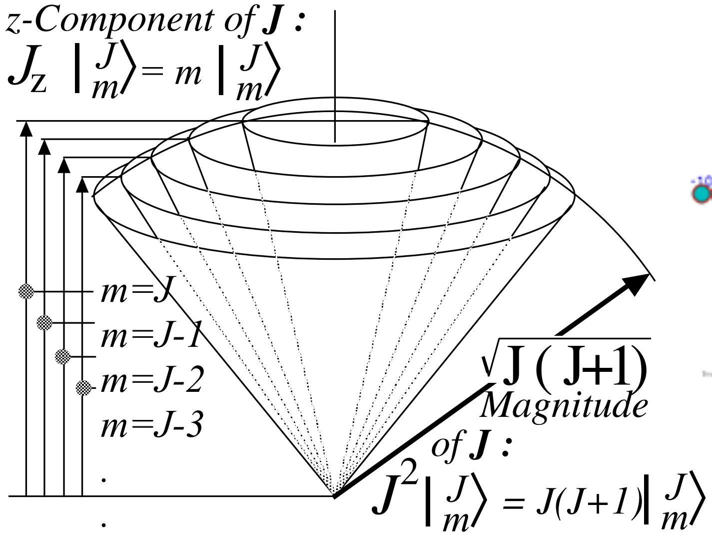


$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

$n=7$

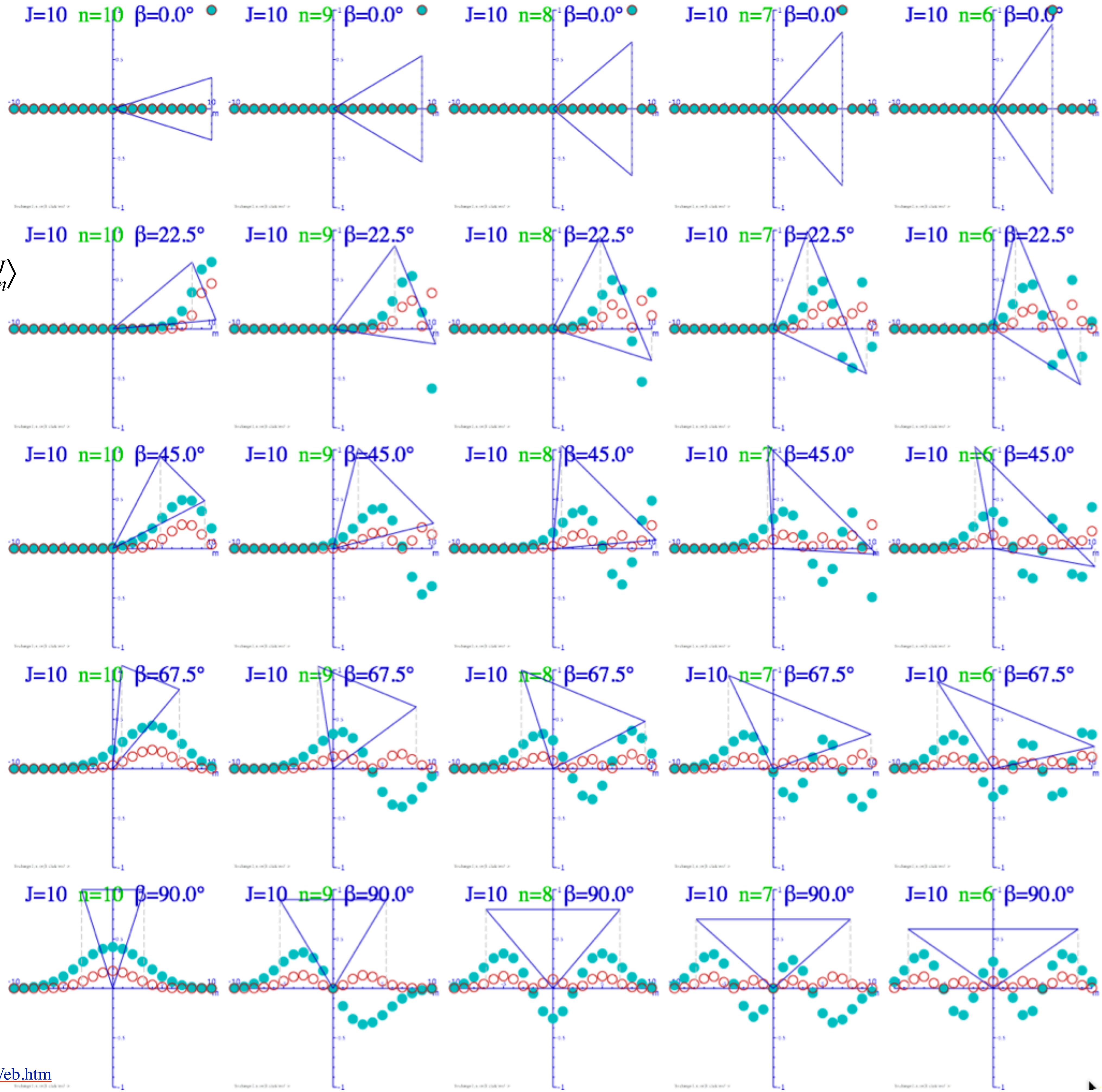


http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

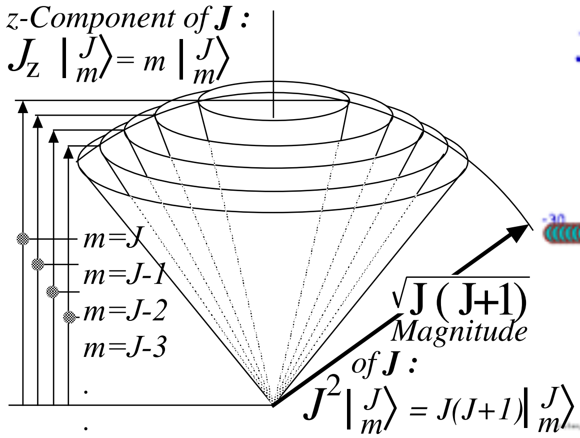


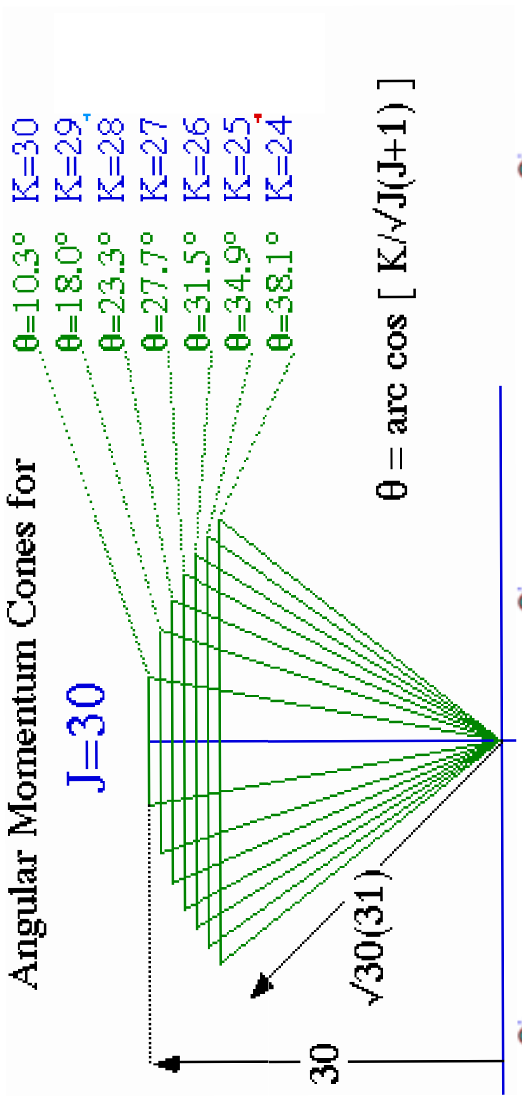
$D^J_{m,n}(0\beta 0)$
plotted
vs. m
for fixed
$J=10, \beta, n$

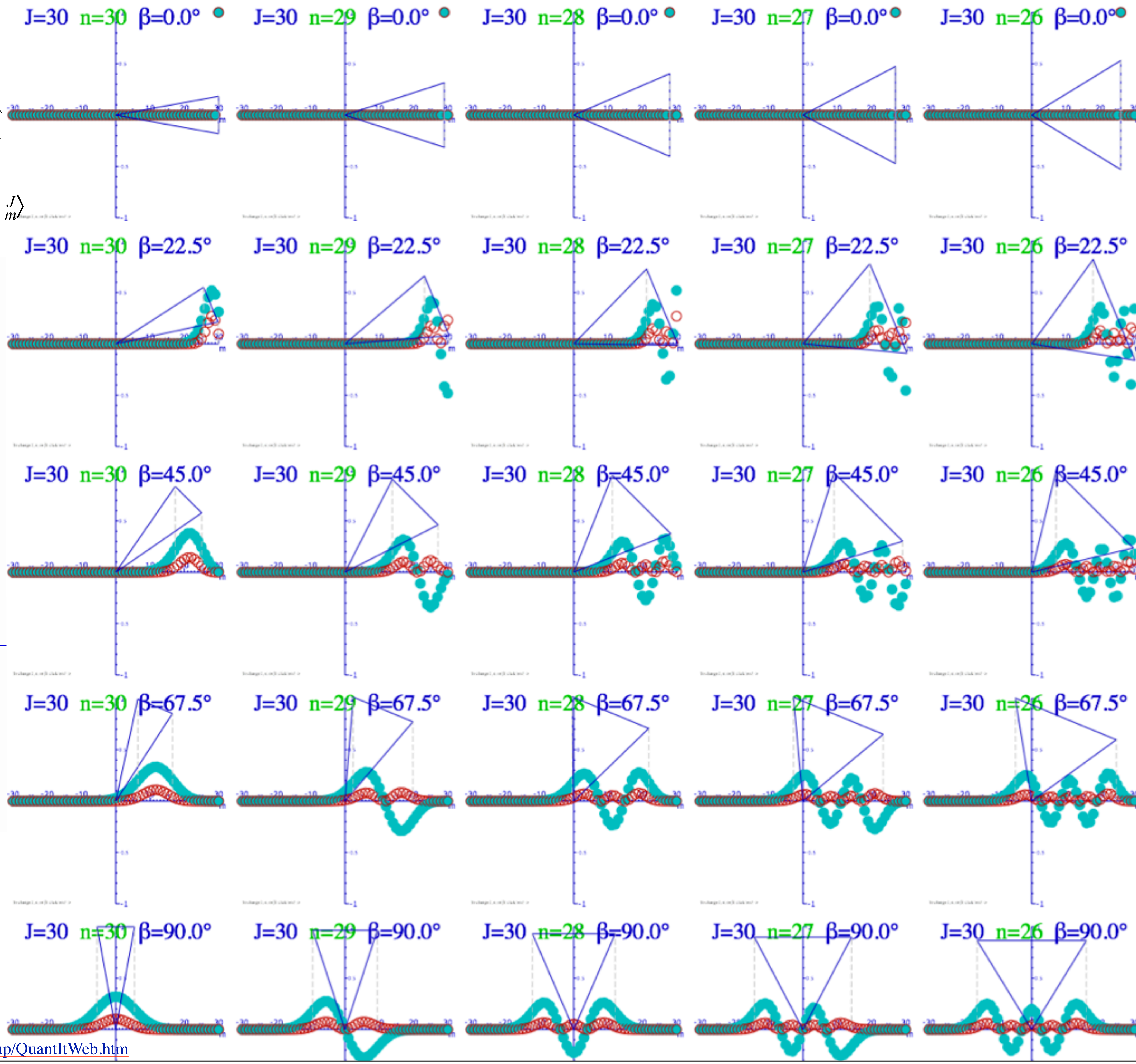
$n=6$



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







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

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 $\mathbf{T}^k_q$ *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*

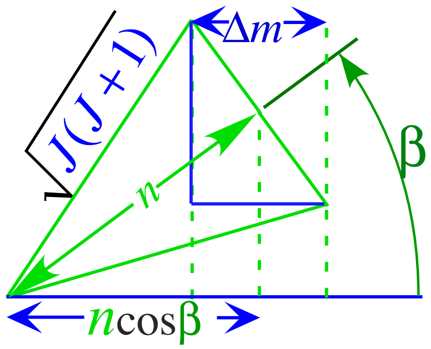
Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

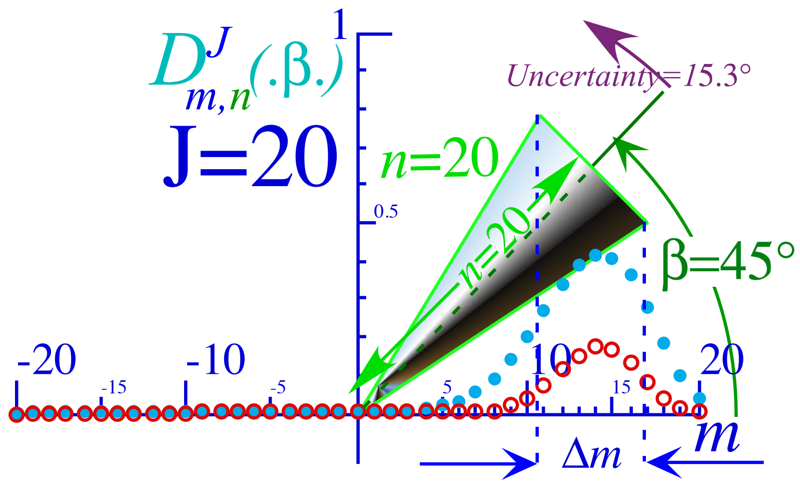
Asymmetric Top eigensolutions for J=1-2

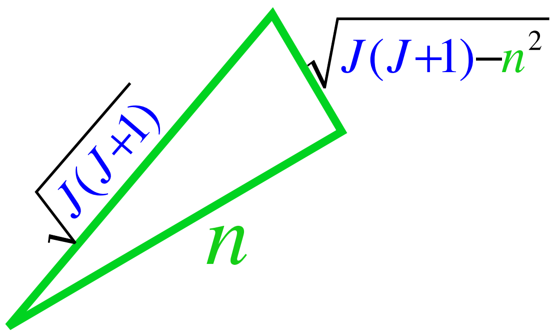
Angular momentum cones and high J properties

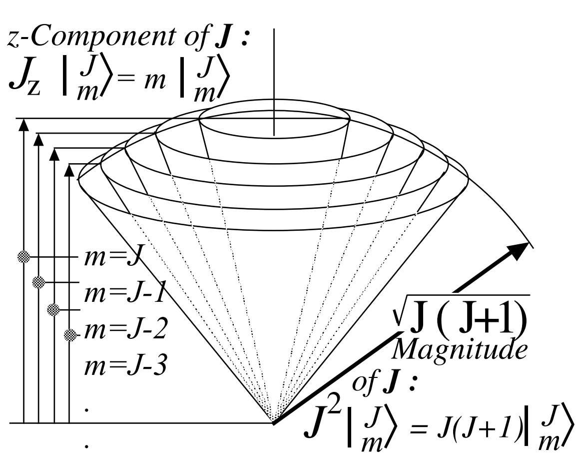
Using literal interpretation of $\left|\begin{smallmatrix} J \\ m \end{smallmatrix}\right\rangle$ to derive approximate number Δm of "most-busy" counters and determine most probable m-values.

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





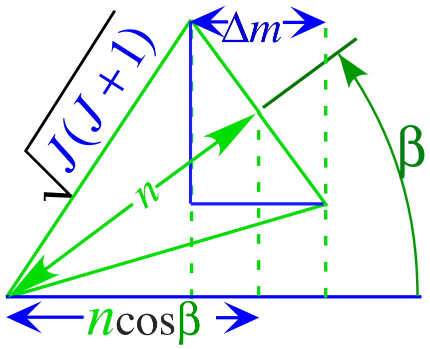




http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

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.

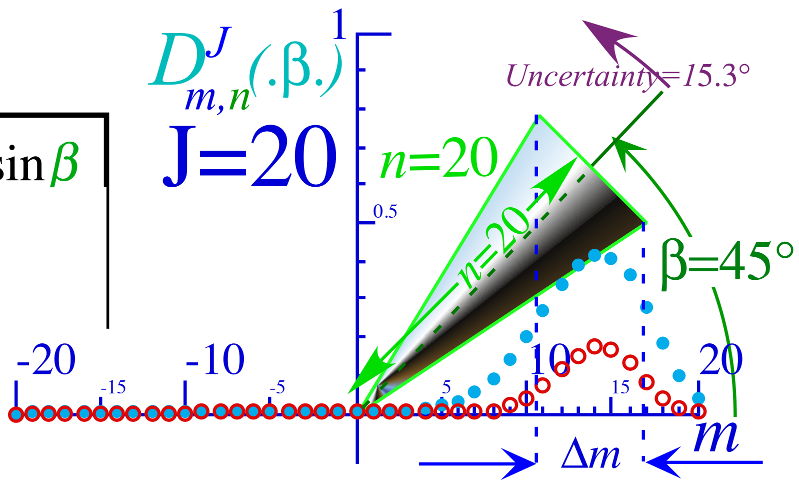
$$\Delta m = 2\sqrt{J(J+1) - n^2} \cdot \sin\beta$$



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

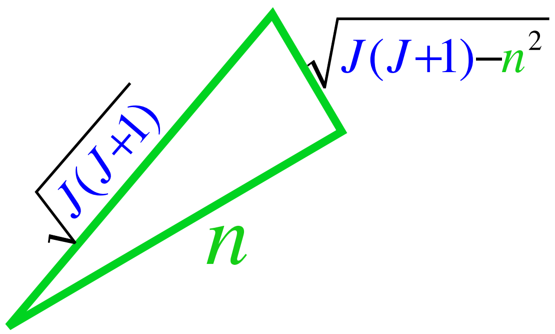
$n=J-1$:

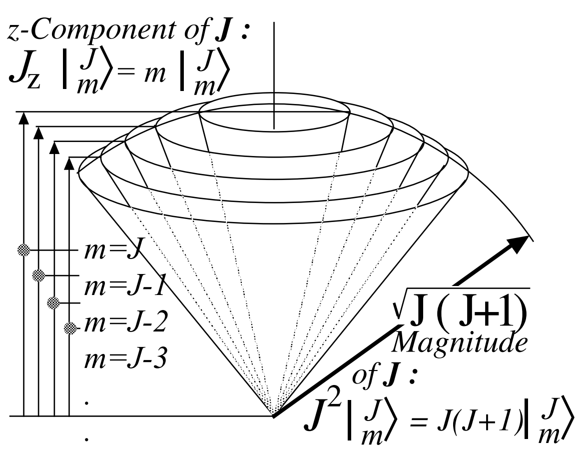
$n=J-2$:



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

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

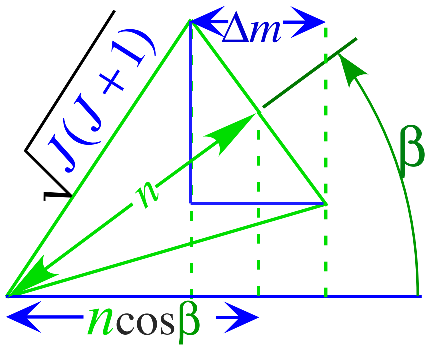




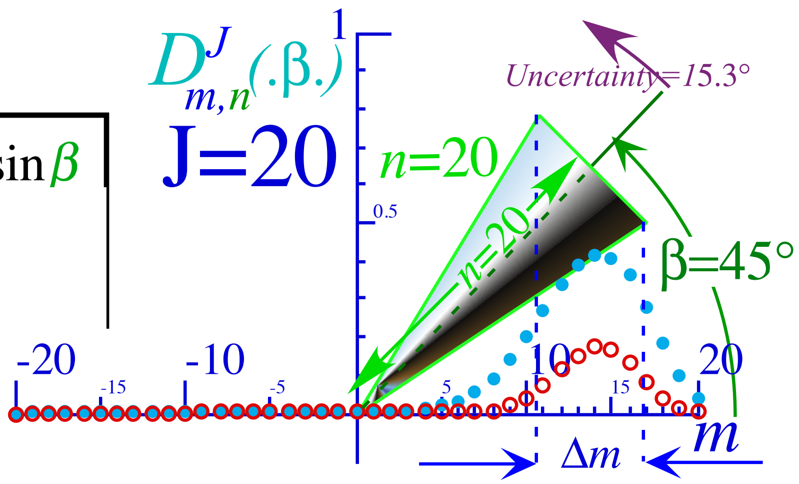
http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

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.

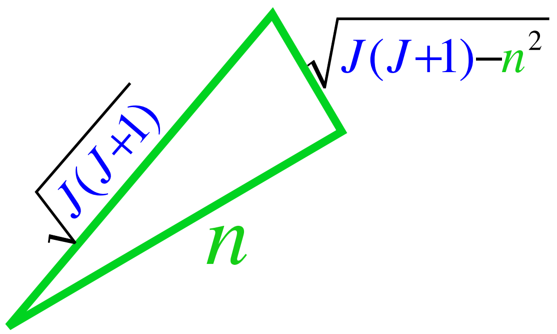
$$\Delta m = 2\sqrt{J(J+1) - n^2} \cdot \sin\beta$$



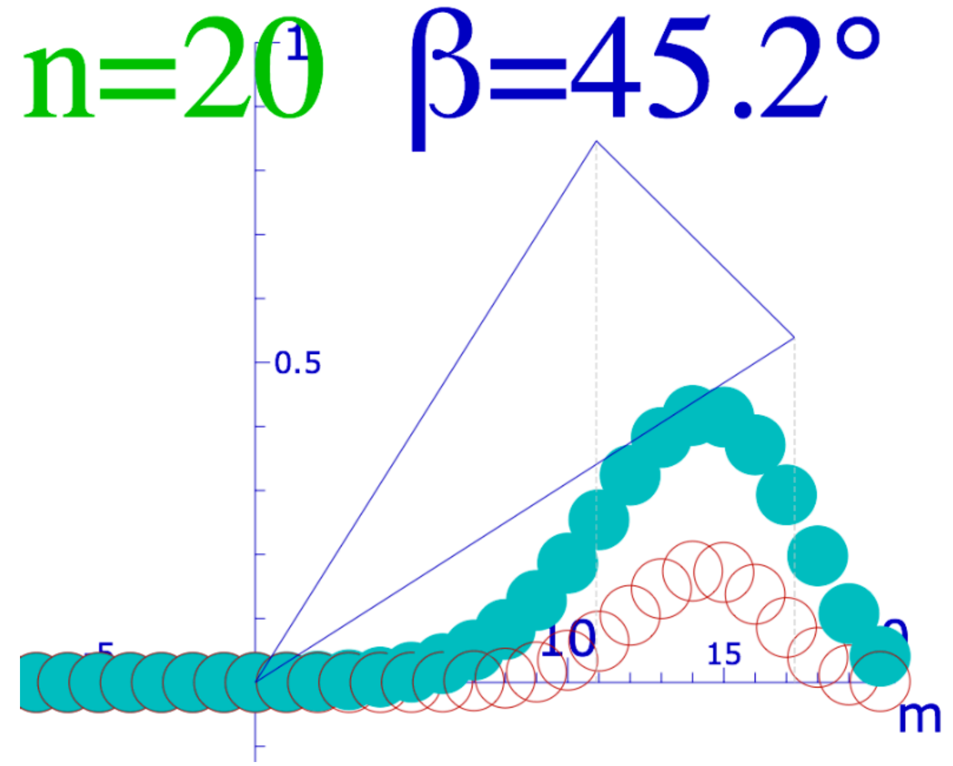
$n=J$:	$\Delta m = 2\sqrt{J} \quad \sin\beta$
$n=J-1$:	
$n=J-2$:	



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



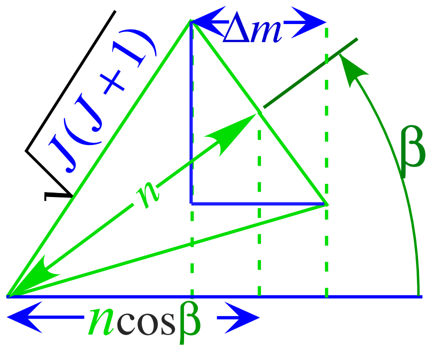
Testing formula with $J=20$ for $\beta=45°$...



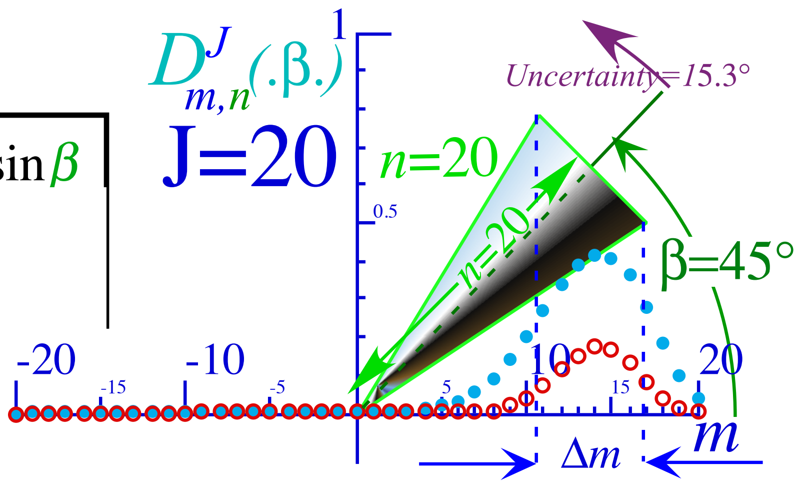
http://www.uark.edu/ua/modphys/markup/QuantItWeb.htm

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.

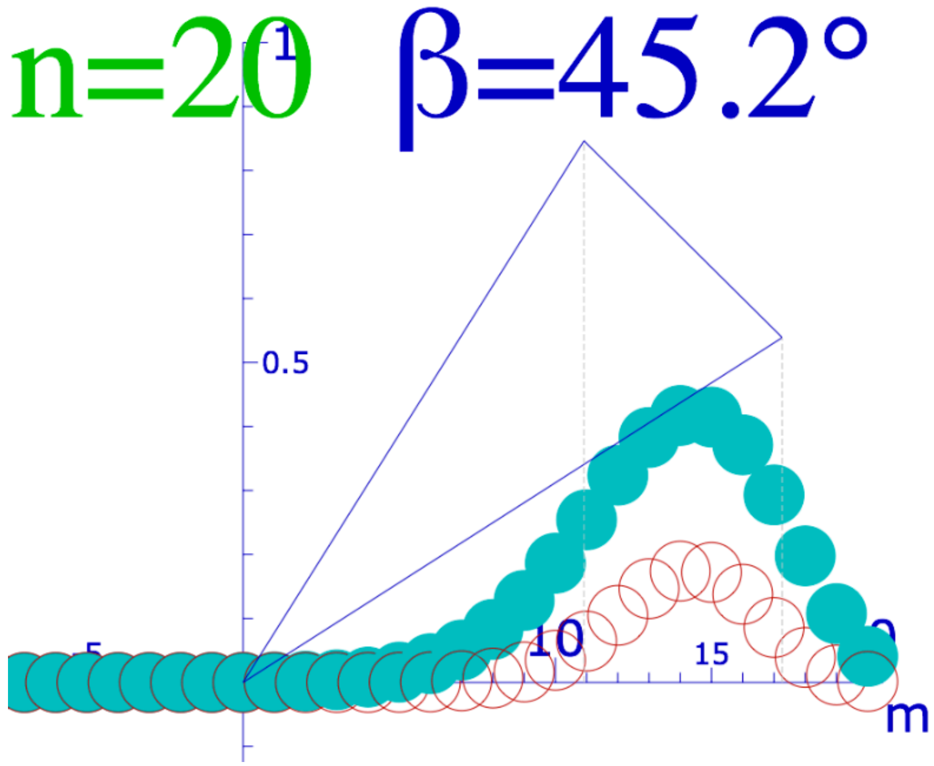
$$\Delta m = 2\sqrt{J(J+1)-n^2}\cdot \sin\beta$$

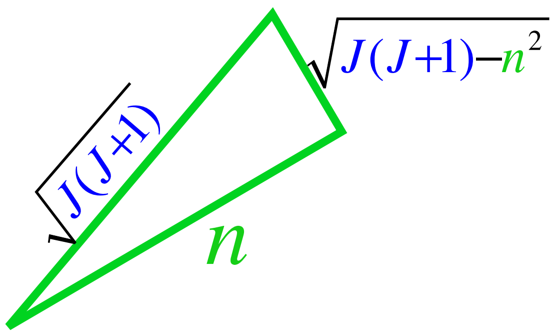


$n=J$:	$\Delta m = 2\sqrt{J}\ \sin\beta$
$n=J-1$:	
$n=J-2$:	



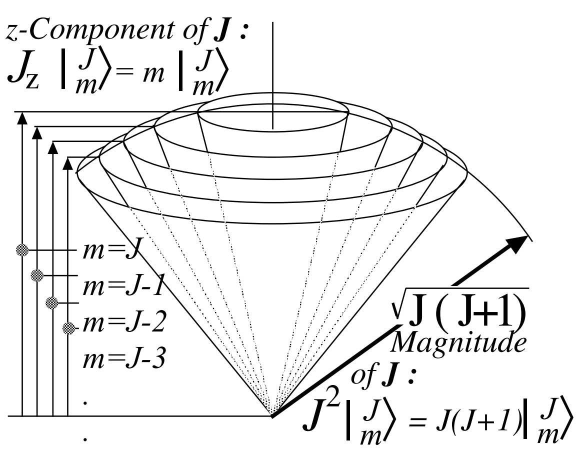
$\Delta m = 2\sqrt{20}\sin 45° = \sqrt{40} = 6.2$

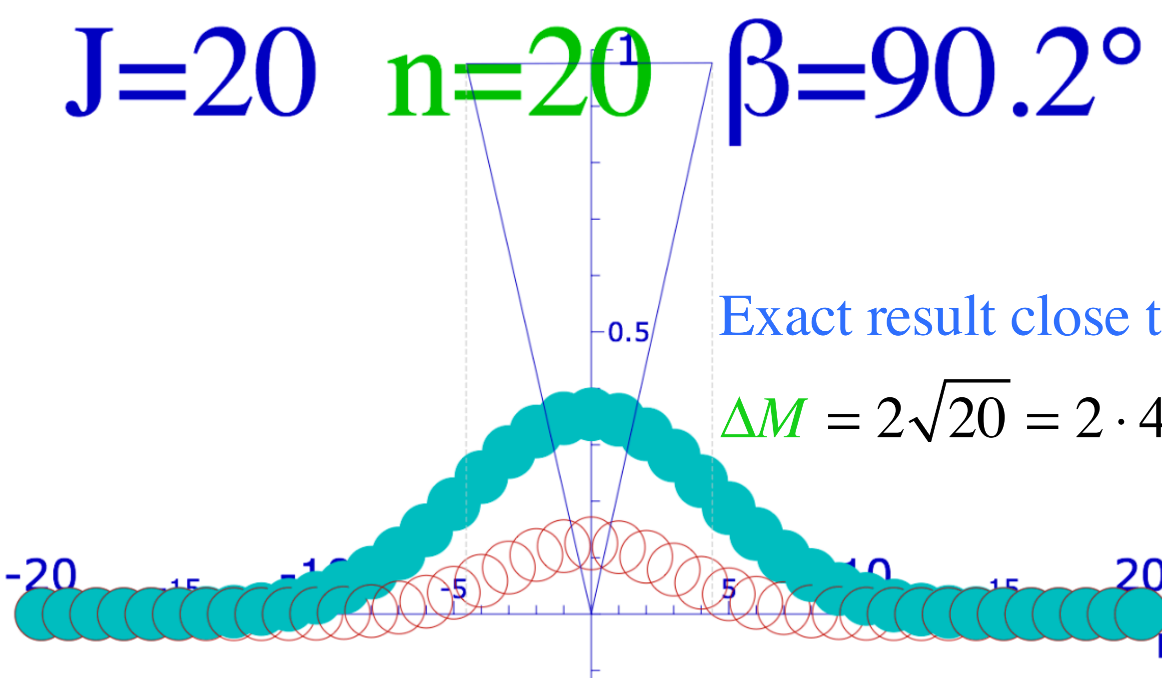




Testing formula with $J=20$ for $\beta=45°$...

...and for $\beta=90°$





Exact result close to:

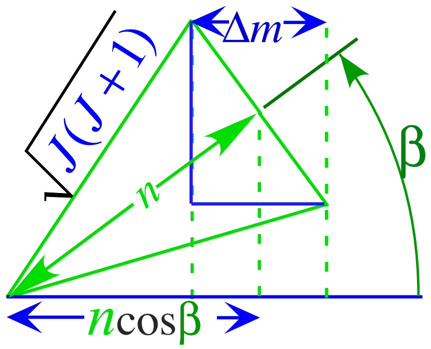
$\Delta M = 2\sqrt{20} = 2\cdot 4.47 = 8.94$

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

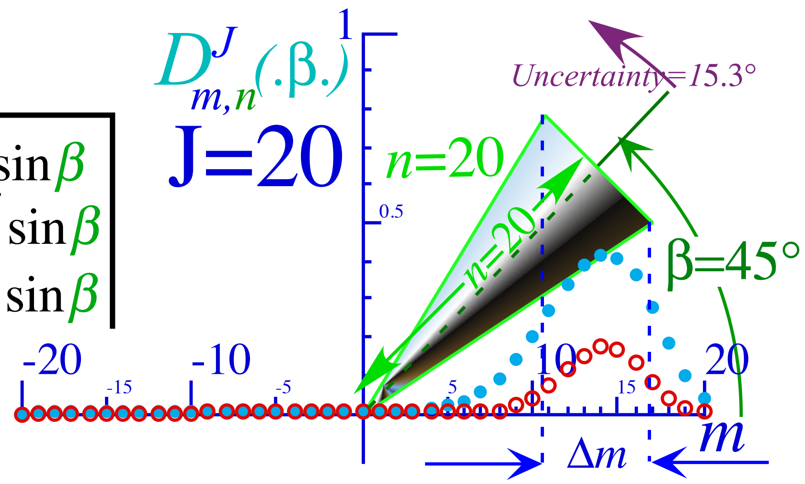
Angular momentum cones and high J properties

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.

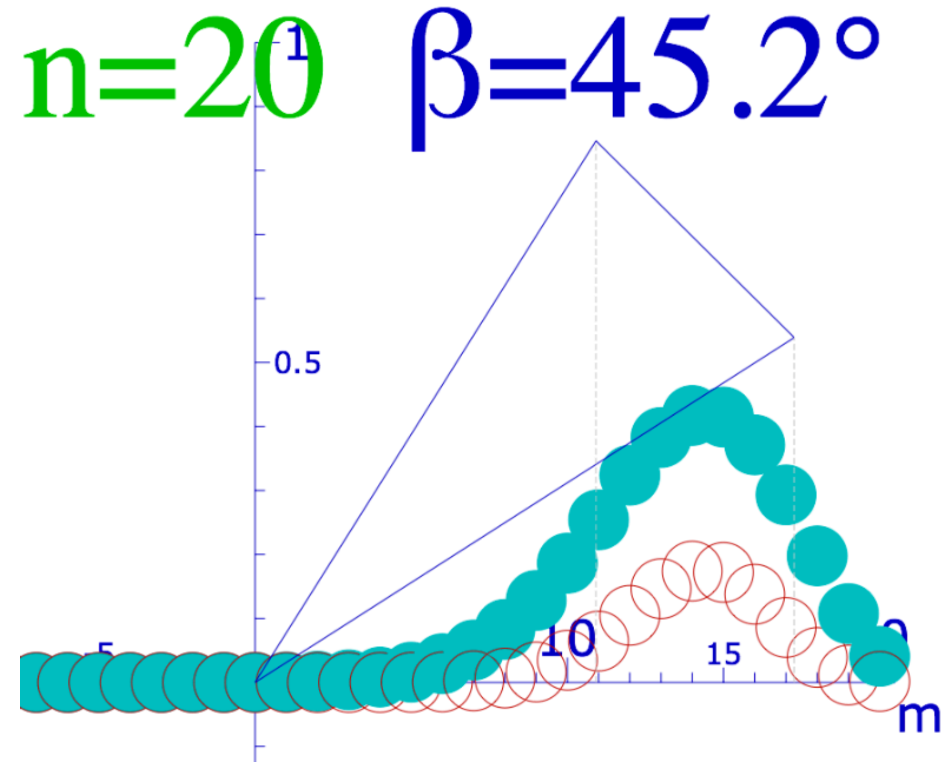
$$\Delta m = 2\sqrt{J(J+1)-n^2}\cdot \sin\beta$$

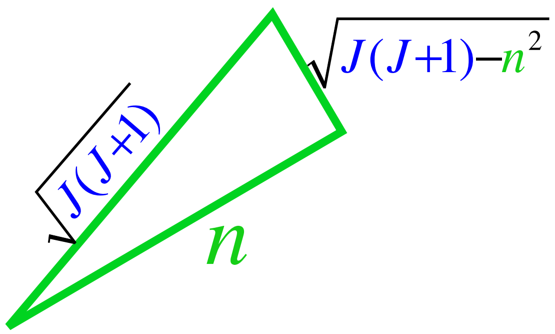


$n=J$: $\Delta m = 2\sqrt{J}\ \sin\beta$
$n=J-1$: $\Delta m = 2\sqrt{3J-1}\ \sin\beta$
$n=J-2$: $\Delta m = 2\sqrt{5J-1}\ \sin\beta$



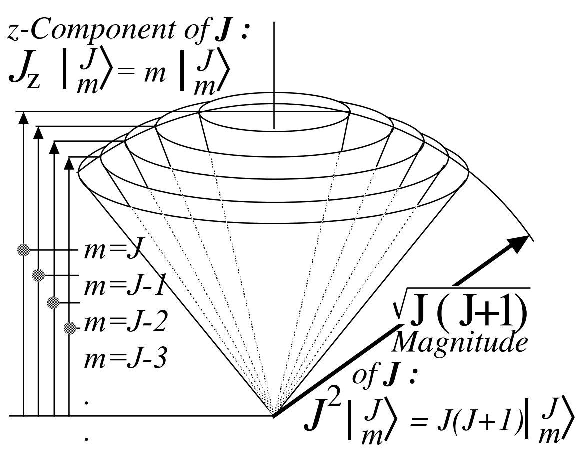
$\Delta m = 2\sqrt{20}\sin 45° = \sqrt{40} = 6.2$

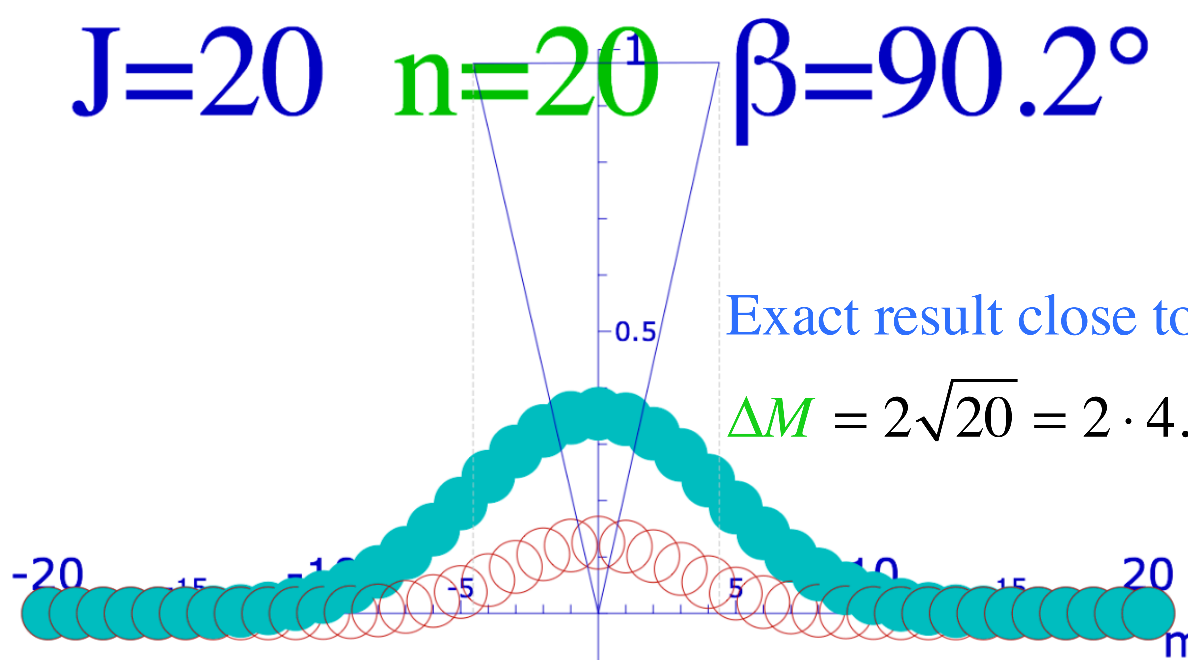




Testing formula with $J=20$ for $\beta=45°$...

...and for $\beta=90°$





Exact result close to:

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

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

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

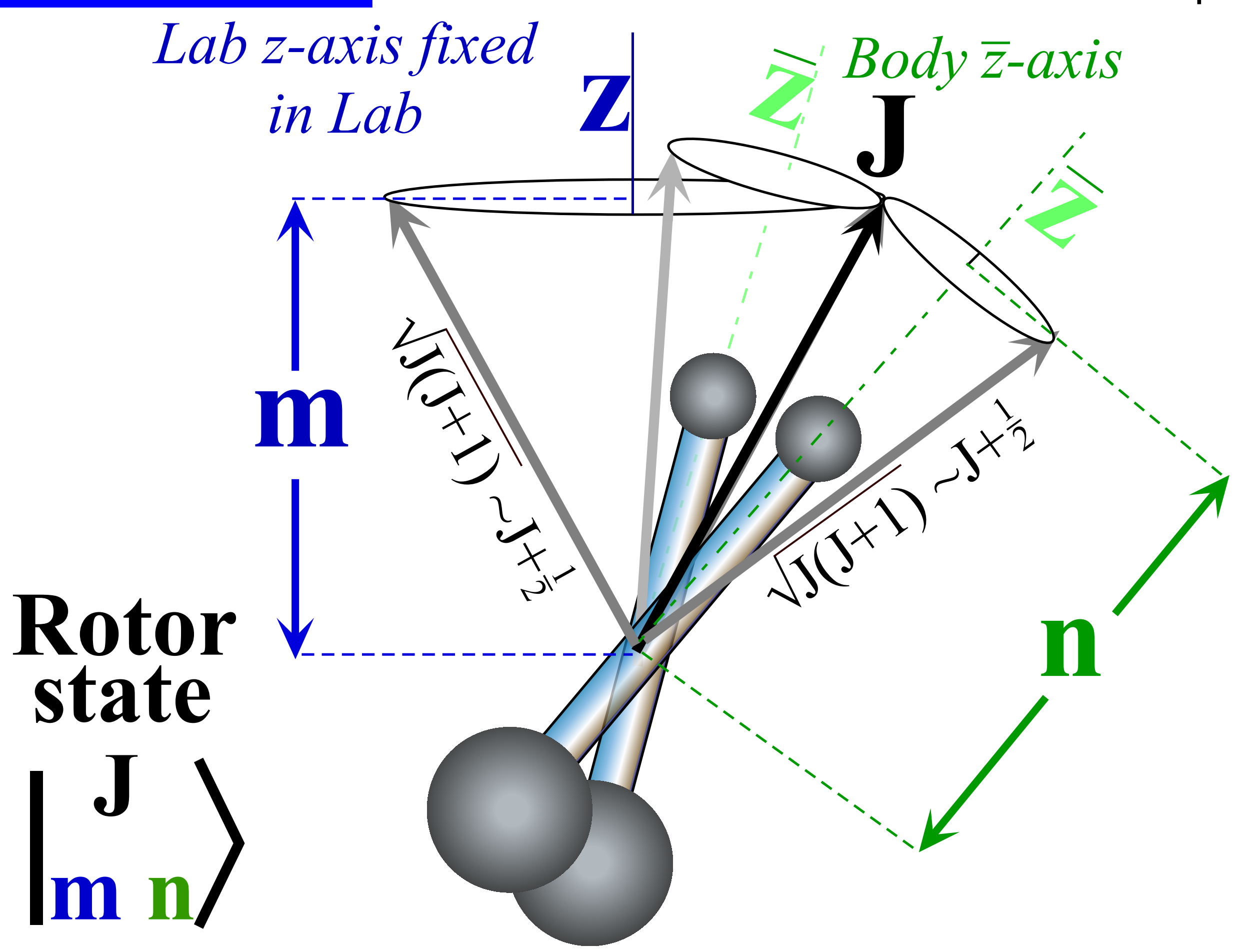
Example of CO_2 *rovibration* $(\upsilon=0)\Leftrightarrow(\upsilon=1)$*bands*

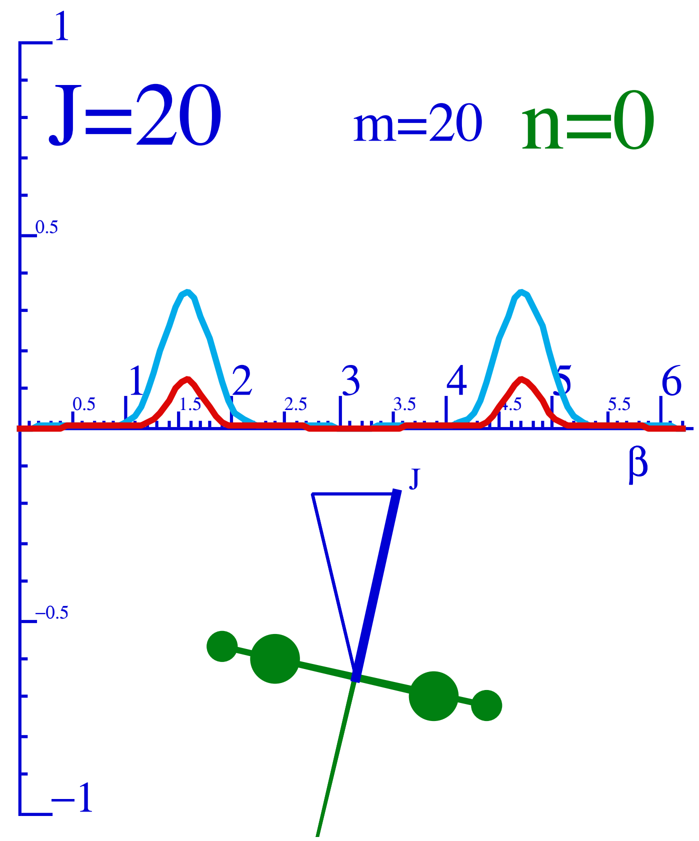
Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

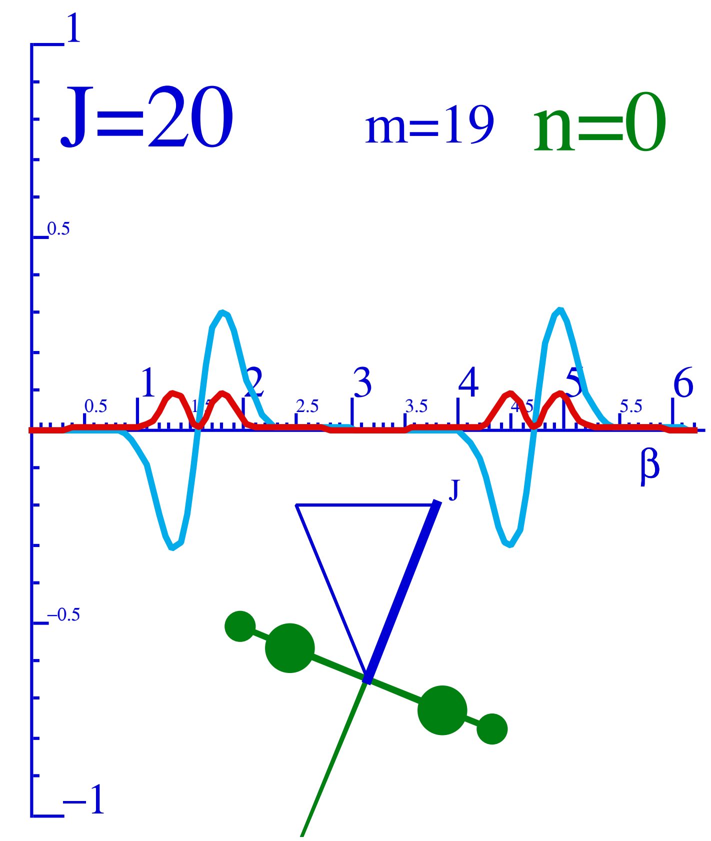
Asymmetric Top eigensolutions for J=1-2

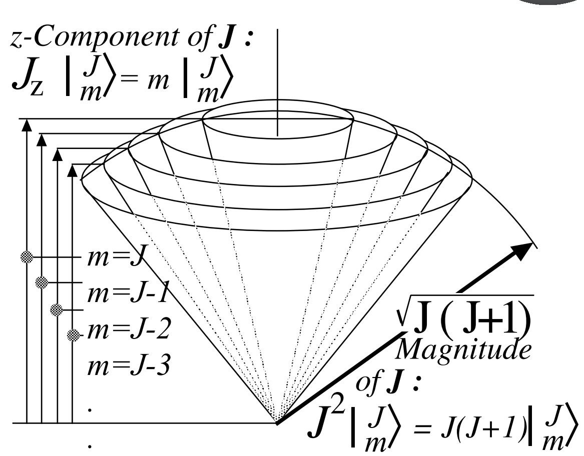
$D^{J=20}_{m,n}(0\beta 0)$
plotted
vs. β
for fixed
J=20,m,n

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







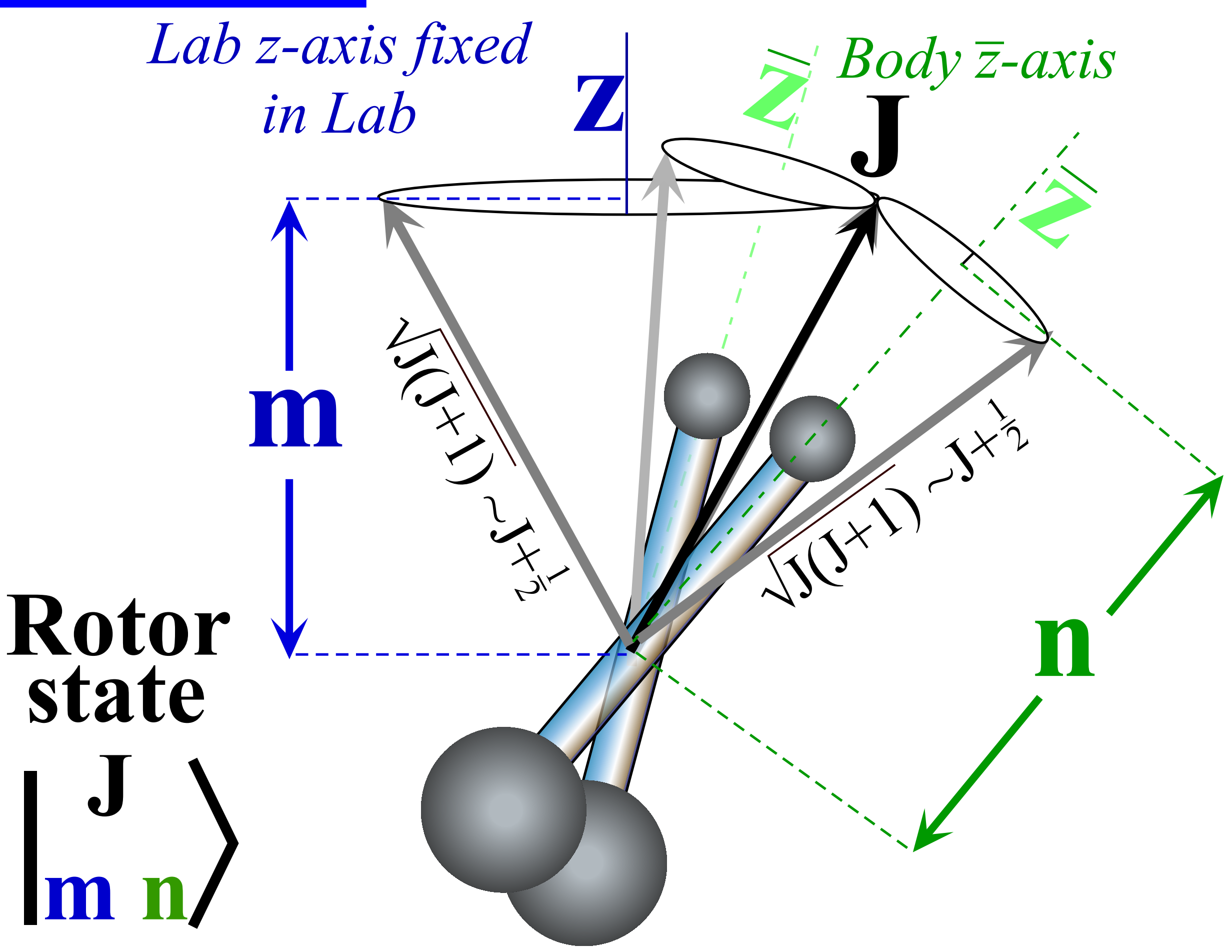


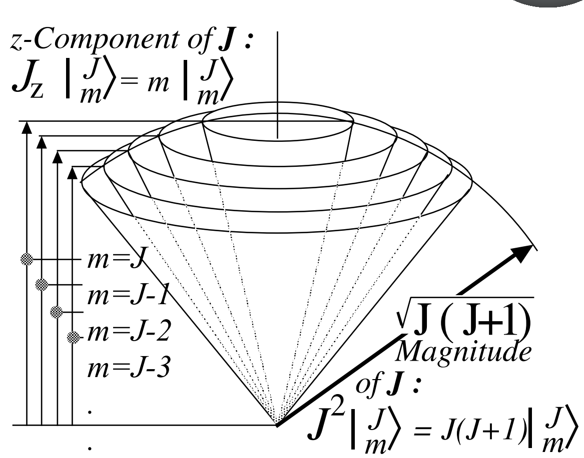
QTforCA Unit 8. Ch. 23 Fig. 23.2.4

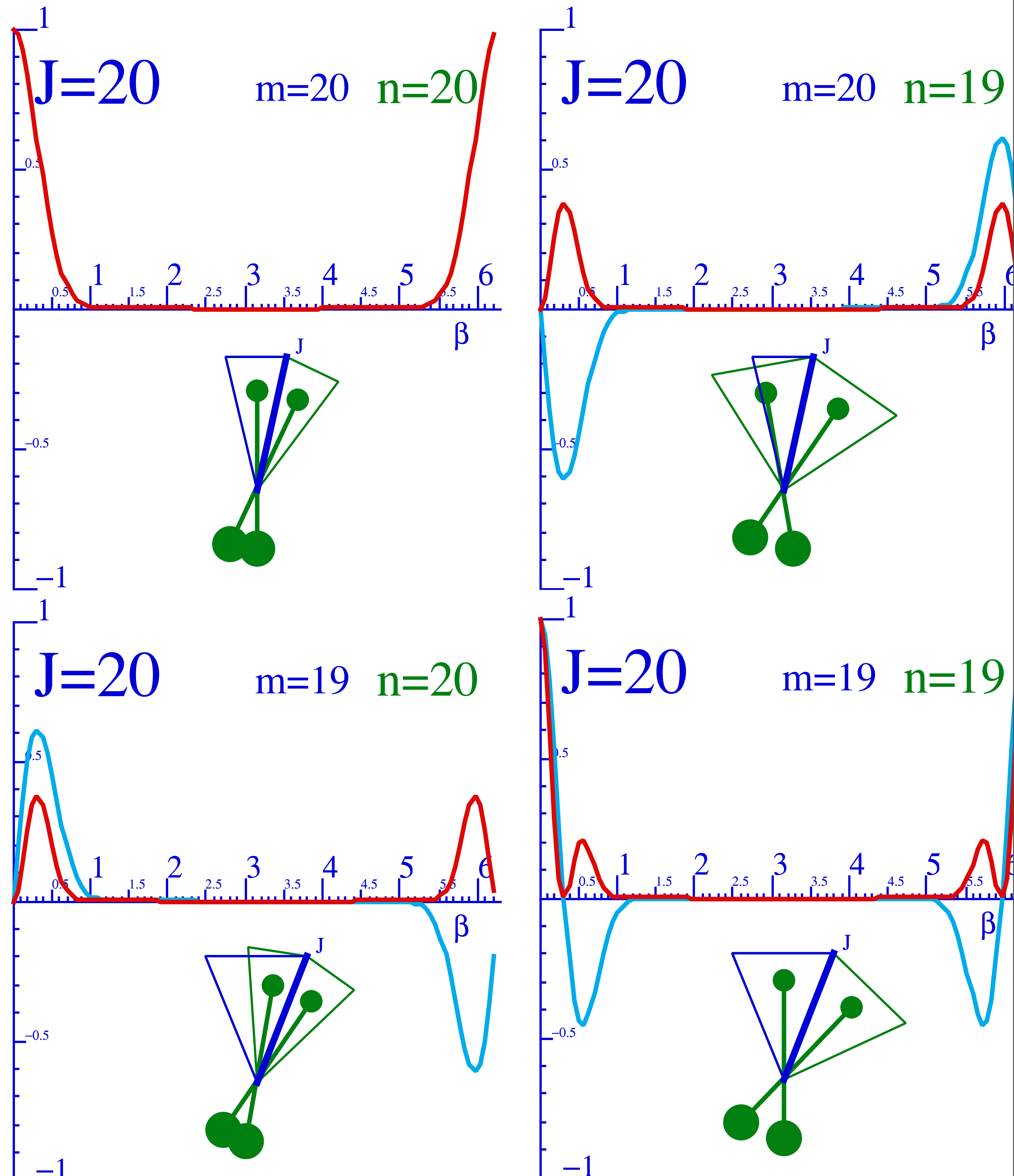
QTforCA Unit 8. Ch. 23 Fig. 23.2.7

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

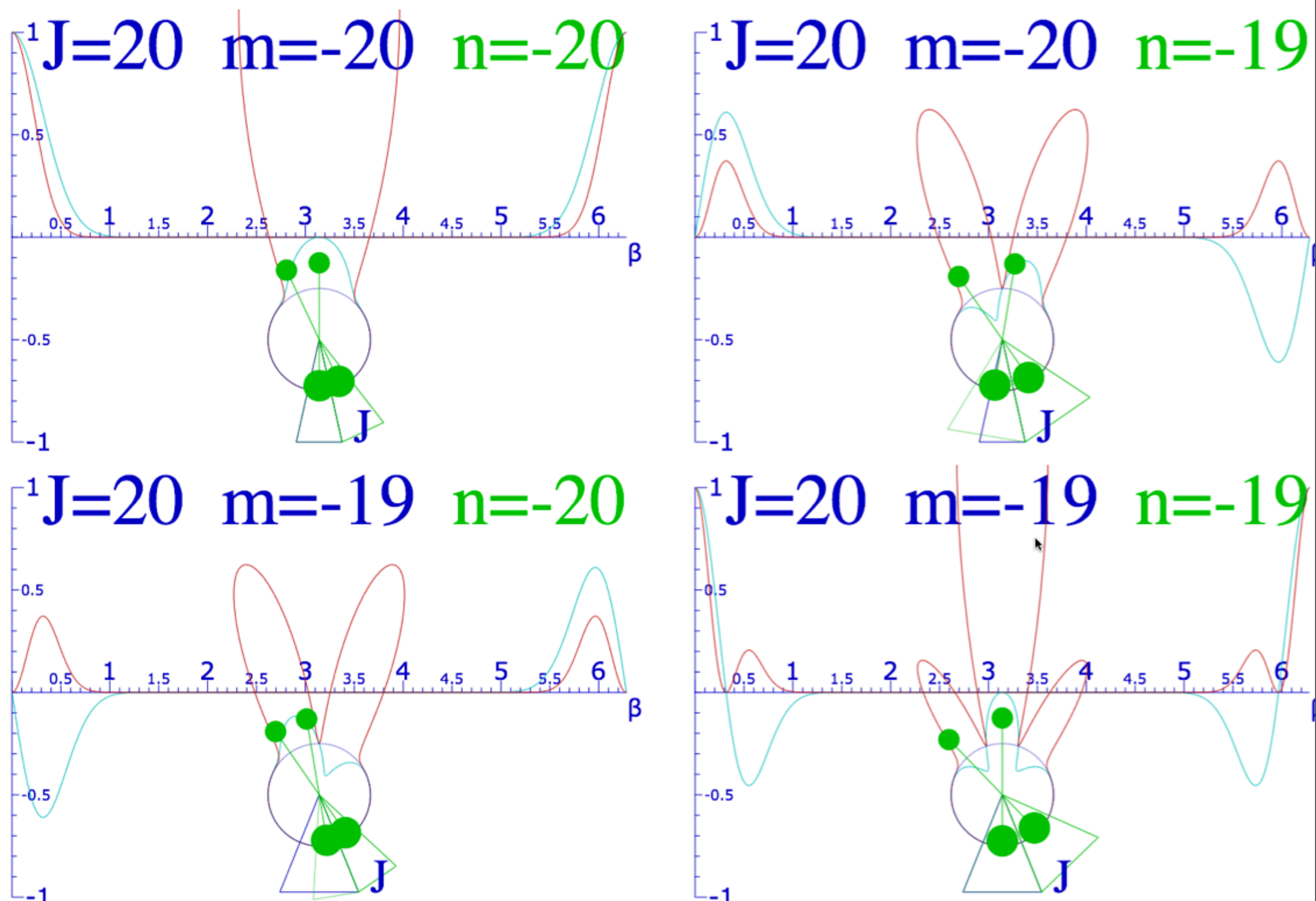


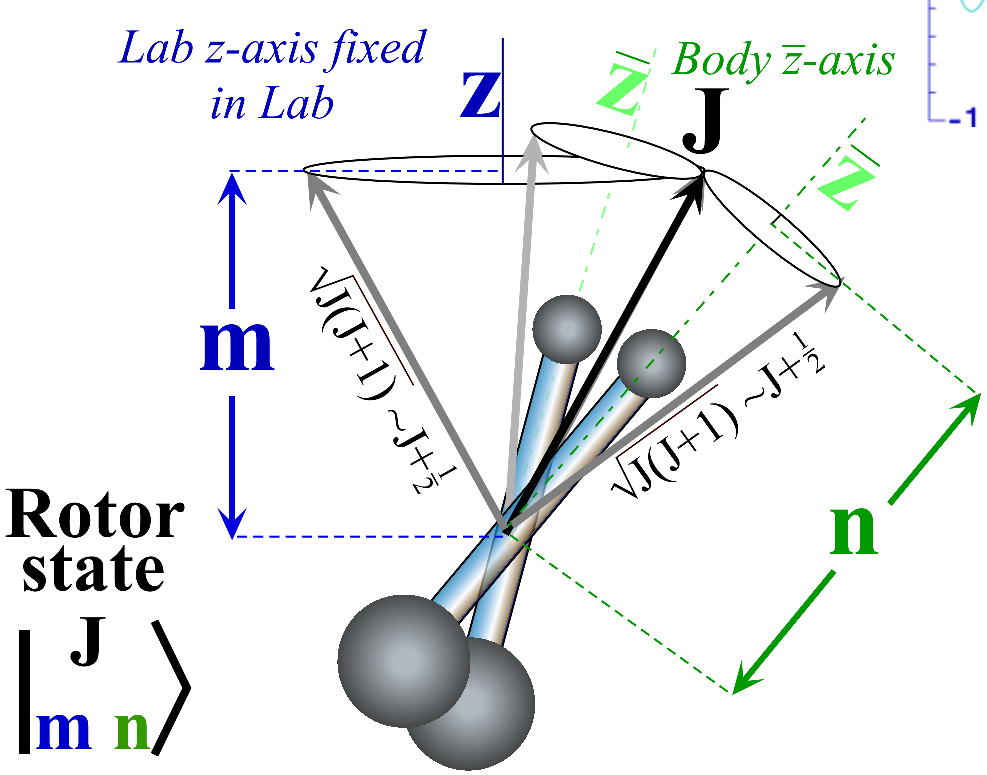




Angular momentum cones and high J properties of LAB vs BOD wavefunctions

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





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

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

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

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).

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

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

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

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

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

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

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).

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

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

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

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

→

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

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

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

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).

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

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

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

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

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

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

→

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

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

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

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).

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

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

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

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

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

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

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

$$X^2_2(\phi\theta 0) = \sqrt{\frac{3}{8}} r^2 e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x+iy)^2 = \sqrt{\frac{3}{8}}(x^2+2ixy-y^2)$$

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

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

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).

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

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

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

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

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

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

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

$$X^2_2(\phi\theta 0) = \sqrt{\frac{3}{8}}r^2 e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x+iy)^2 = \sqrt{\frac{3}{8}}\left(x^2+2ixy-y^2\right)$$

$$X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{8}}e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x-iy)^2 = \sqrt{\frac{3}{8}}\left(x^2-2ixy-y^2\right)$$

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

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

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).

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

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

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

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

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

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

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

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

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

$$X^2_2(\phi\theta 0) = \sqrt{\frac{3}{8}} r^2 e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x+iy)^2 = \sqrt{\frac{3}{8}}\left(x^2+2ixy-y^2\right)$$

$$+\; X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x-iy)^2 = \sqrt{\frac{3}{8}}\left(x^2-2ixy-y^2\right)$$

$$= X^2_2(\phi\theta 0)+X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{2}} r^2\frac{e^{i2\phi}+e^{-i2\phi}}{2}\sin^2\theta = \sqrt{\frac{3}{2}}\left(x^2-y^2\right) = \sqrt{\frac{3}{2}} r^2\cos 2\phi\sin^2\theta$$

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).

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

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

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

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

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

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

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

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

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

$$X^2_2(\phi\theta 0) = \sqrt{\frac{3}{8}} r^2 e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x+iy)^2 = \sqrt{\frac{3}{8}}(x^2+2ixy-y^2)$$

$$+\ X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x-iy)^2 = \sqrt{\frac{3}{8}}(x^2-2ixy-y^2)$$

$$=\ X^2_2(\phi\theta 0)+X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{2}} r^2\frac{e^{i2\phi}+e^{-i2\phi}}{2}\sin^2\theta = \sqrt{\frac{3}{2}}(x^2-y^2) = \sqrt{\frac{3}{2}} r^2\cos 2\phi\sin^2\theta$$

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

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).

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

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

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

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

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

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

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

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

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

$$X^2_2(\phi\theta 0) = \sqrt{\frac{3}{8}} r^2 e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x+iy)^2 = \sqrt{\frac{3}{8}}(x^2+2ixy-y^2)$$

$$+\quad X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{-i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}(x-iy)^2 = \sqrt{\frac{3}{8}}(x^2-2ixy-y^2)$$

$$= X^2_2(\phi\theta 0)+X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{2}} r^2\frac{e^{i2\phi}+e^{-i2\phi}}{2}\sin^2\theta = \sqrt{\frac{3}{2}}(x^2-y^2) = \sqrt{\frac{3}{2}} r^2\cos 2\phi\sin^2\theta$$

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

-

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

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

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*

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

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

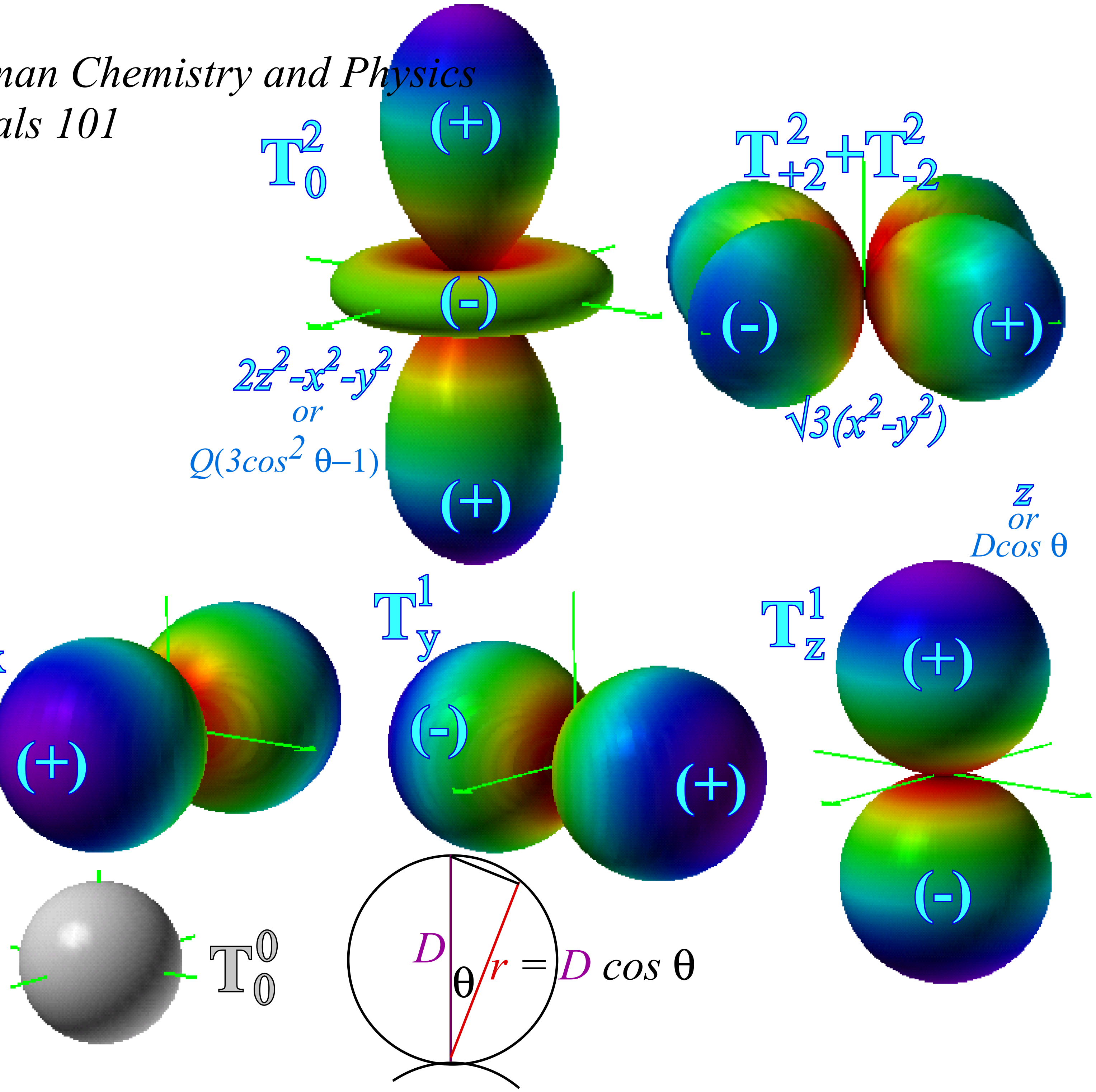
$$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\,\frac{\mathbf{J}_x^{\;2}-\mathbf{J}_y^{\;2}}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

Review of freshman Chemistry and Physics
Electronic orbitals 101

Quadrupoles
(d-orbitals)

Dipoles
(p-orbitals)

Monopole
(s-orbital)



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*

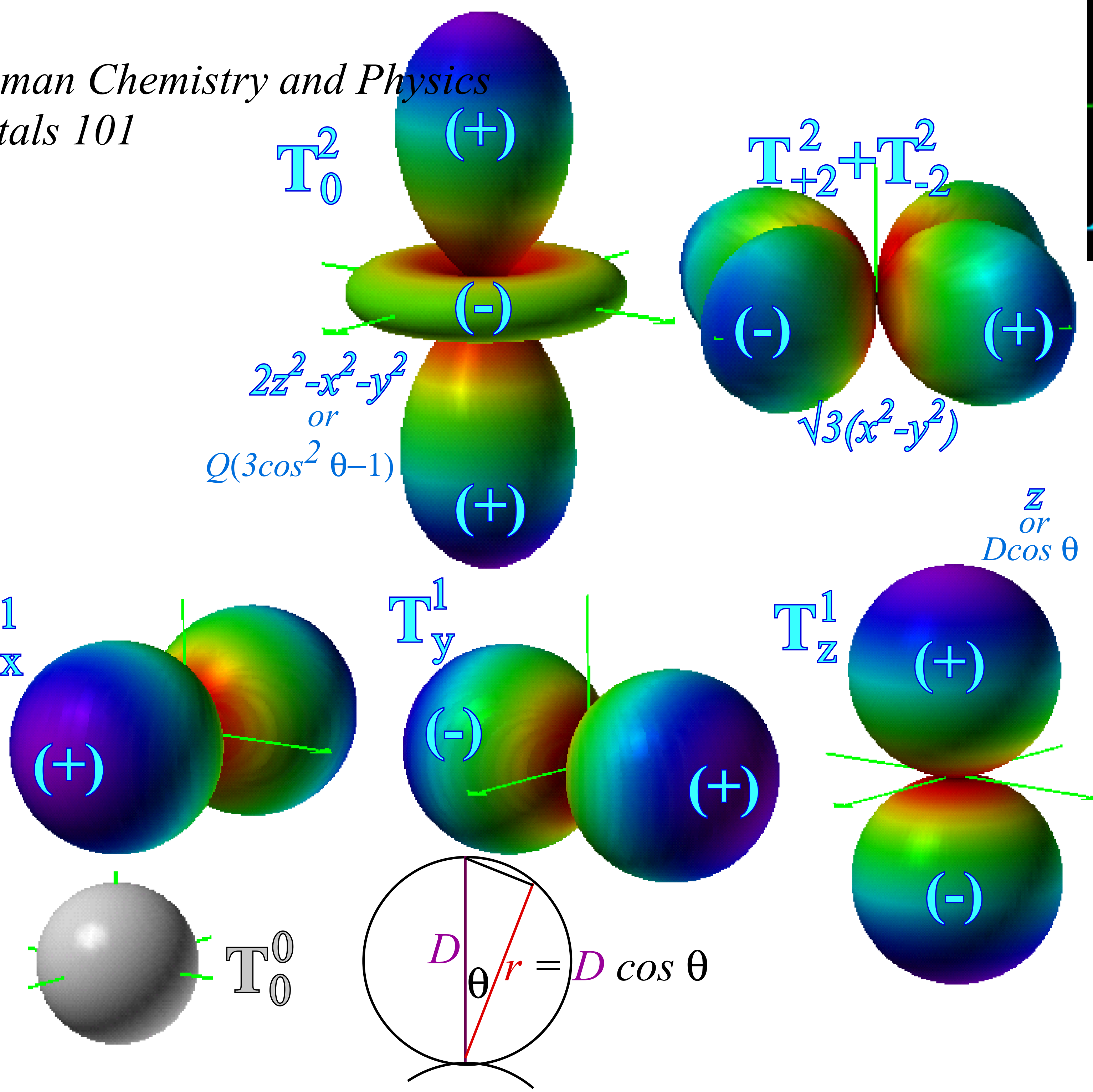
$\mathbf{T}_0^0=\mathbf{J}_x{}^2+\mathbf{J}_y{}^2+\mathbf{J}_z{}^2=\mathbf{J}^2$	$\mathbf{T}_0^2=\frac{2\mathbf{J}_z{}^2-\mathbf{J}_x{}^2-\mathbf{J}_y{}^2}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$	$\mathbf{T}_2^2+\mathbf{T}_{-2}^2=\sqrt{6}\frac{\mathbf{J}_x{}^2-\mathbf{J}_y{}^2}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos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

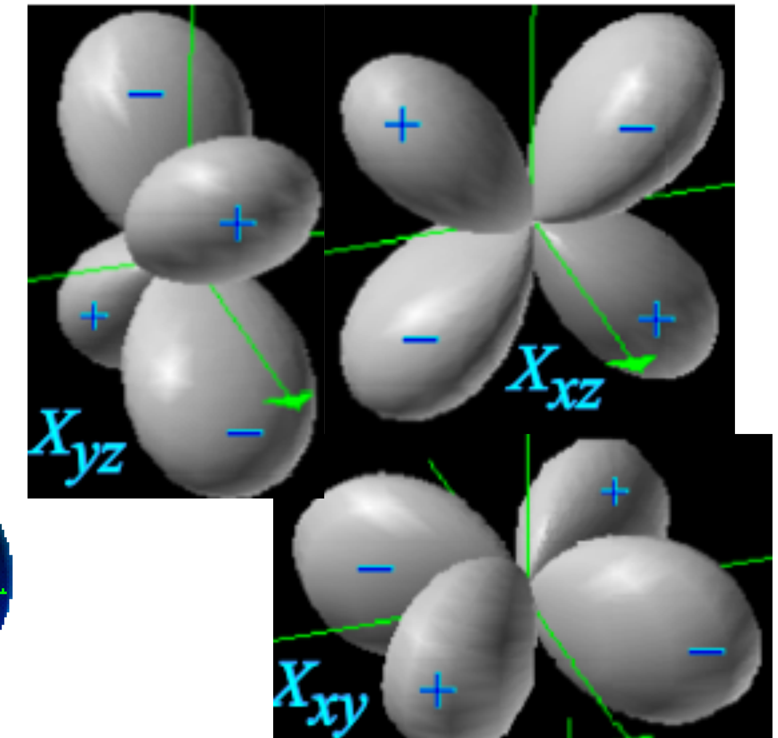
Review of freshman Chemistry and Physics
Electronic orbitals 101

Quadrupoles
(d-orbitals)

Dipoles
(p-orbitals)

Monopole
(s-orbital)





This triplet not needed for the diagonalized rotor Hamiltonian that has no $\mathbf{J}_x\mathbf{J}_y$, $\mathbf{J}_x\mathbf{J}_z$, *or* $\mathbf{J}_y\mathbf{J}_z$

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*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

*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*

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

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

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

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

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

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

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

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

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

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

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*

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

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

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

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

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

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

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*

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

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

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:

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

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*

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

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

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

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

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

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

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

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

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:

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

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

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 $\mathbf{T}^k_q$ *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

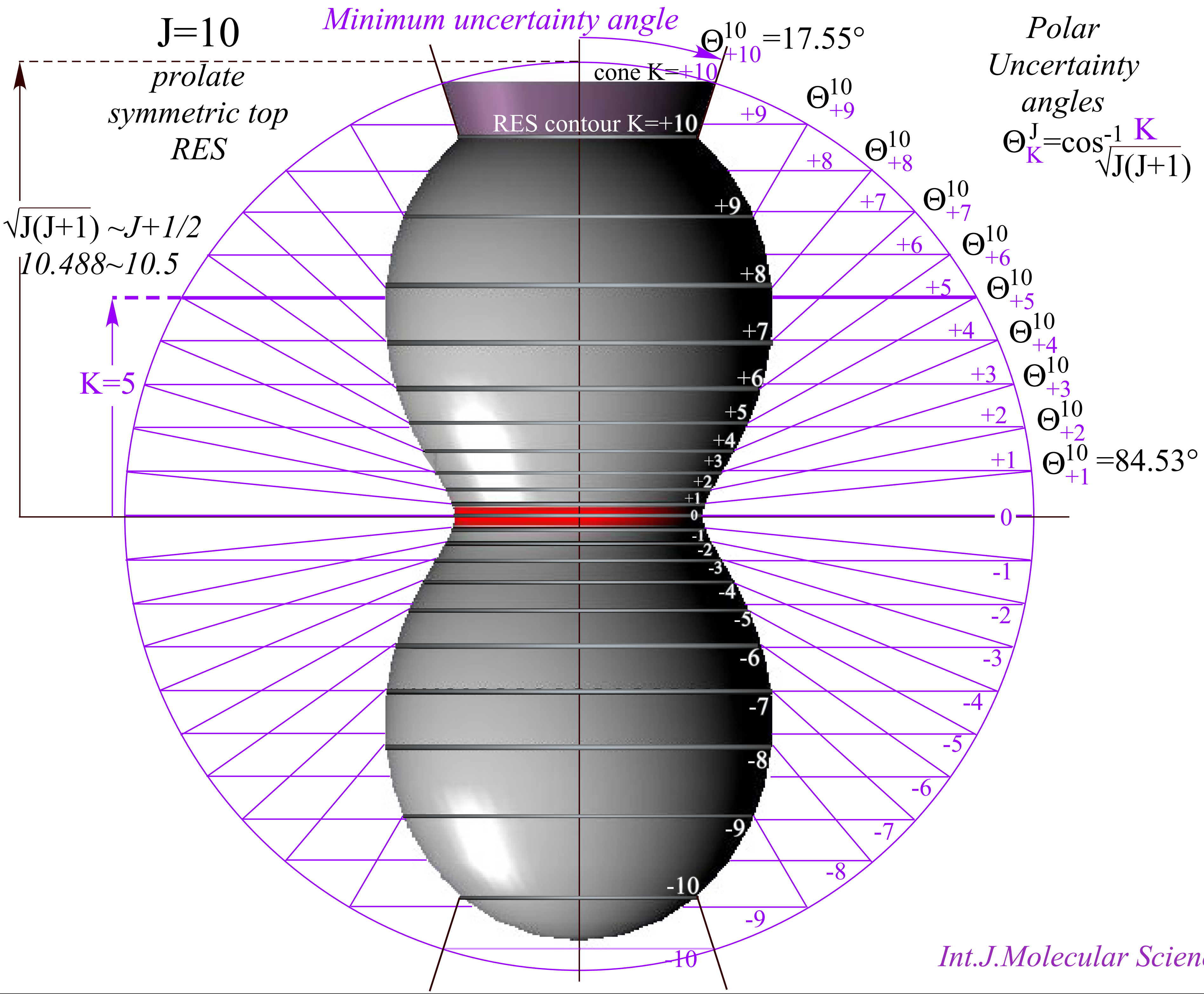
Rotational Energy Surfaces (RE or RES) of symmetric rotor and eigensolutions

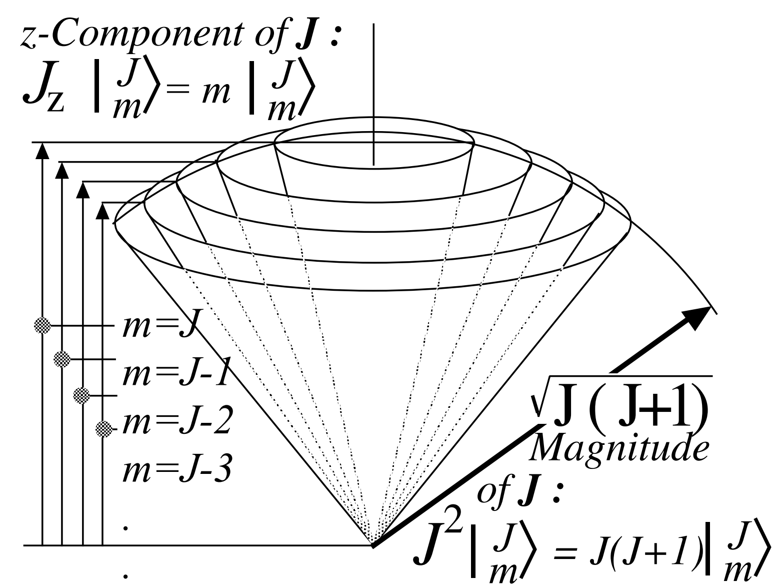
Plot Hamiltonian $\mathbf{H}=B\mathbf{J}^2+(C-B)\mathbf{J}_z^{\,2}$ radially as $H(\Theta)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta$

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

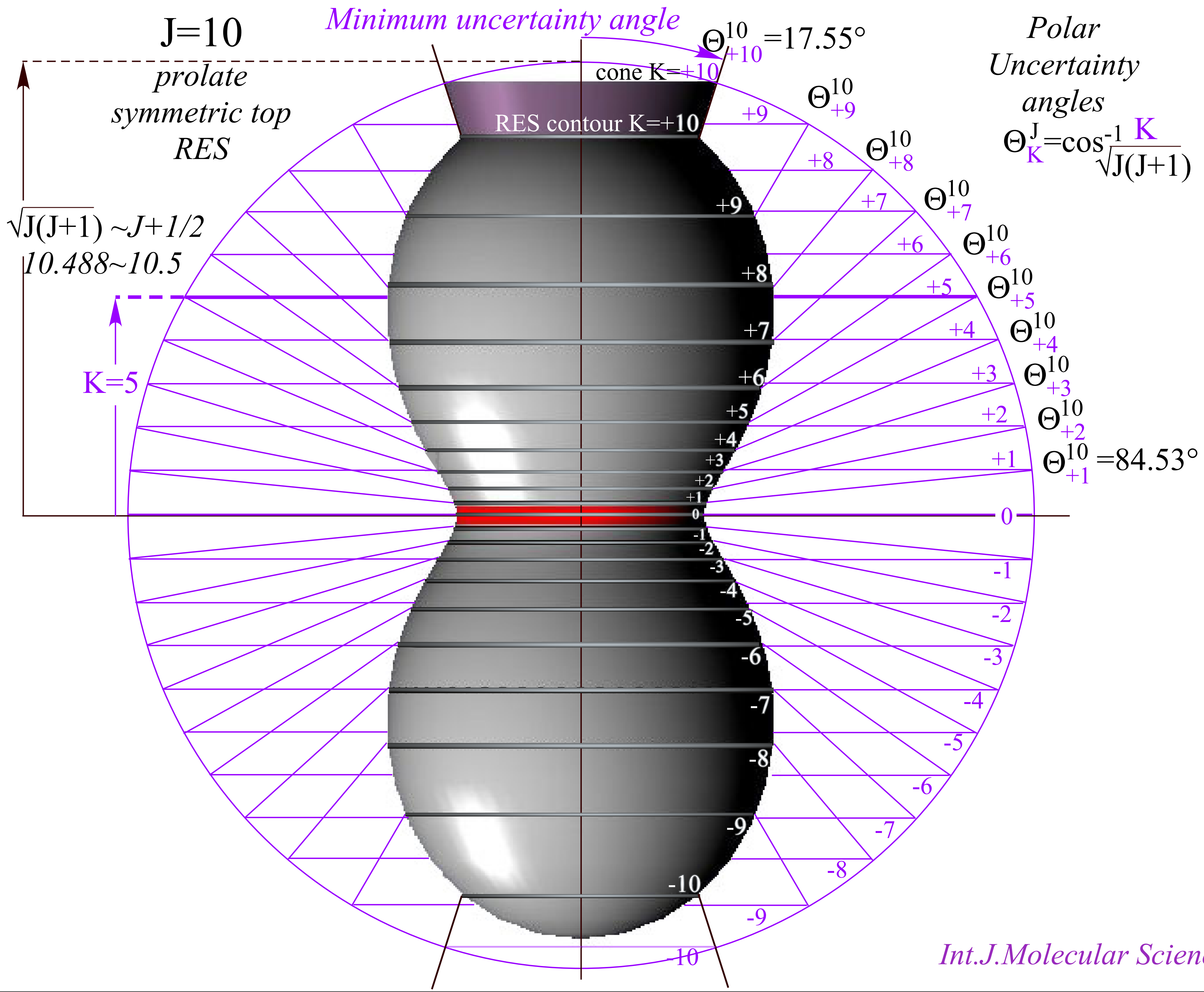
$H(\Theta^J_K)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta^J_K$

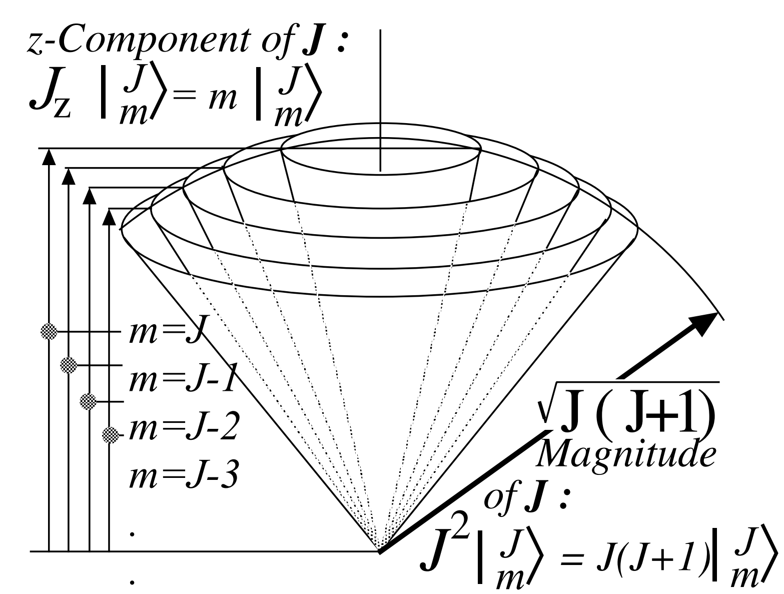
where : $\mathbf{J}_z = |\mathbf{J}|\cos\Theta = \sqrt{J(J+1)}\cos\Theta$

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

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

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

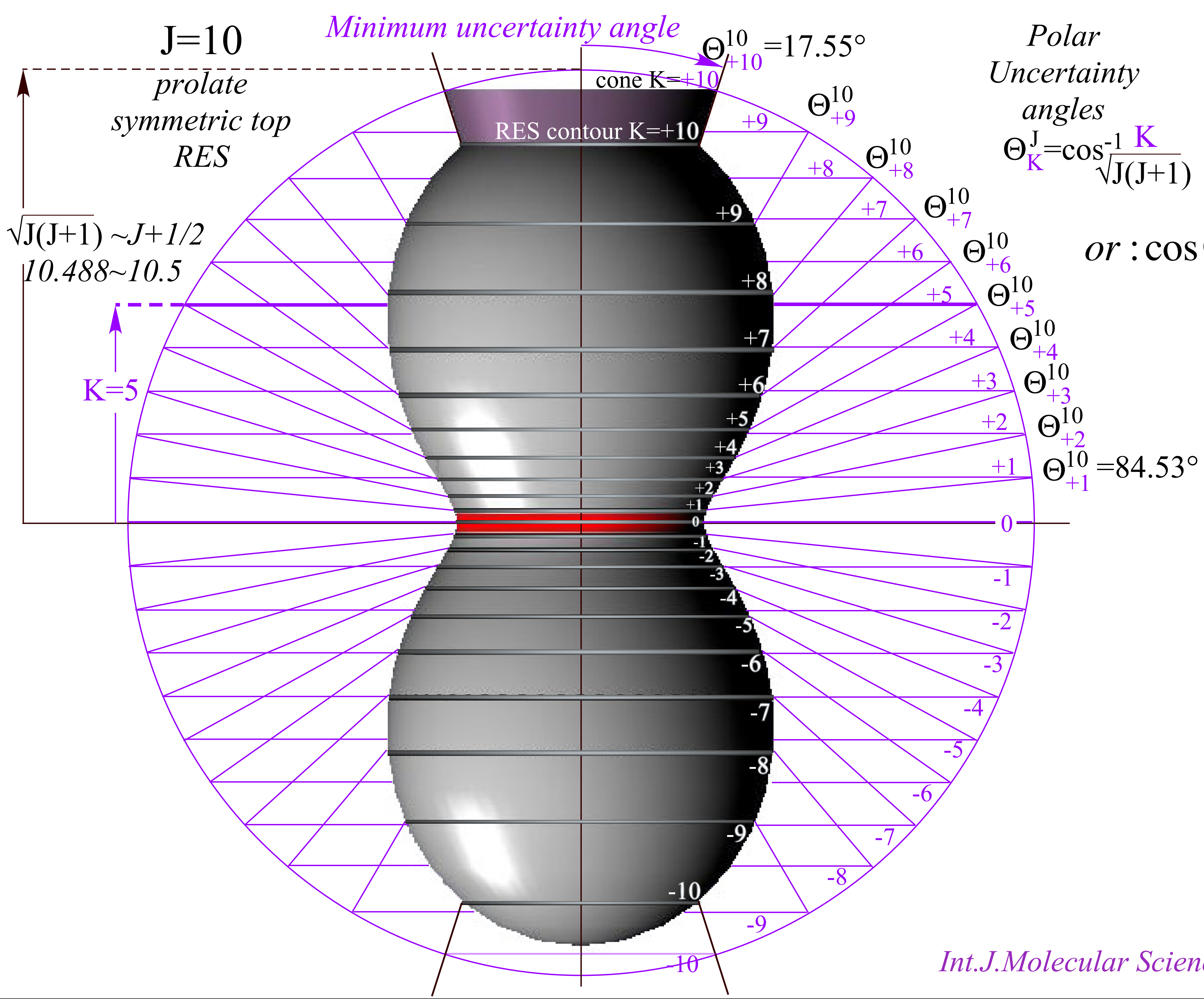
where : $\mathbf{J}_z=|\mathbf{J}|\cos\Theta=\sqrt{J(J+1)}\cos\Theta$

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

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

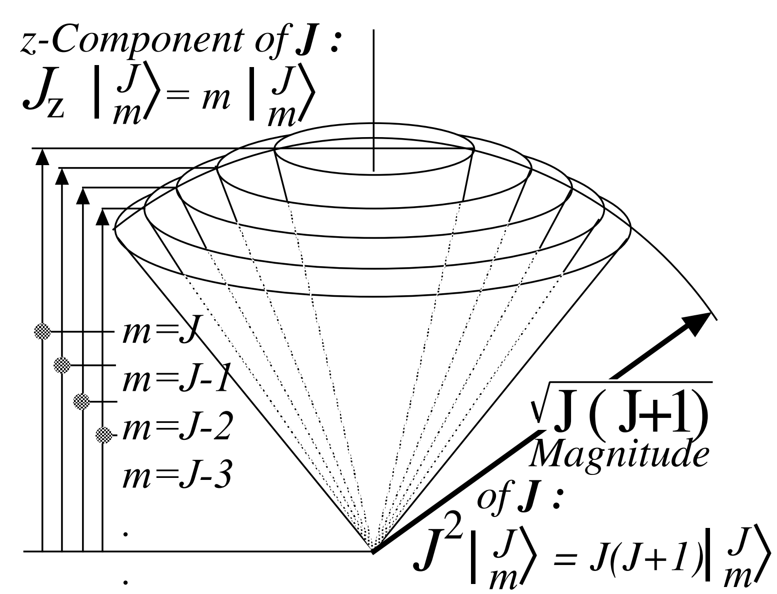
LAB $m=M$ *BOD* $n=K$

(Here this gives exact quantum eigenvalues!)



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

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



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 $|{}^J_{mn}\rangle = \mathbf{P}^J_{mn}|(0,0,0)\rangle = \int d(\alpha,\beta,\gamma) D^{J*}_{mn}(\alpha,\beta,\gamma)\mathbf{R}(\alpha,\beta,\gamma)|(0,0,0)\rangle$

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 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

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

Kinetic energy inertial coefficients:

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

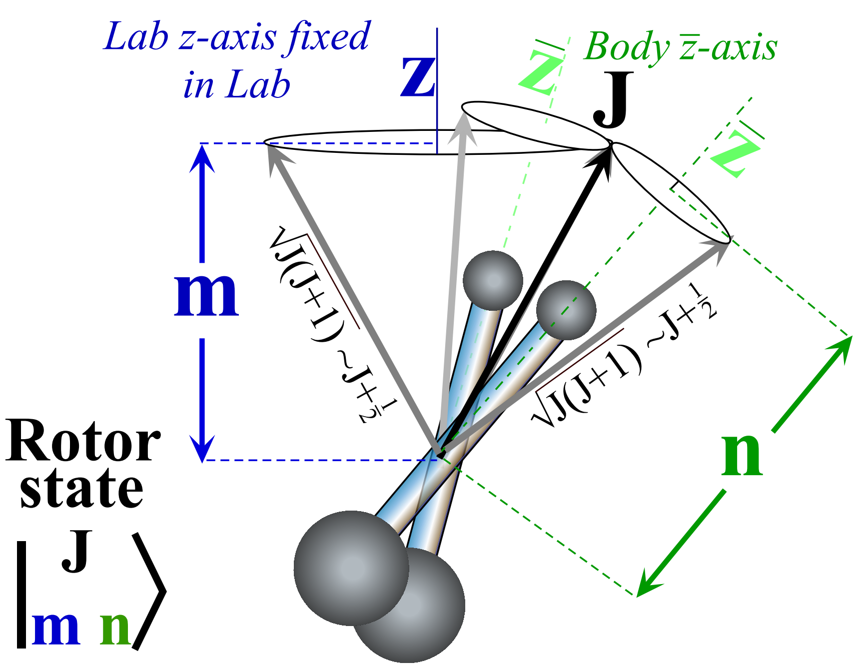
Eigensolution equations:

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

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

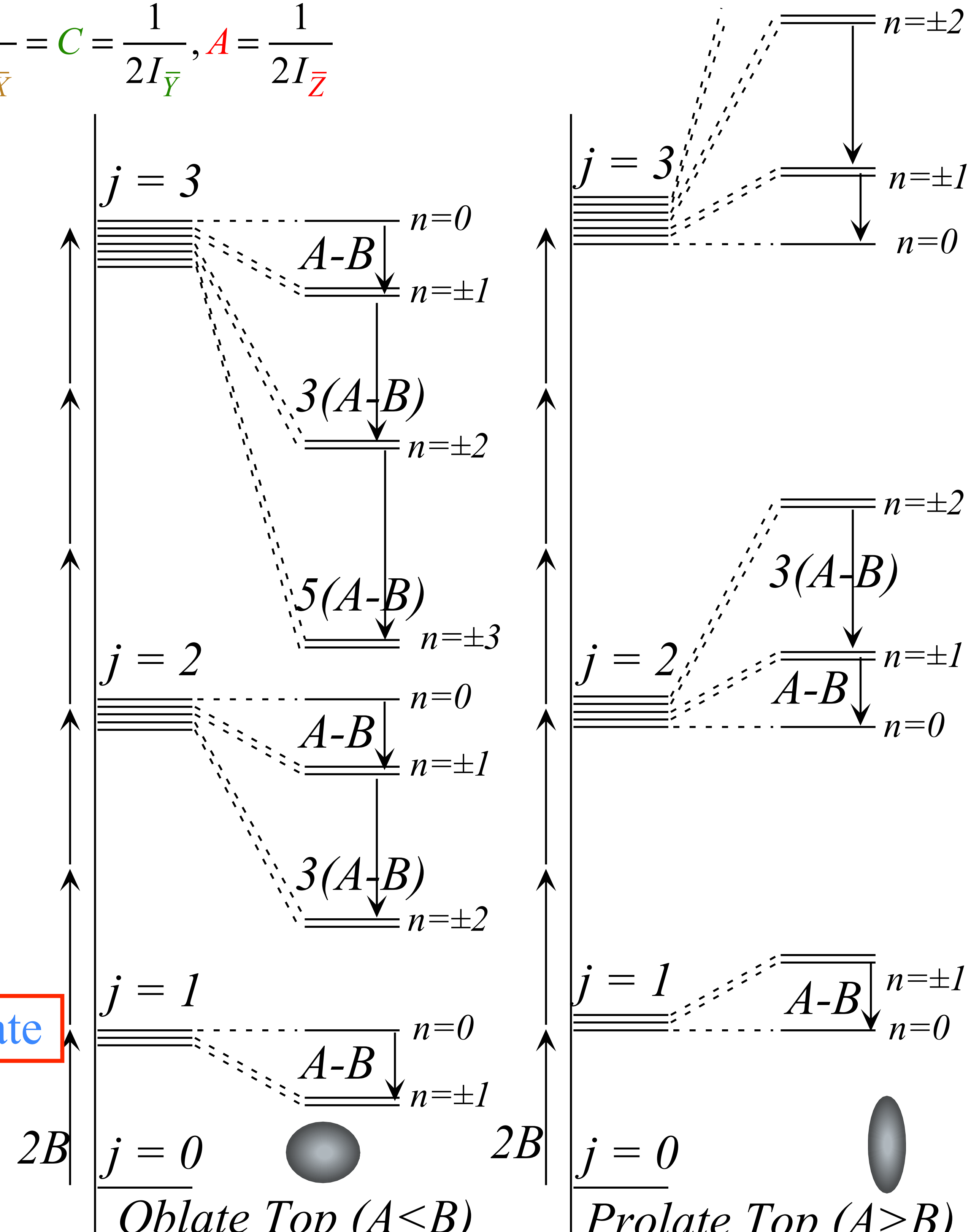
$$= \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

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



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

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



QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

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

Kinetic energy inertial coefficients:

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

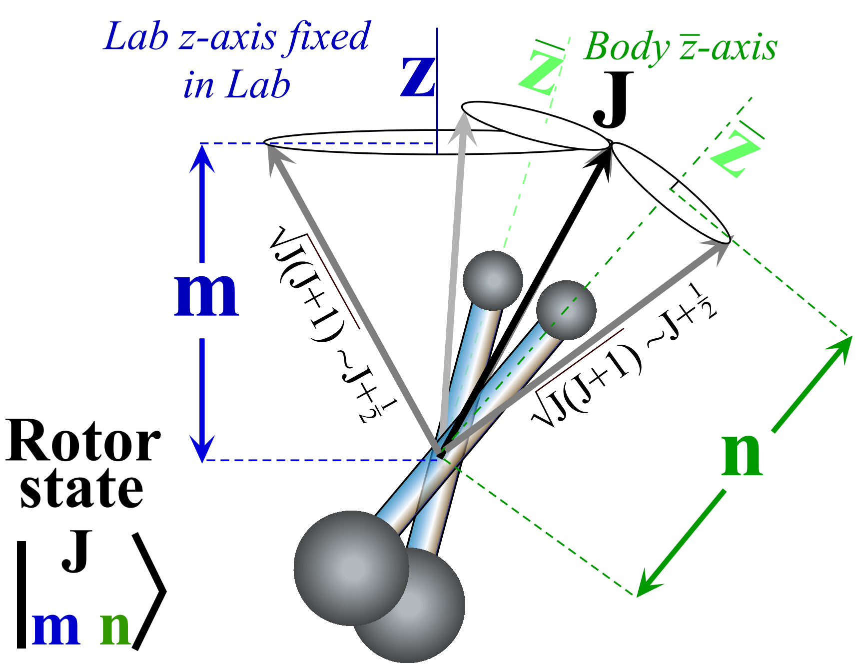
Eigensolution equations:

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

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

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

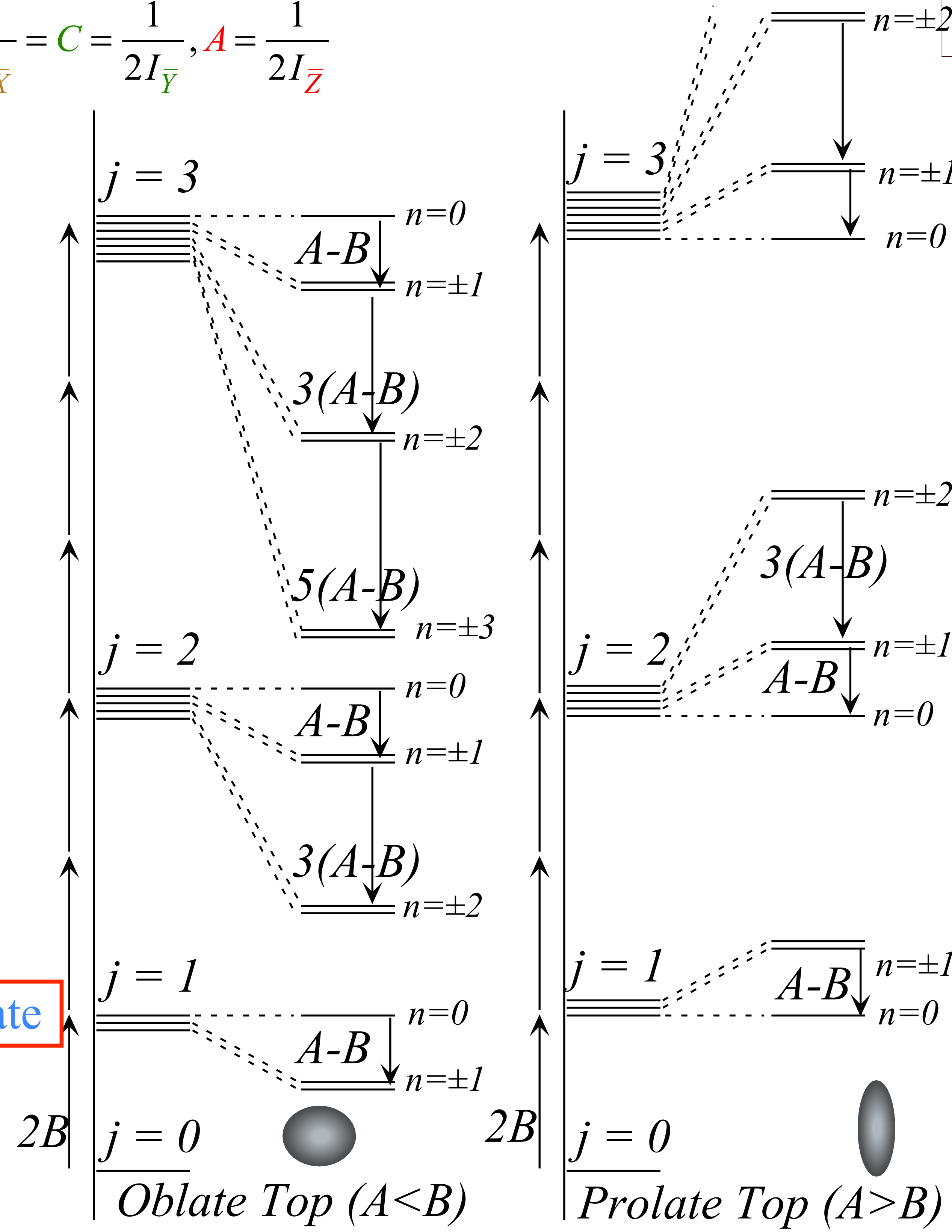
Mock-Mach-Multiplicity is $(2j+1)^2$ for each j

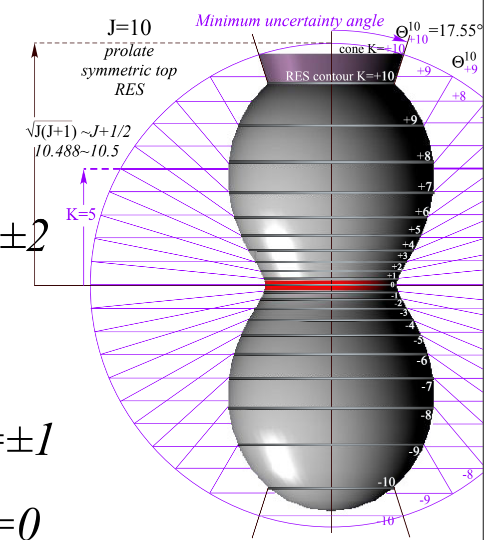


Even n=0 levels are $2j+1$-fold degenerate

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

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

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

Kinetic energy inertial coefficients:

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

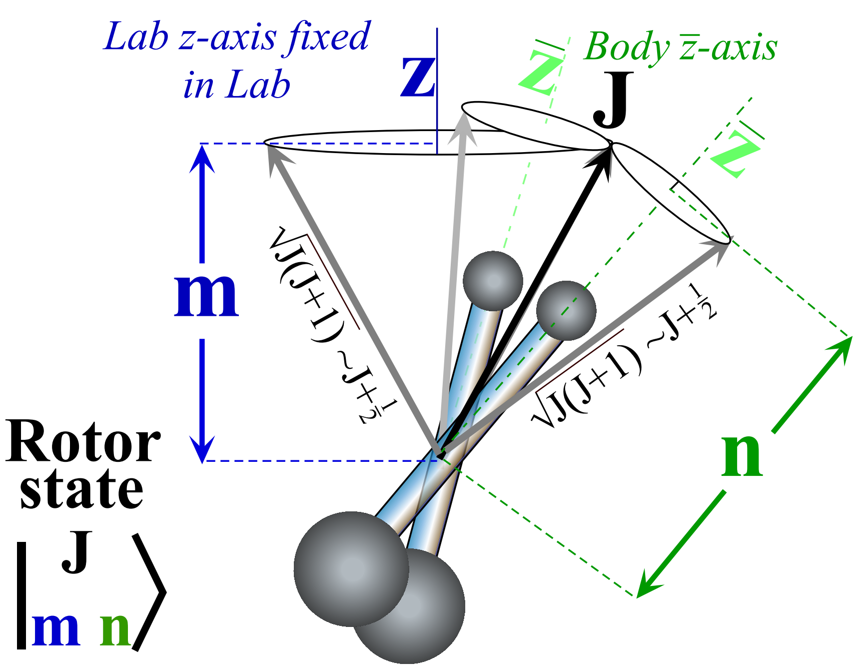
Eigensolution equations:

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

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

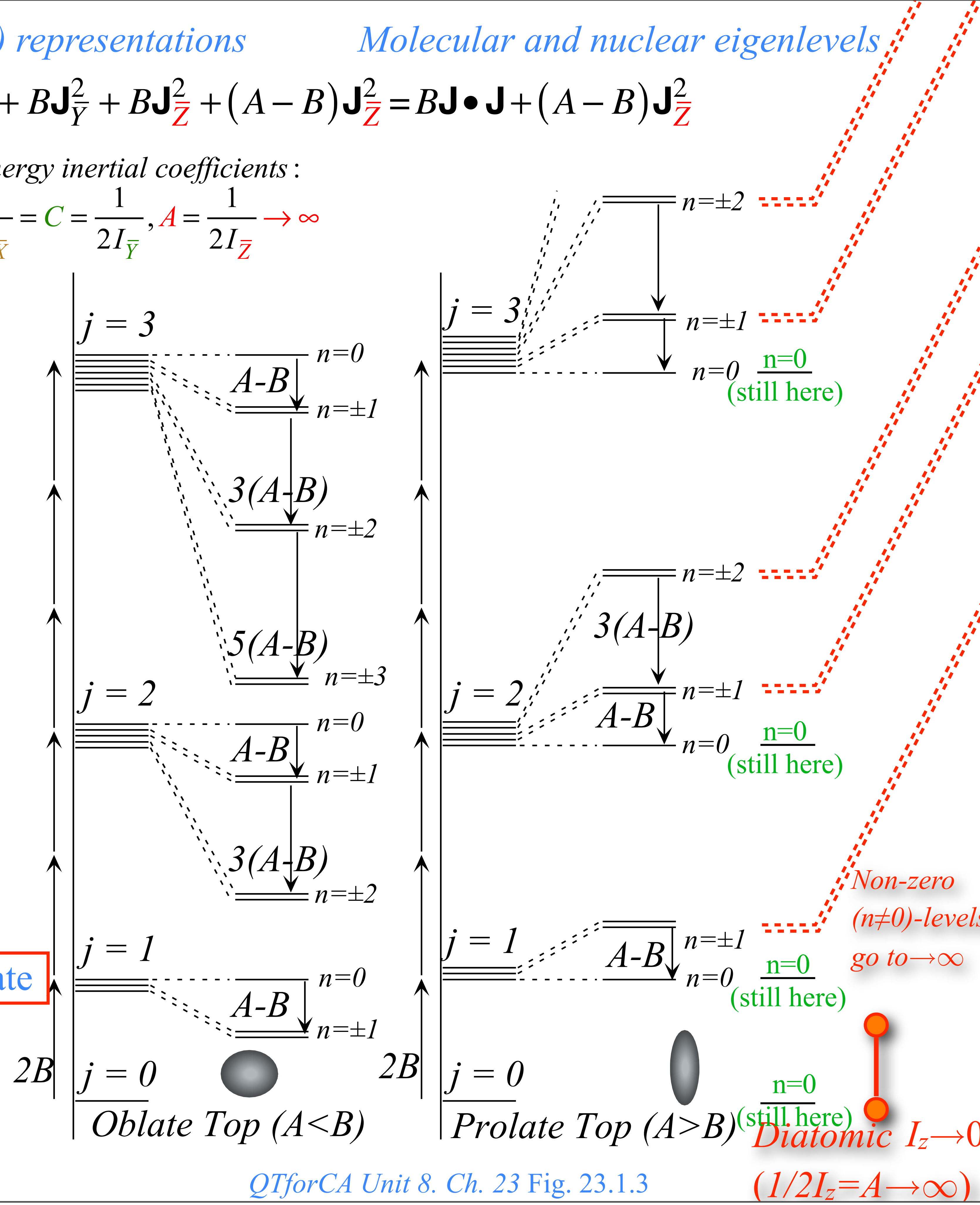
$$= \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{smallmatrix} j \\ m,n \end{smallmatrix}\right\rangle$$

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:

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

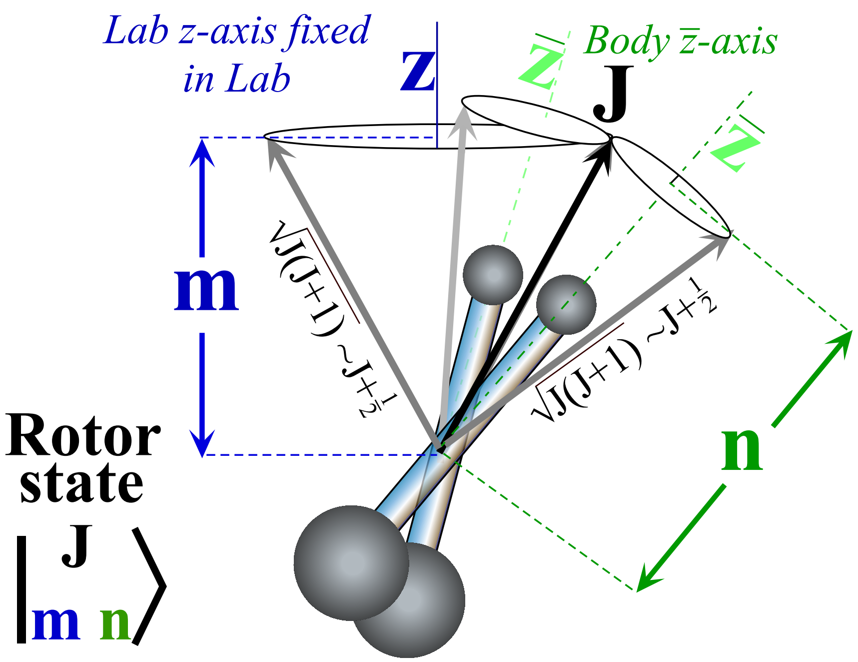
Eigensolution equations:

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

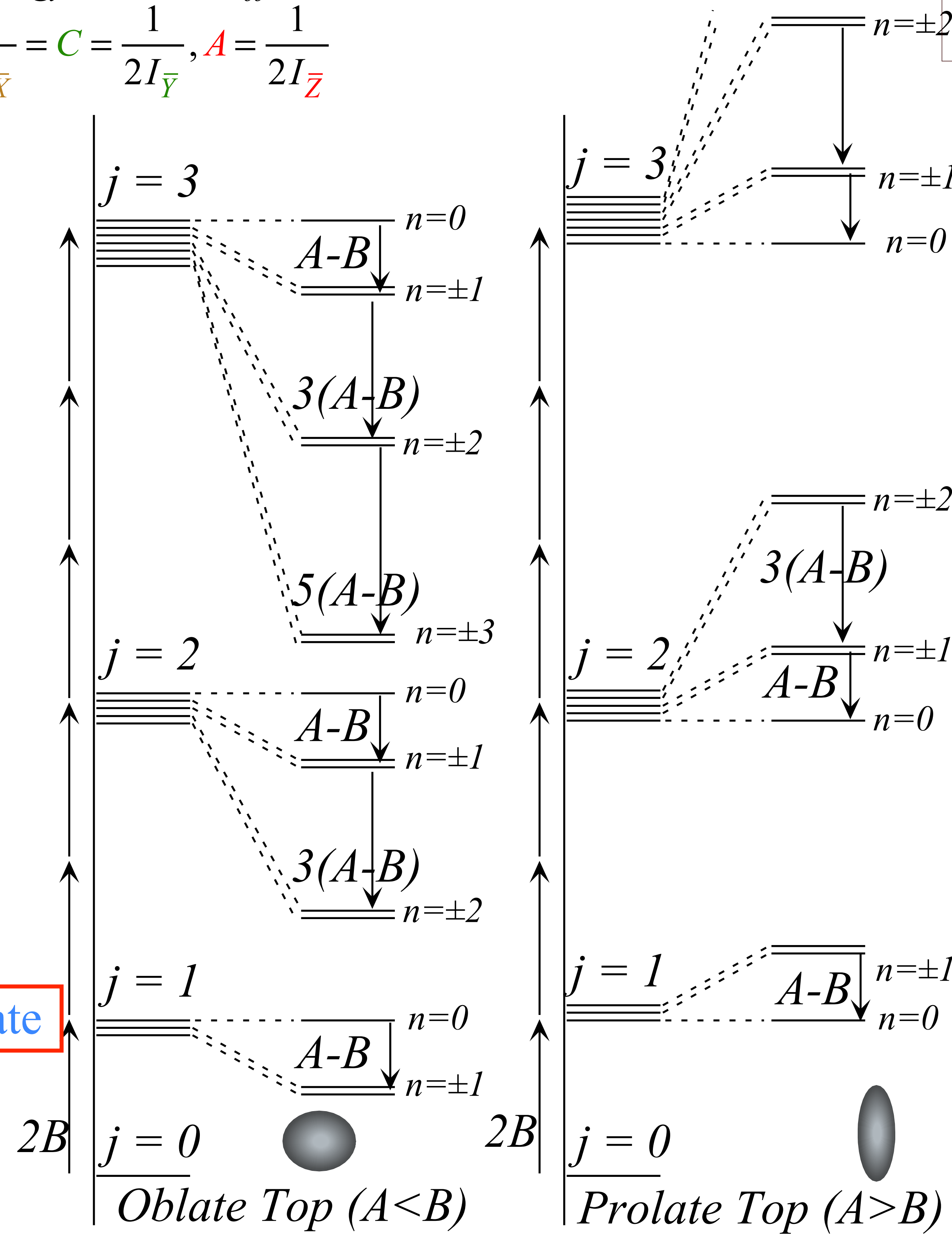
$$= B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2 \left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

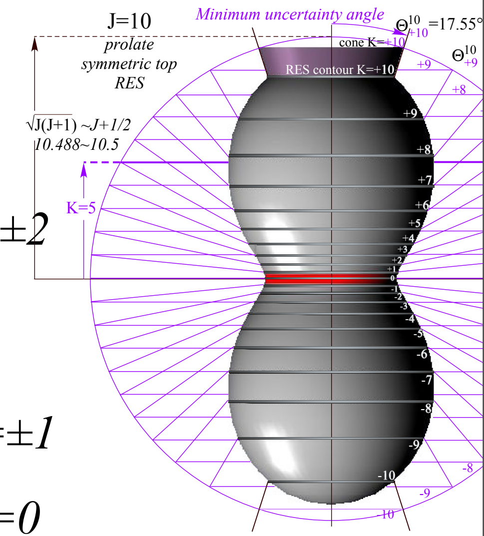
$$= \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

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



Even n=0 levels are $2j+1$-fold degenerate
If n is non-zero the degeneracy is $4j+2$.





QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

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

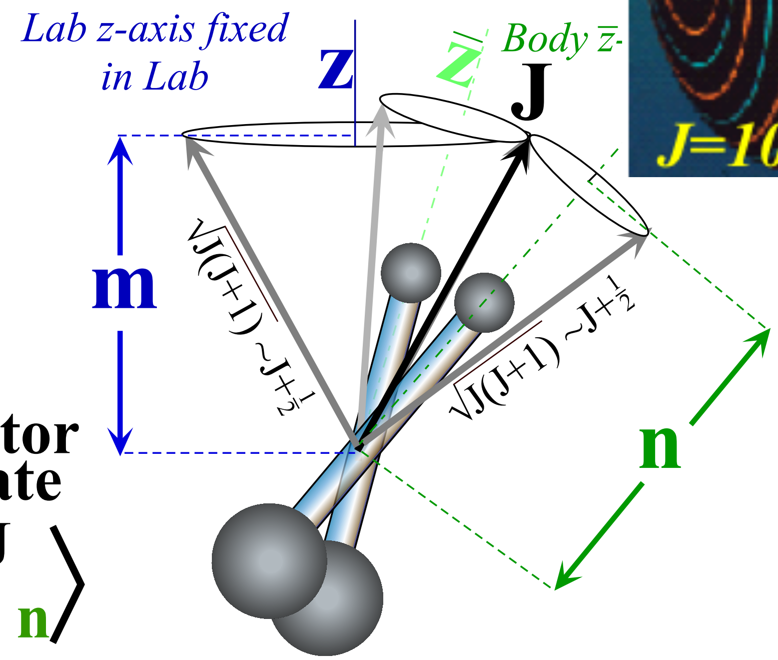
Kinetic energy inertial coefficients:

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

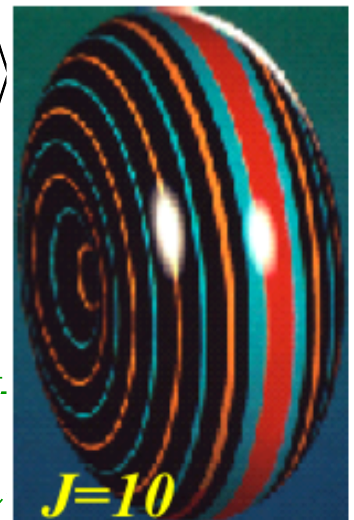
Eigensolution equations:

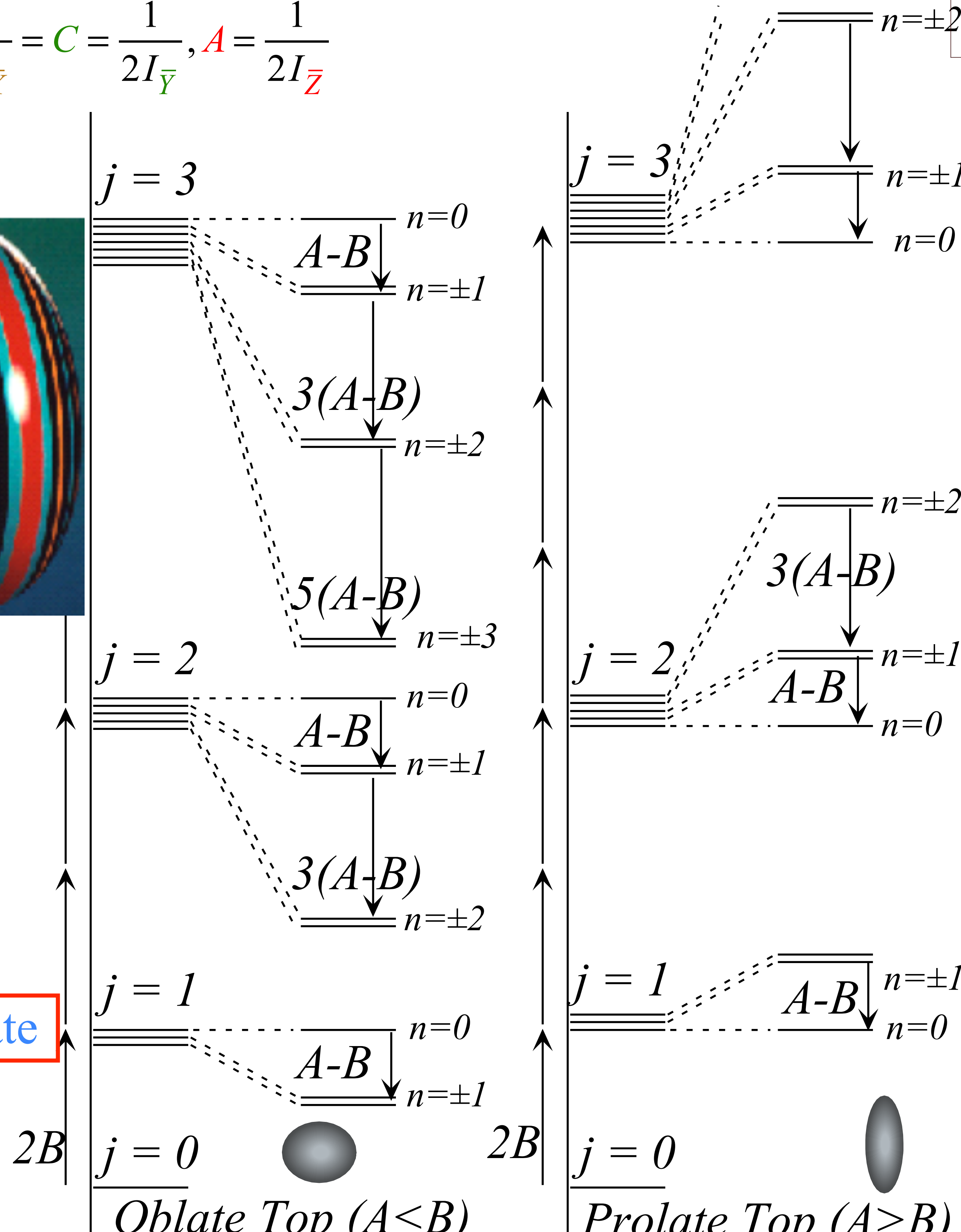
$$\mathbf{H}_{symmetric\ top}\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle = B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle = \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

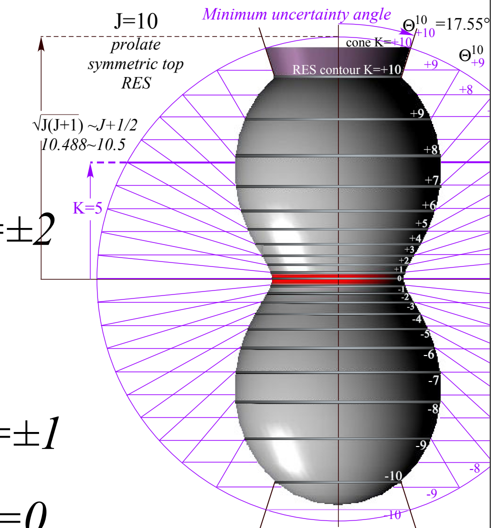
Mock-Mach-Multiplicity is $(2j+1)^2$ for each j

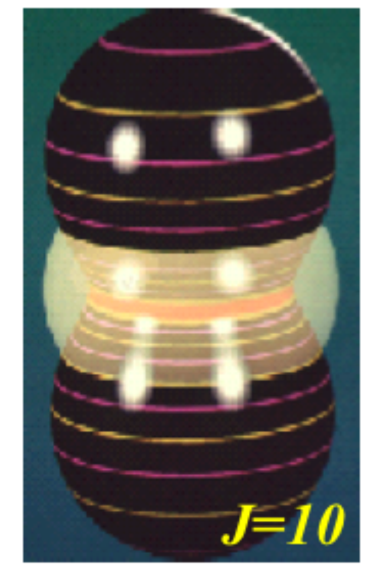


Rotor state $\left|\begin{matrix} \mathbf{J} \\ \mathbf{m}\ \mathbf{n} \end{matrix}\right\rangle$









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 $\mathbf{R}(\alpha,\beta,\gamma)|{}^J_{mn}\rangle = \Sigma_{m'} D^J_{m'n}(\alpha,\beta,\gamma)|{}^J_{m'n}\rangle$

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

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

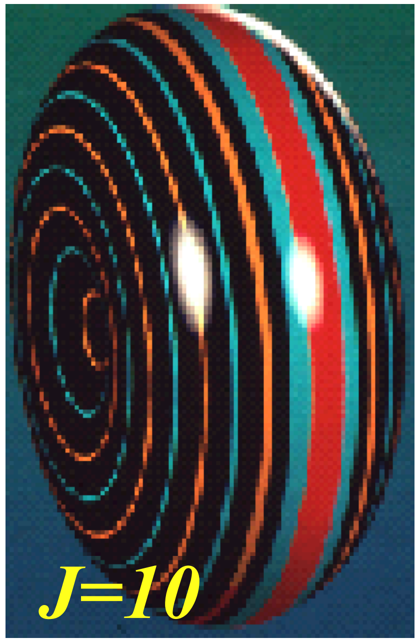
Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

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

Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

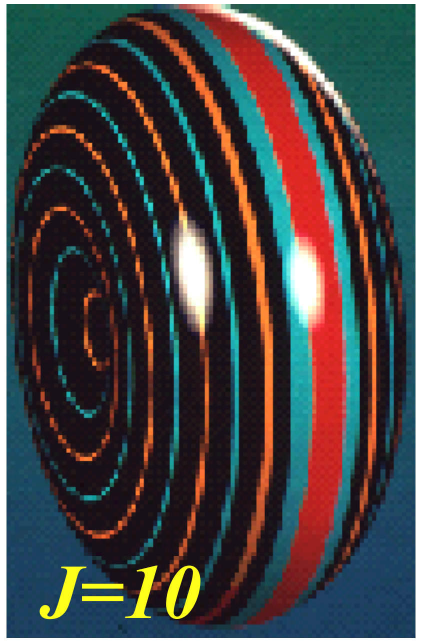
Asymmetric Top eigensolutions for J=1-2

RES of symmetric rotor (Prolate and Oblate)



after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

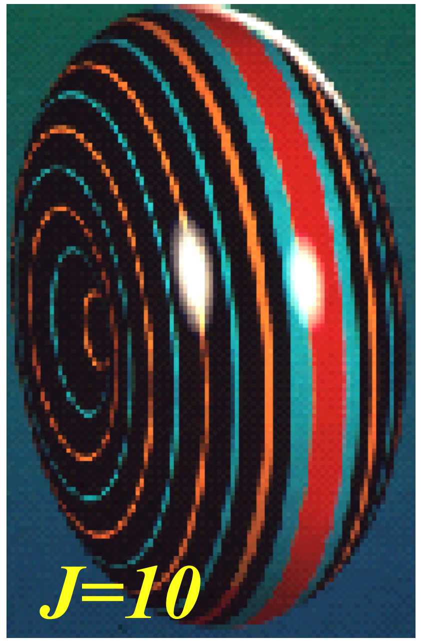
RES of symmetric rotor (Prolate and Oblate)



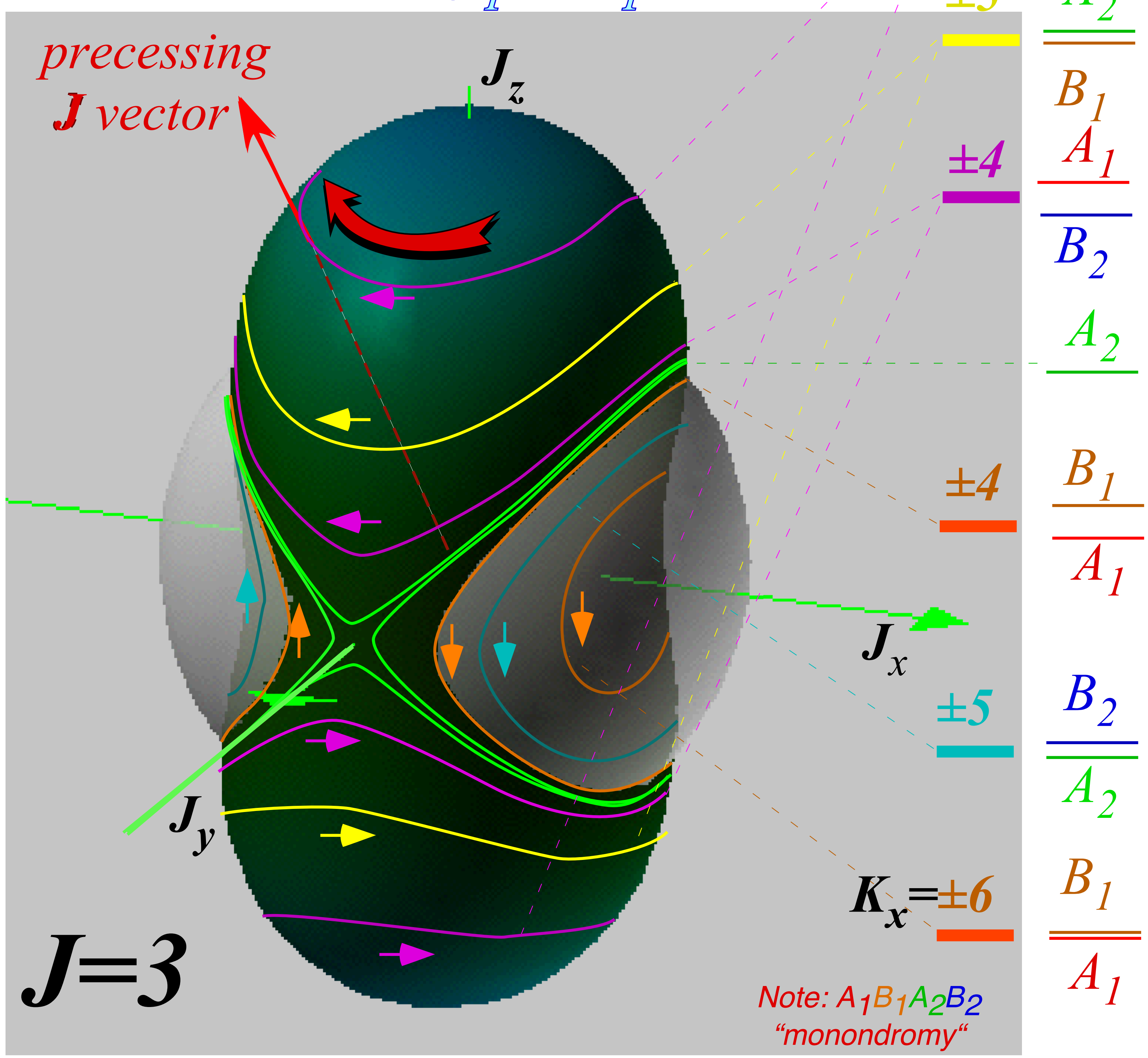
Asymmetric Top Eigensolutions
Related to RE Surface
and semi-classical J-phase paths

after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

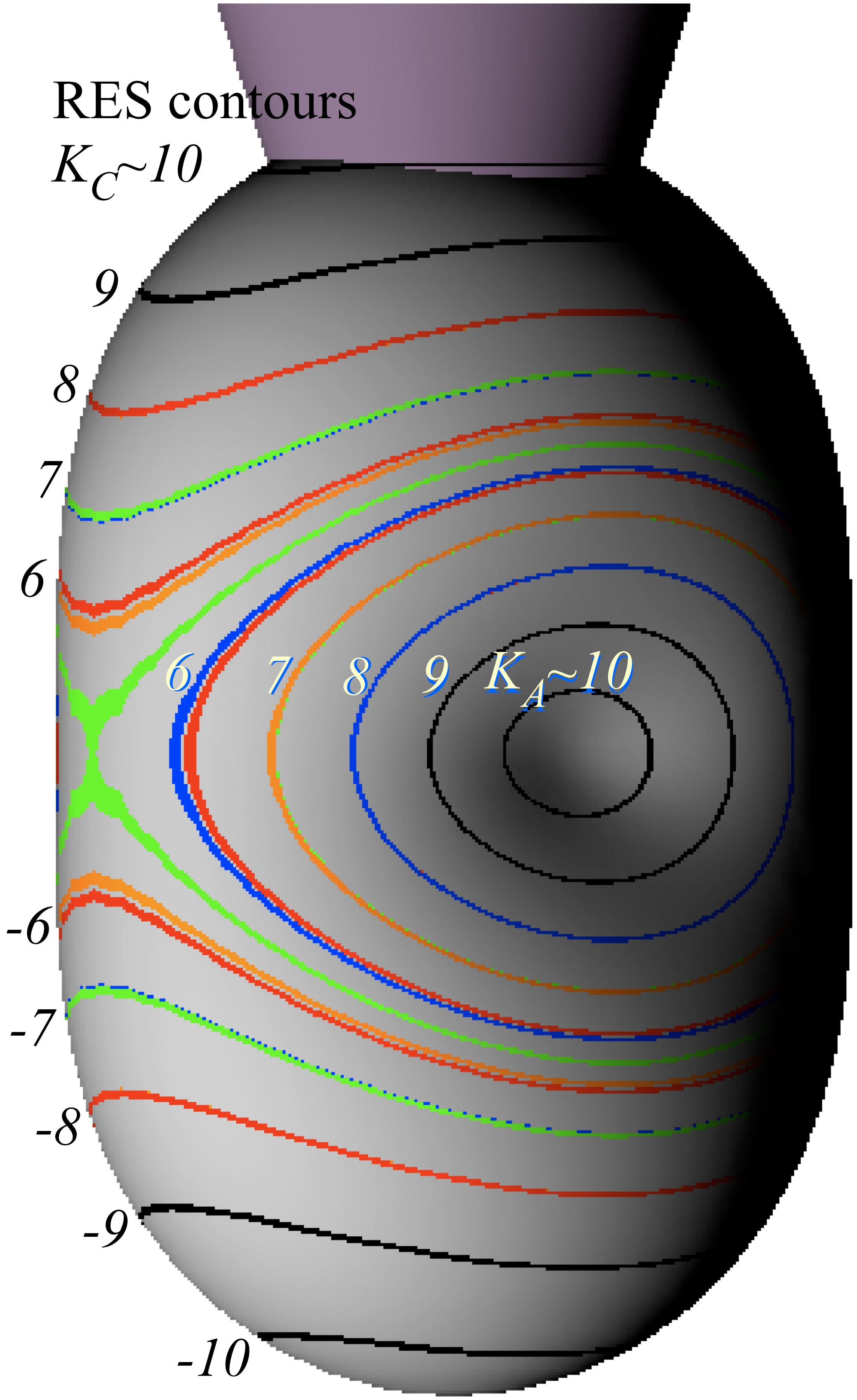
RES of symmetric rotor (Prolate and Oblate)



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

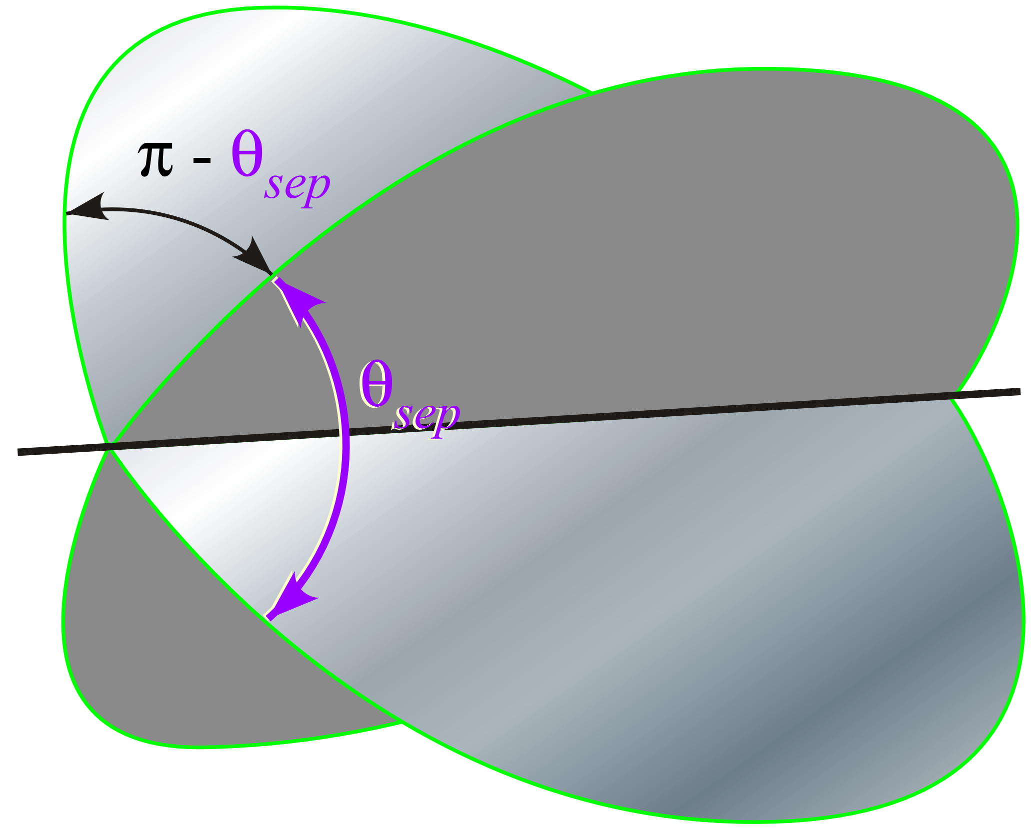


after QTforCA Unit 8. Ch. 25 Fig. 25.4.1



Separatrix circle pair dihedral angle

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



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

Molecular Symmetry and Dynamics | 32.2 Rotational Energy Surfaces and Semiclassical Rotational Dynamics

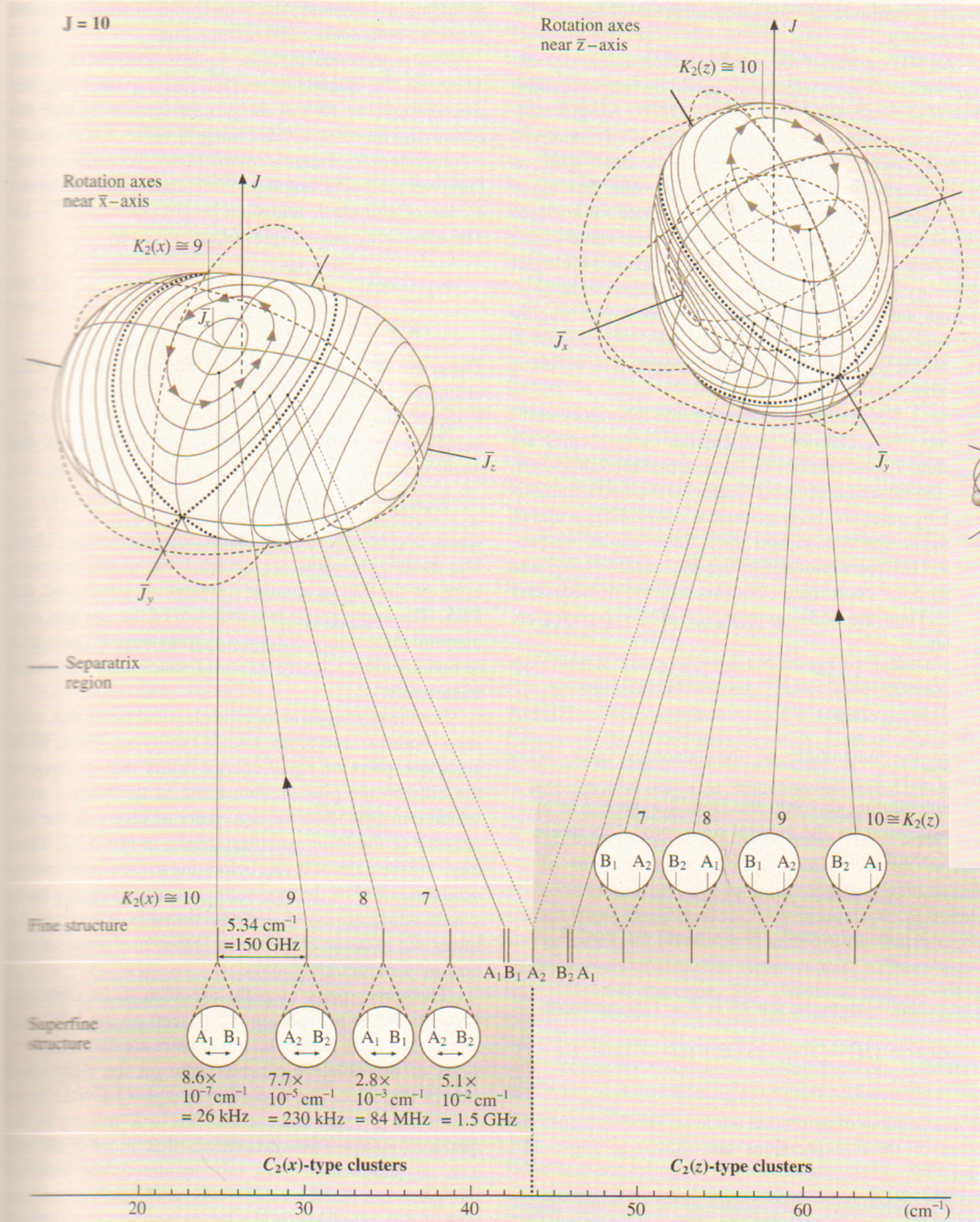
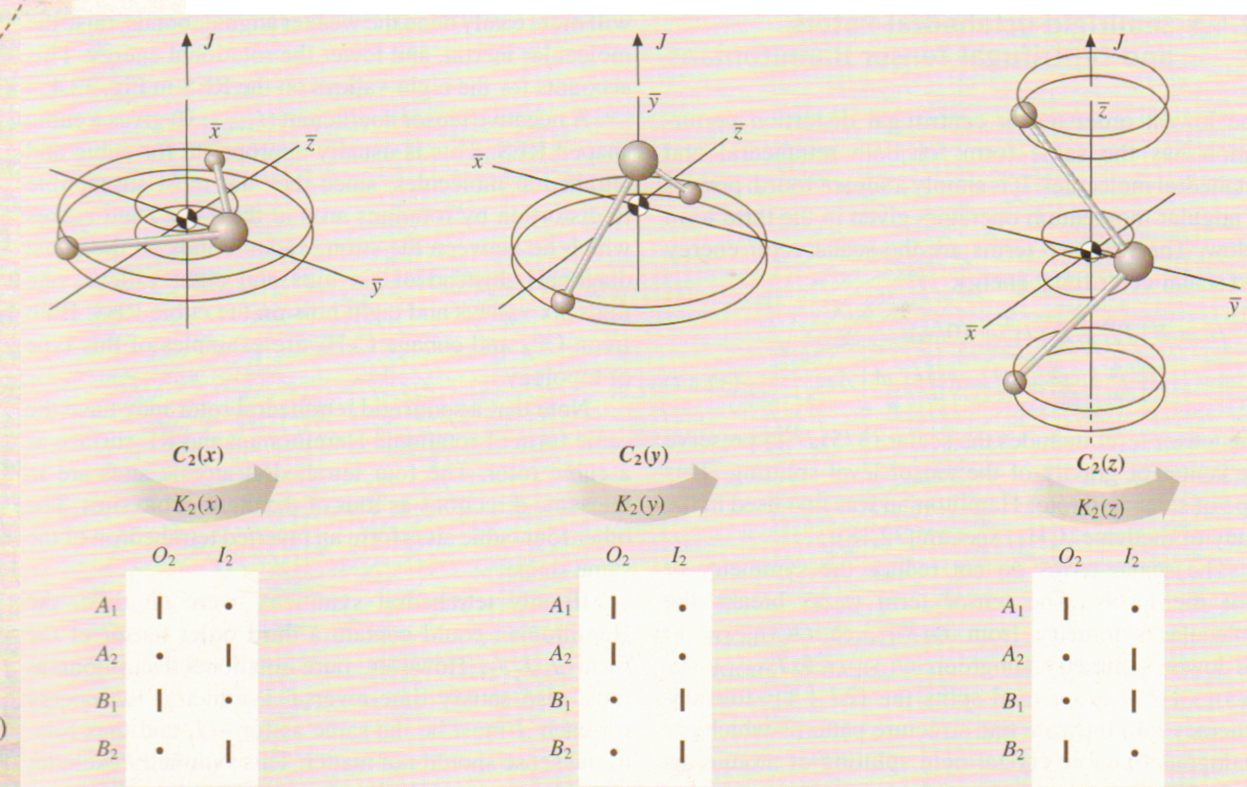


Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator ($A = 0.2$, $B = 0.4$, $C = 0.6\,\text{cm}^{-1}$)

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*

"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

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

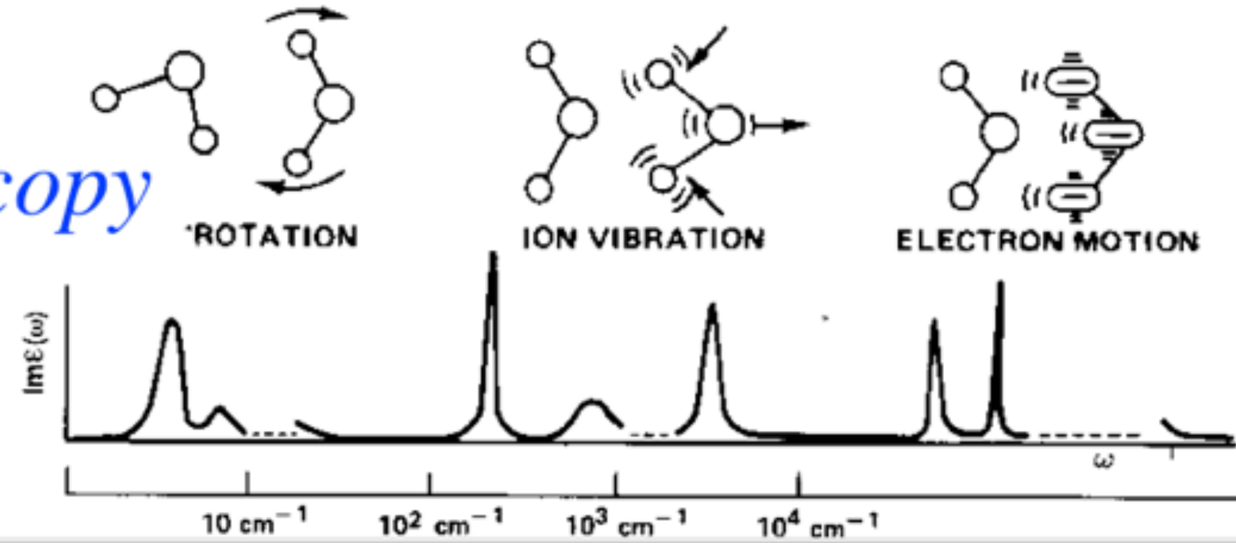
Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

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

A sketch of modern molecular spectroscopy

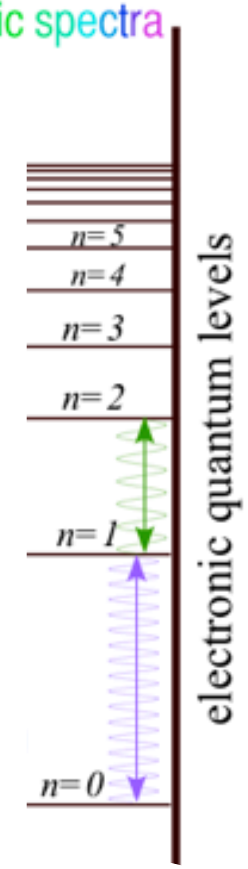


From Fig. 6.5.5.
Principles of Symmetry, Dynamics, and Spectroscopy
W. G. Harter, Wiley Interscience, NY (1993)

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
$1/\lambda=2\cdot10^6 m^{-1}$
$=2\cdot10^4 cm^{-1}$
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

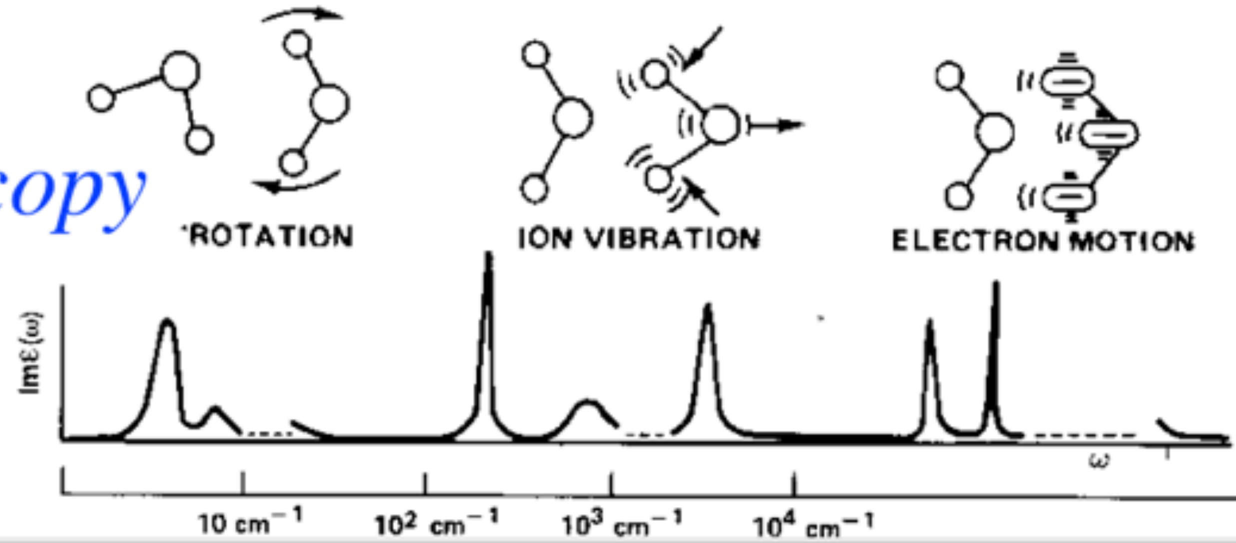
Frequency υ
Hertz(sec^{-1})
THz $10^{12}s^{-1}$
GHz $10^9 s^{-1}$
MHz $10^6 s^{-1}$
kHz $10^3 s^{-1}$

Wavelength λ
meters(m)
fm $10^{-15}m$
pm $10^{-12}m$
nm $10^{-9}m$
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

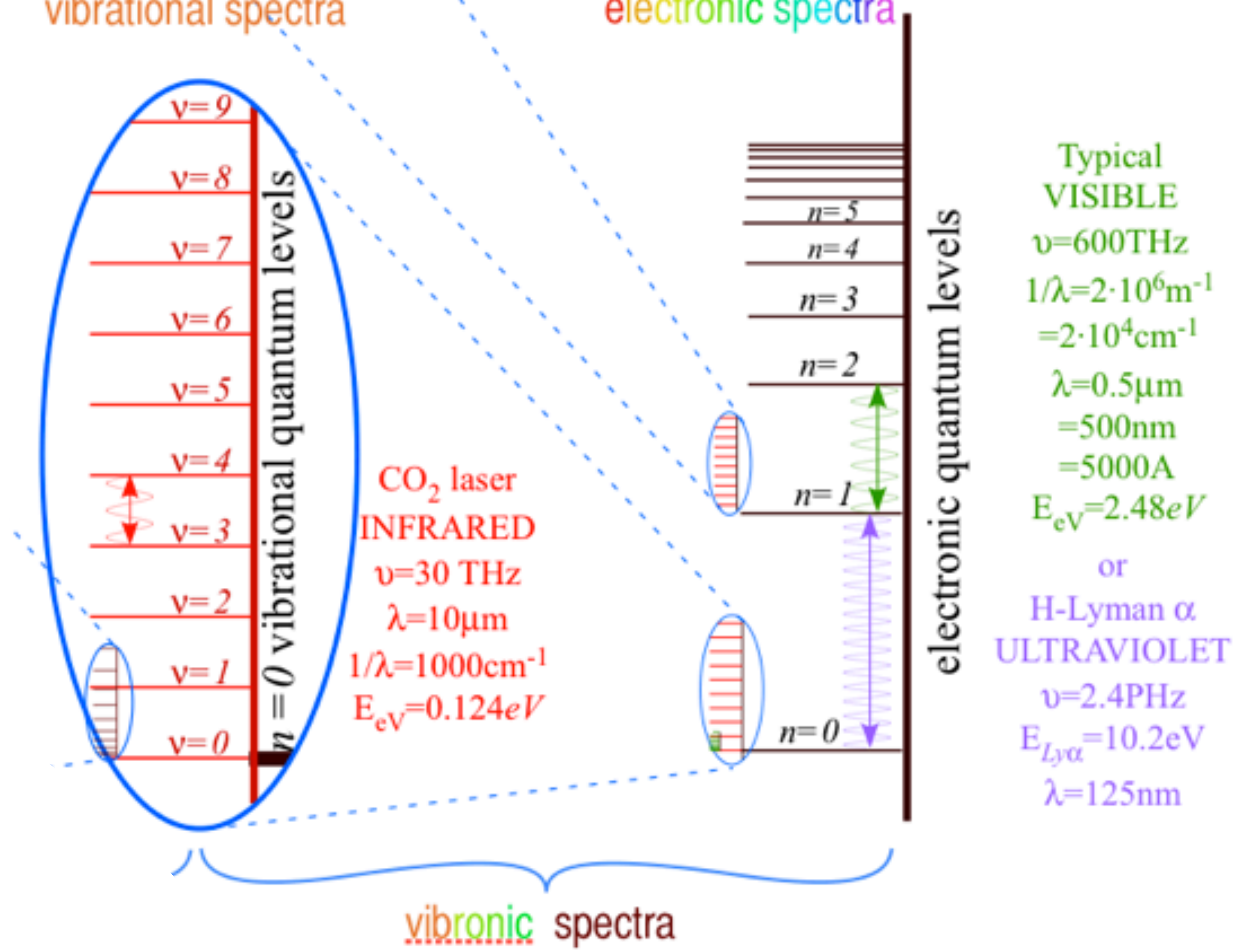


From Fig. 6.5.5.
Principles of Symmetry, Dynamics, and Spectroscopy
W. G. Harter, Wiley Interscience, NY (1993)

The frequency hierarchy

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

rotational | vibrational spectra | electronic spectra



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 $10^{3}m$

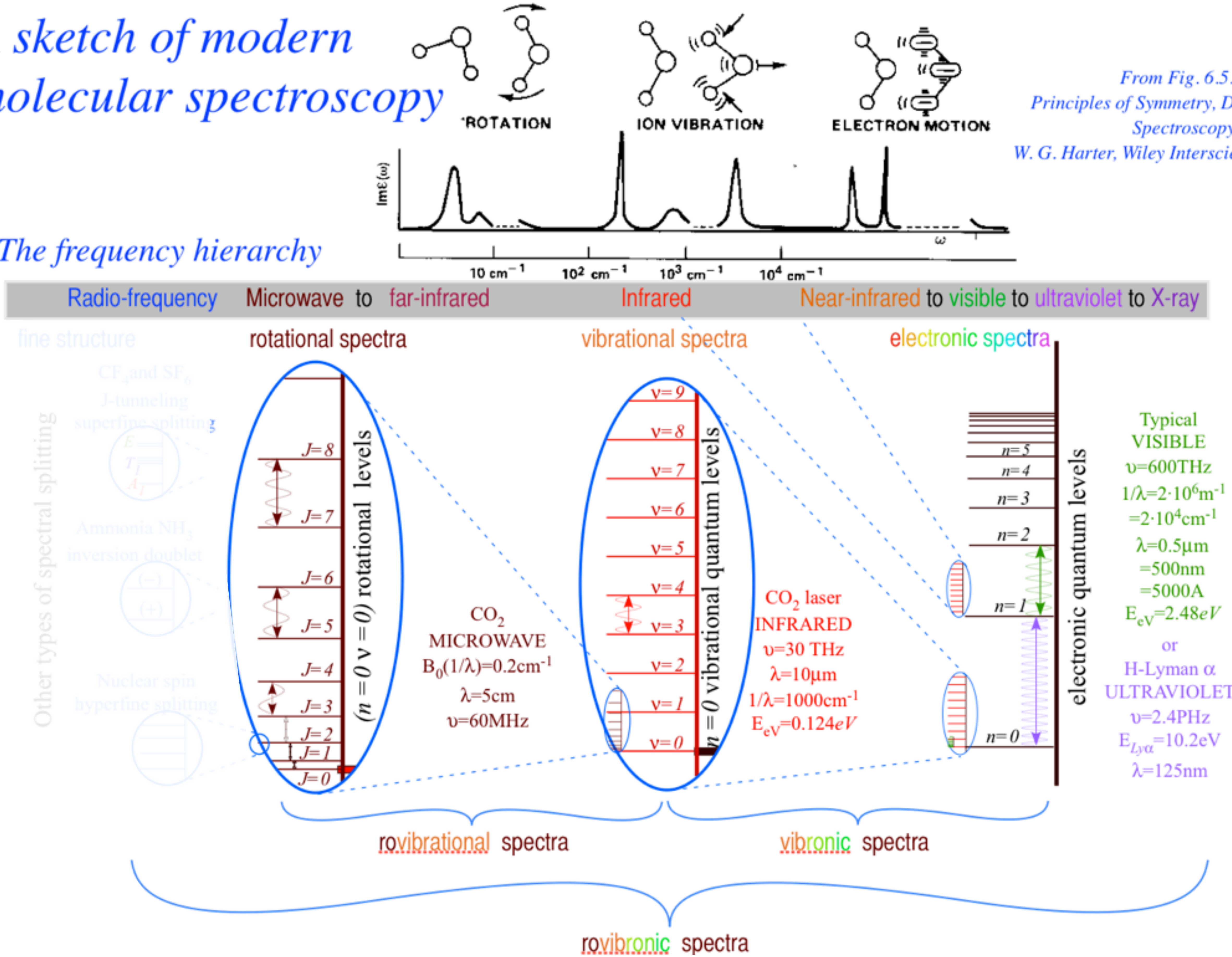
Wavenumber
per meter(m^{-1})
cm^{-1} $10^{2}m^{-1}$

Energy $eh\upsilon$
electonVolts
(eV)

A sketch of modern molecular spectroscopy

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

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 $10^{3}s^{-1}$

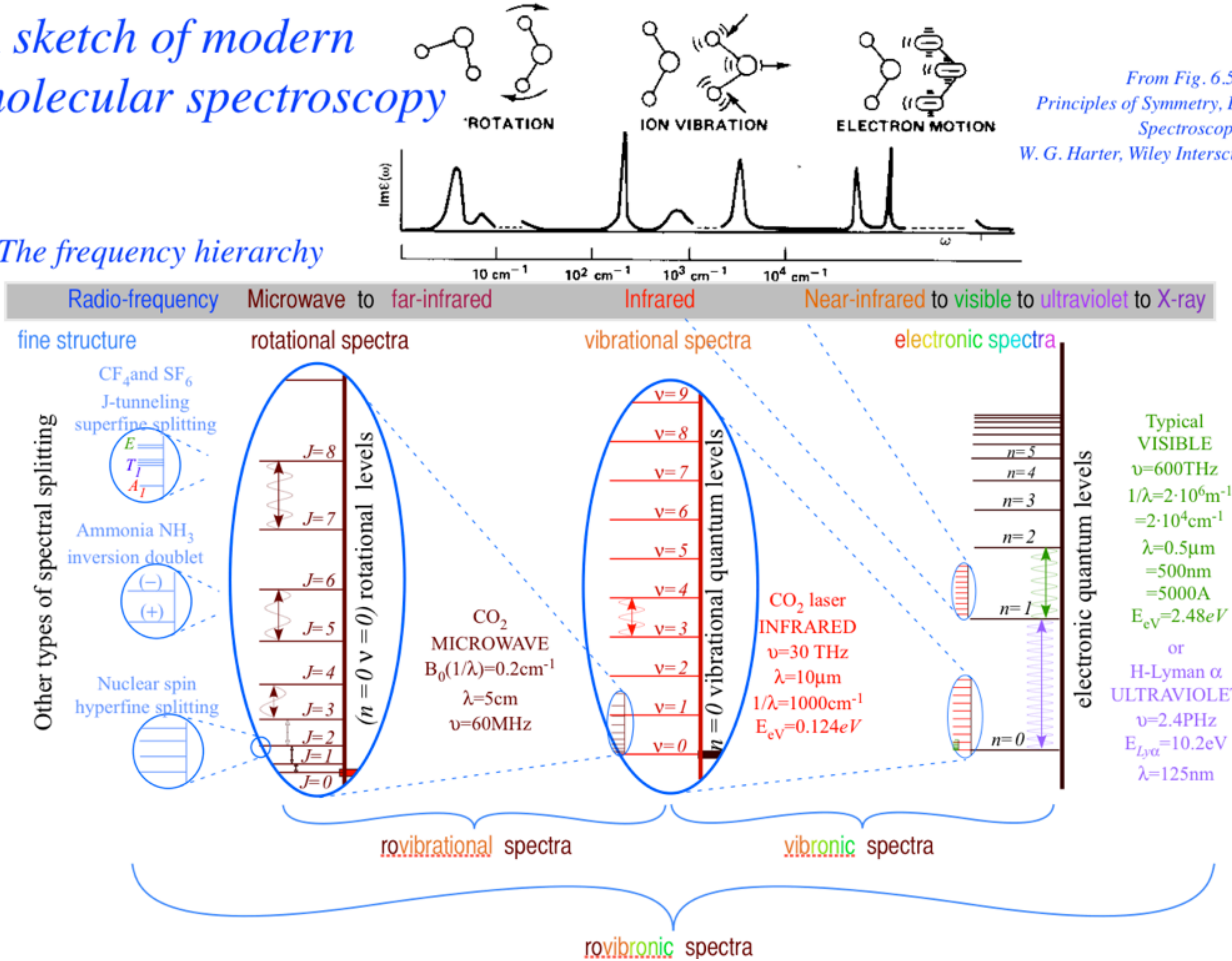
Wavelength λ
meters(m)
fm $10^{-15}m$
pm $10^{-12}m$
nm $10^{-9}m$
μ*m* $10^{-6}m$
mm $10^{-3}m$
cm $10^{-2}m$
km $10^{3}m$

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

Energy $eh\upsilon$
electonVolts (*eV*)

A sketch of modern molecular spectroscopy

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



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)

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

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

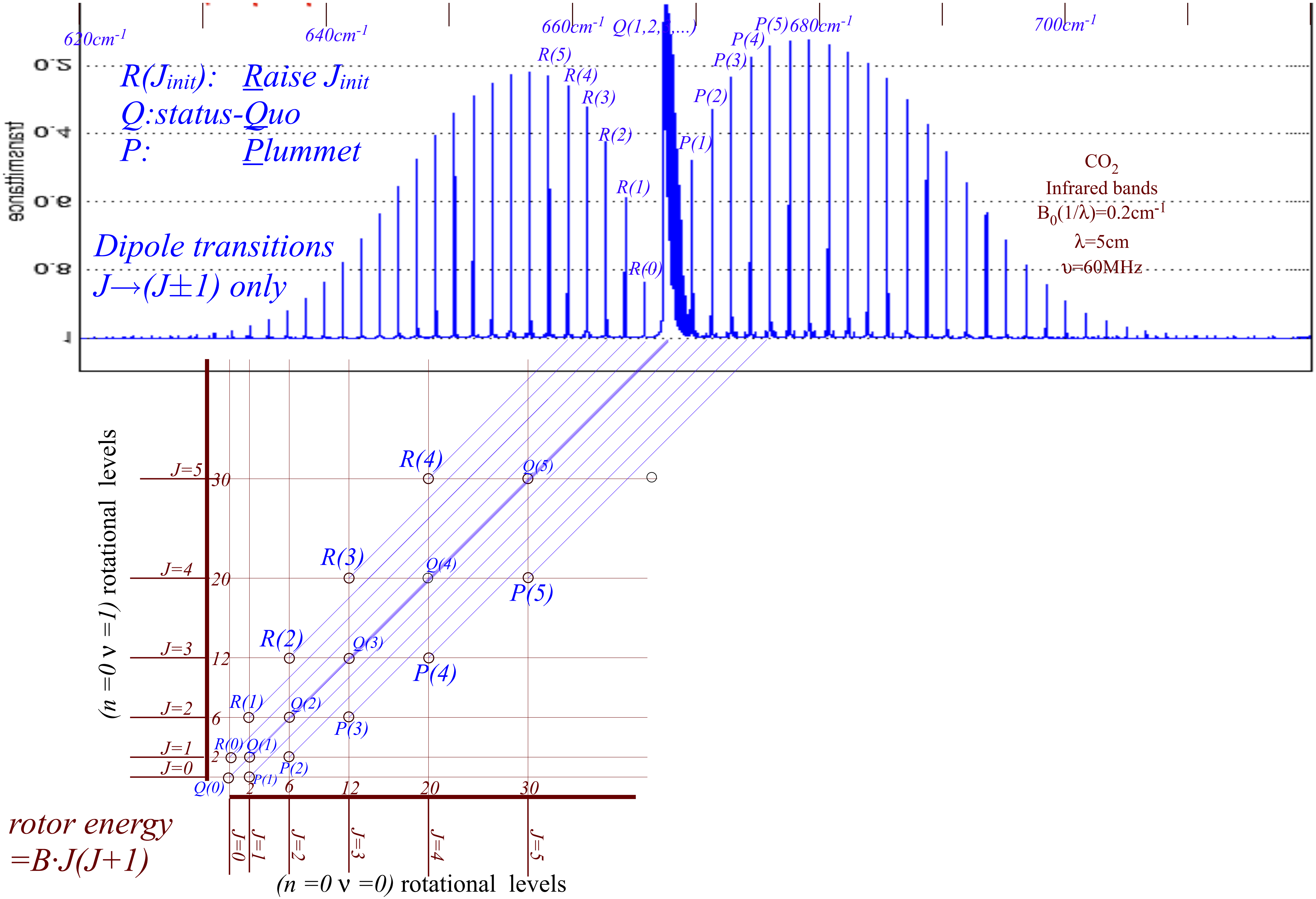
Sketch of modern molecular electronic, vibrational, and rotational spectroscopy

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

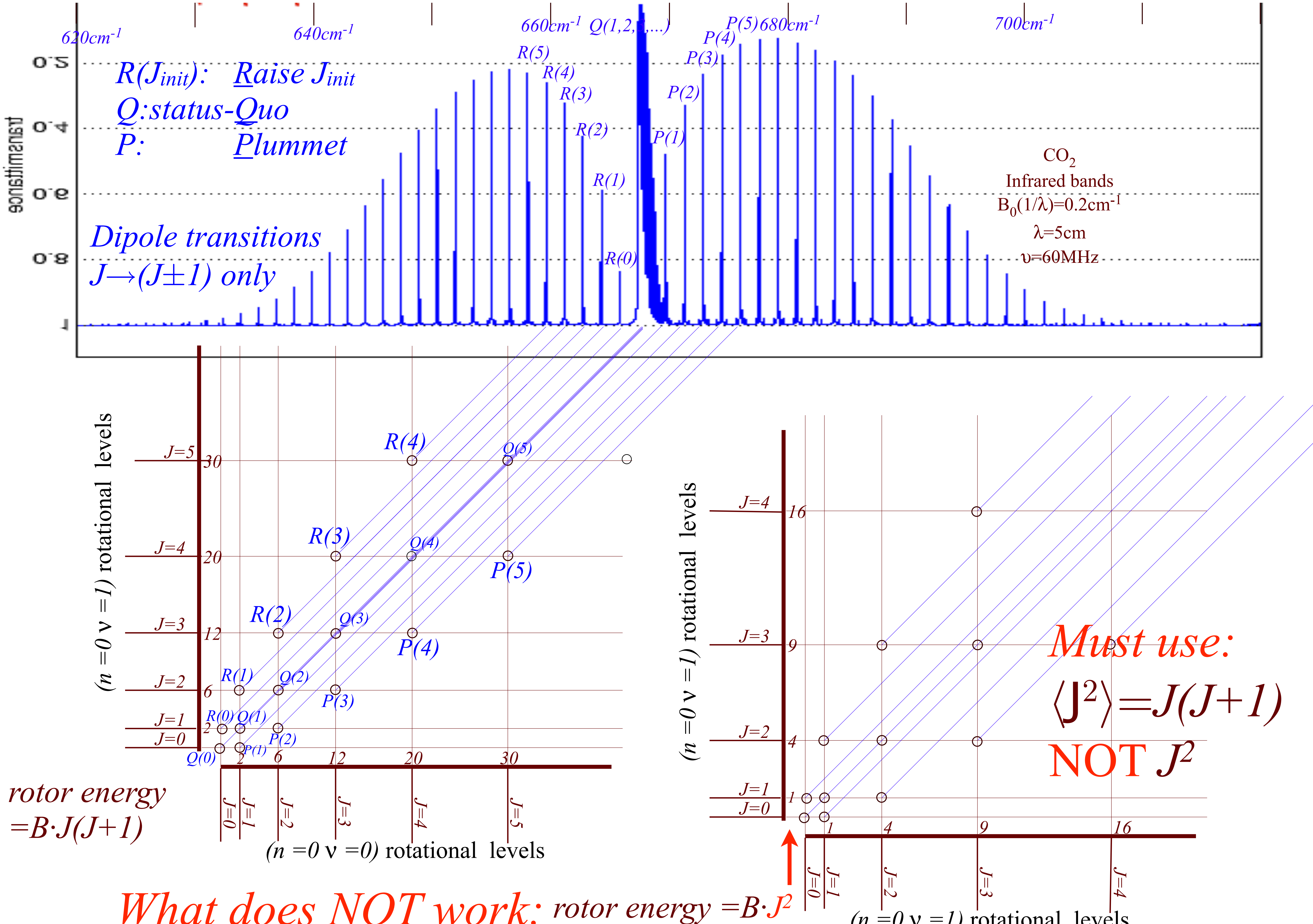
Introduction to RE symmetry and RES analysis of rovibrational Hamiltonians

Asymmetric Top eigensolutions for J=1-2

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

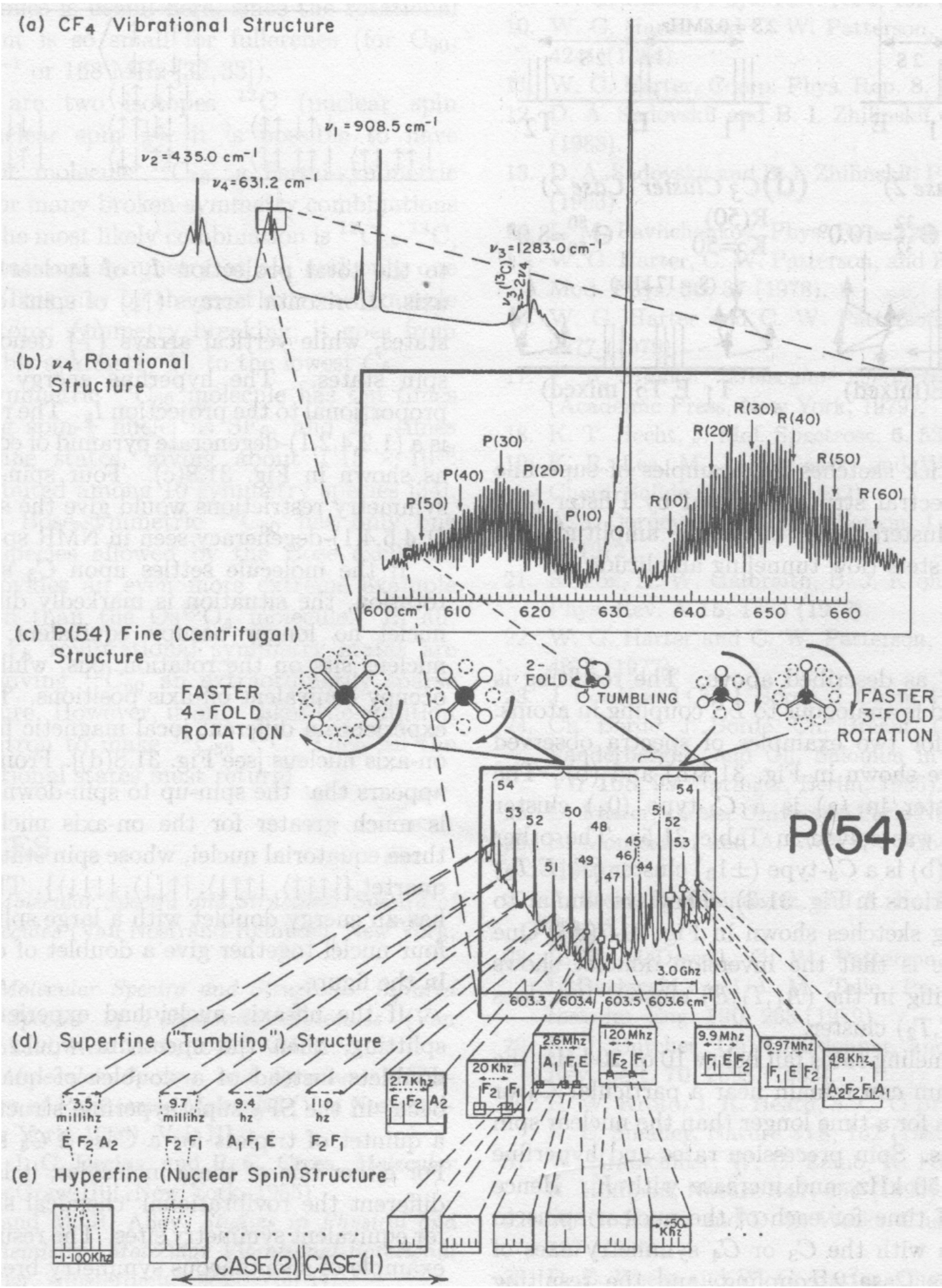


Example of CO_2 rotational $(\upsilon=0)\Leftrightarrow(\upsilon=1)$ bands



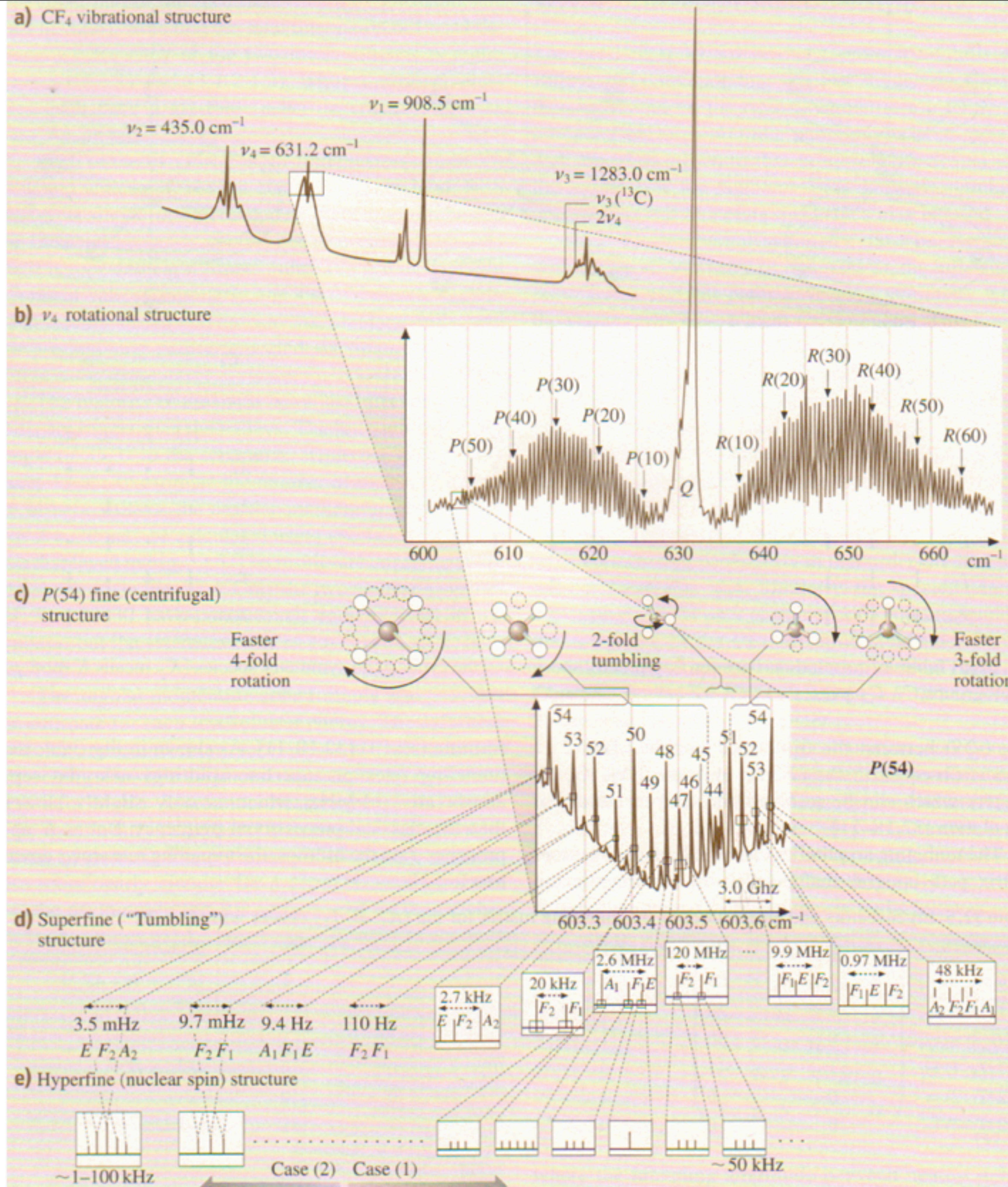
What does NOT work: rotor energy $=B\cdot J^2$

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

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

j,m,n formulas for momentum operator matrix elements: (From Lecture 24 p. 36)

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

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

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

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

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

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

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

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

LAB matrix elements use the usual atomic formula:

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

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

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

BOD matrix elements are the same after switching *m's* into *n's* and changing sign of $\mathbf{J}_2$ matrix (*-conjugation)

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

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

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

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.

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

$$= \tfrac{1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)}\left|{J \atop m,n+2}\right\rangle + \tfrac{1}{4}(j-n)(j+n+1)\left|{J \atop m,n}\right\rangle + \tfrac{1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)}\left|{J \atop m,n-2}\right\rangle + \tfrac{1}{4}(j+n)(j-n+1)\left|{J \atop m,n}\right\rangle$$

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

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

$$= \tfrac{-1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)}\left|{J \atop m,n+2}\right\rangle + \tfrac{1}{4}(j-n)(j+n+1)\left|{J \atop m,n}\right\rangle \tfrac{-1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)}\left|{J \atop m,n-2}\right\rangle + \tfrac{1}{4}(j+n)(j-n+1)\left|{J \atop m,n}\right\rangle$$

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

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

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

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

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

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

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

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

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

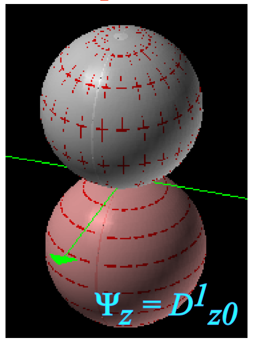
eigen-values: $(B+C=5,\ \ A+B=3,\ \ A+C=4)$

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

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

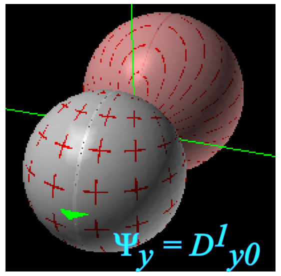
$$\left|A+B\right\rangle = +\left|{}^{1}_{m,0}\right\rangle \quad \textit{z-like}$$

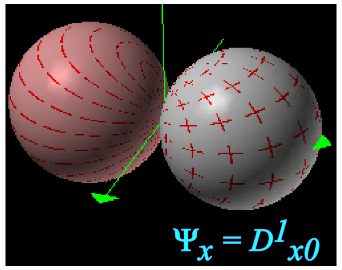
$$\left|A+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle + 1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle \quad \textit{x-like}$$



j = 1
Standing
p-Waves

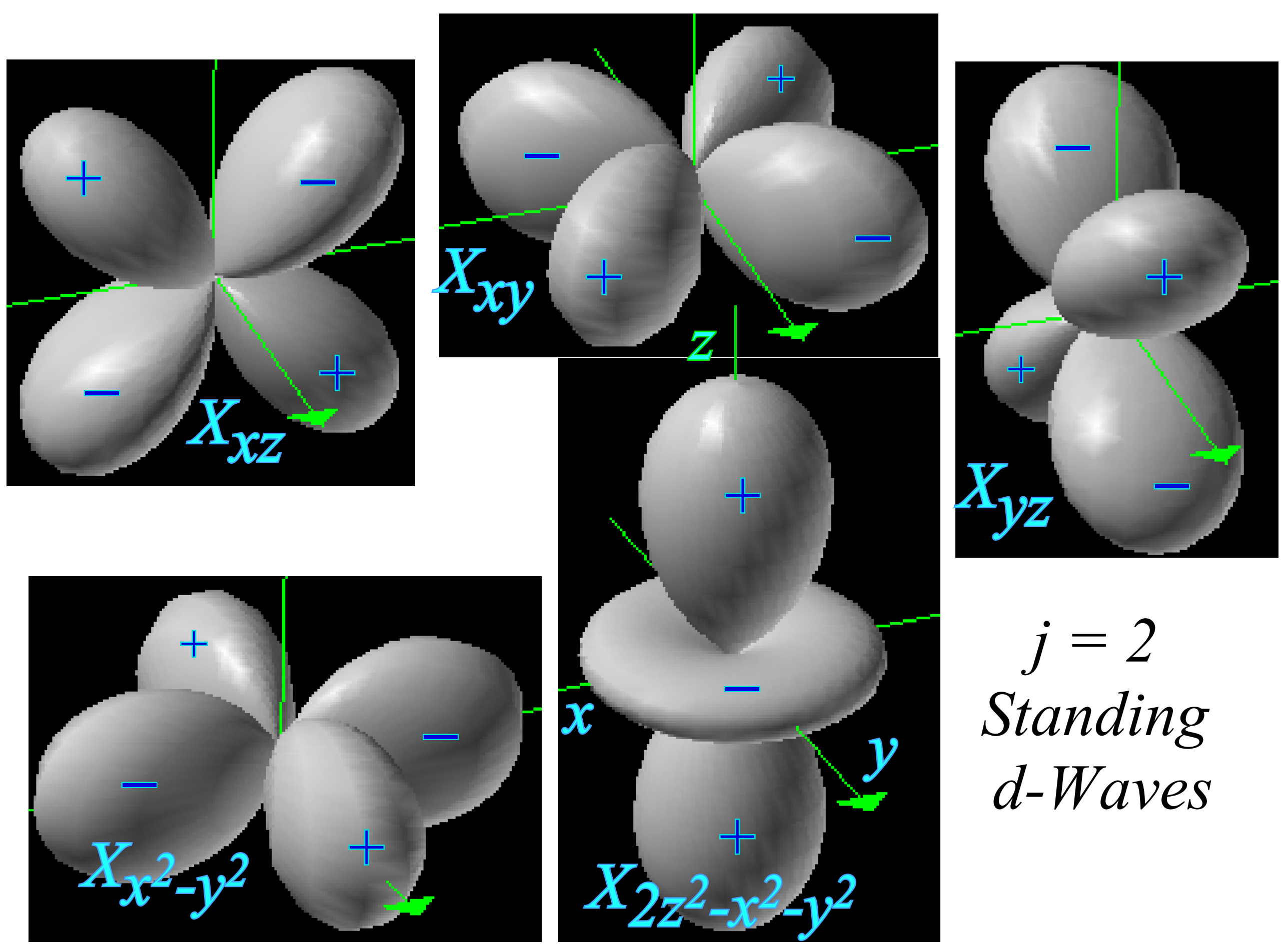
Body-based J=1
vector-like eigenfunctions





($J=2$)-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

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

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

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.

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

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

New D_2 basis:

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

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

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

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

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

Completing diagonalization from new D_2 basis:

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

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

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

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

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

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

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

×

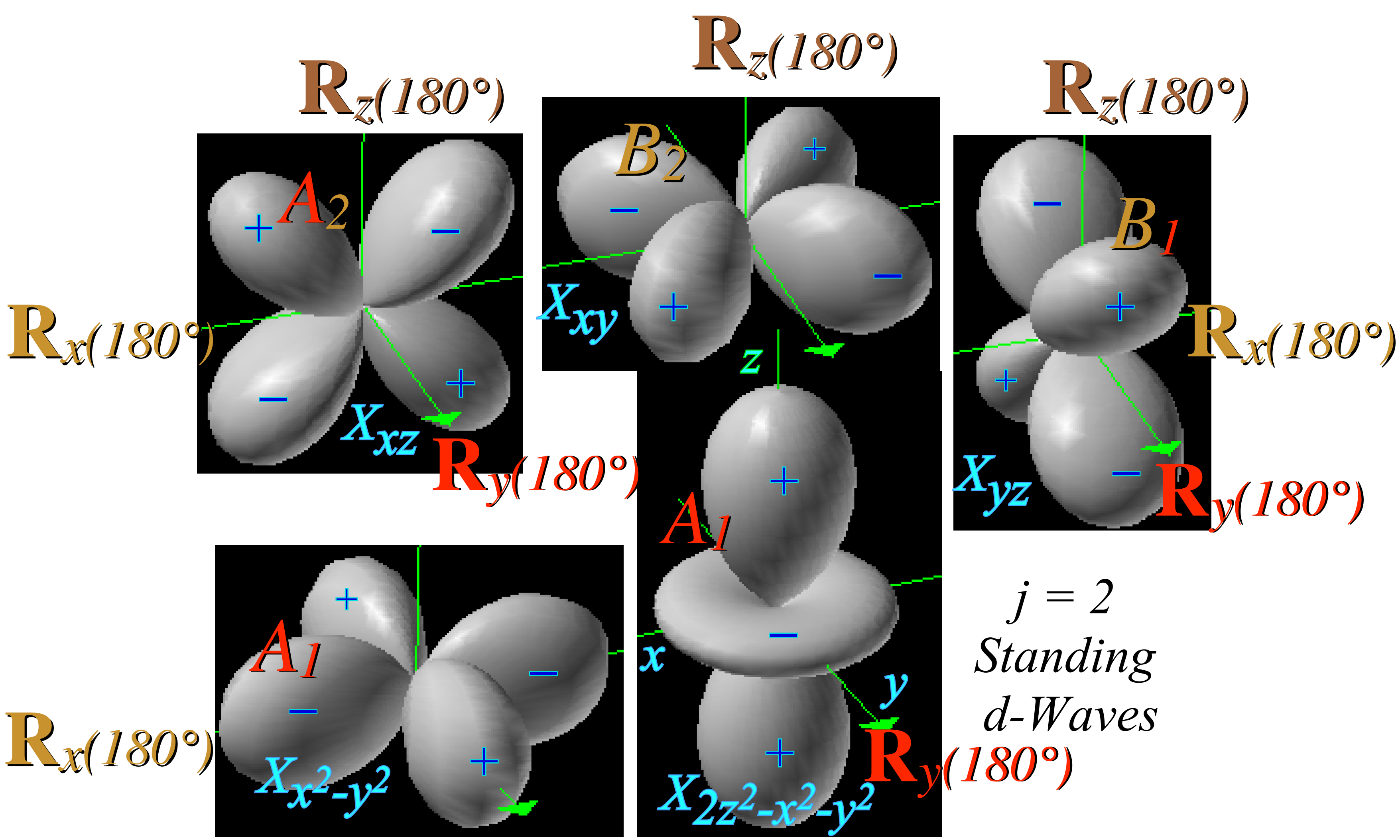
C_2^y	**1**	$\mathbf{R}_y$
+	1	1
−	1	−1

=

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

=

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:

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

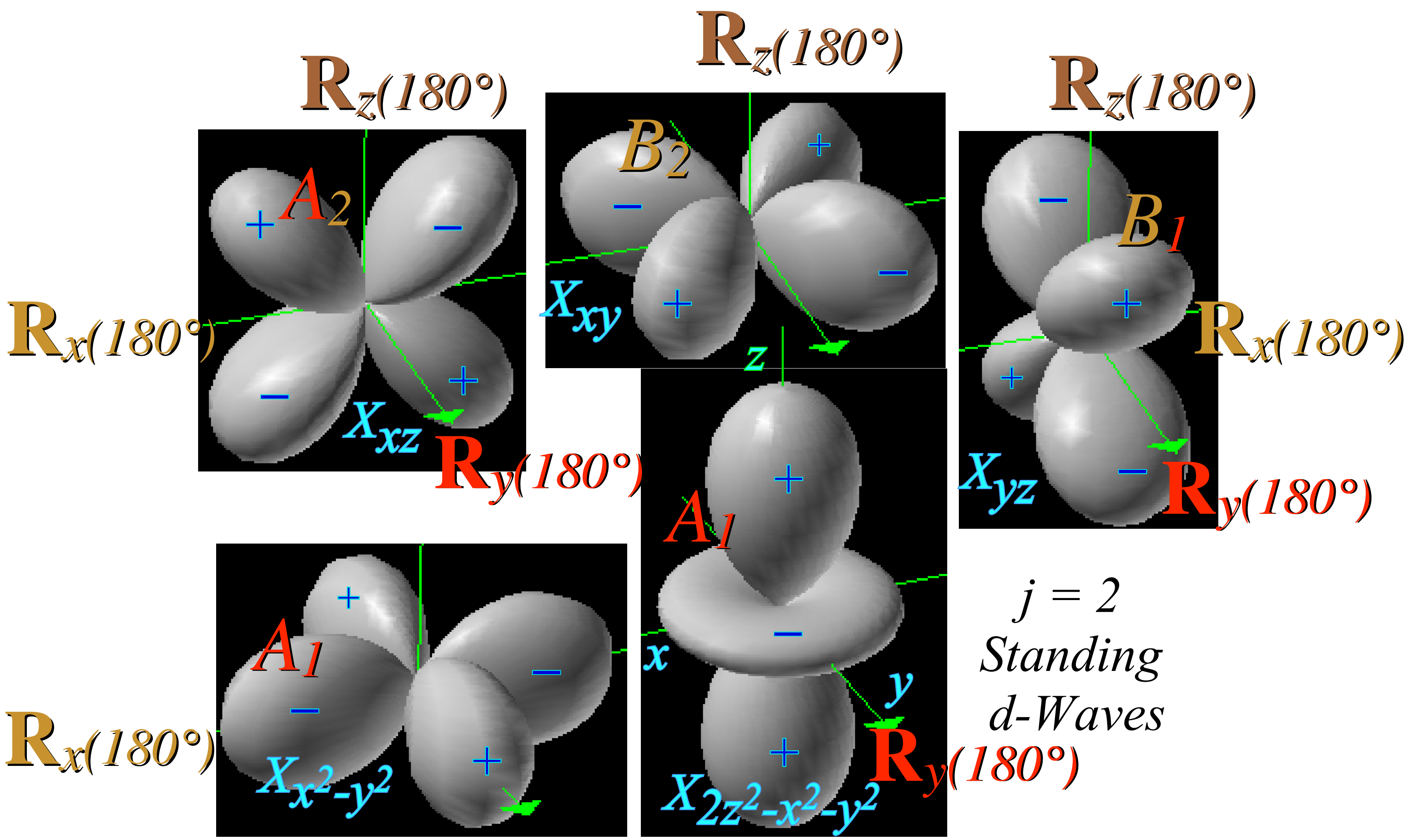
$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_1 1^+\right\rangle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

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



j = 2
Standing
d-Waves

Completing diagonalization from new D_2 basis:

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

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

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

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

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

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

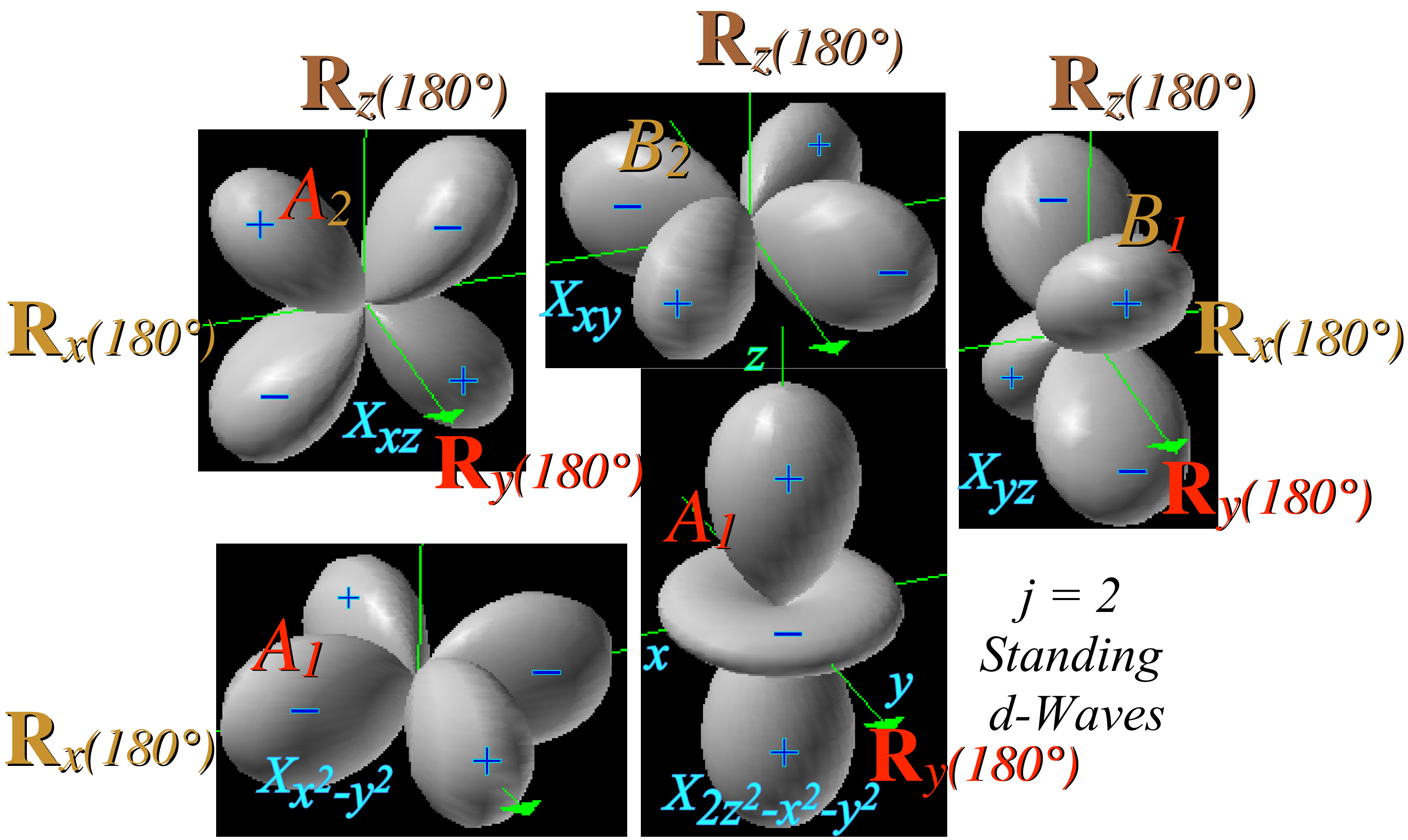
Need only diagonalize the two A_1's:

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

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

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

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



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+)

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

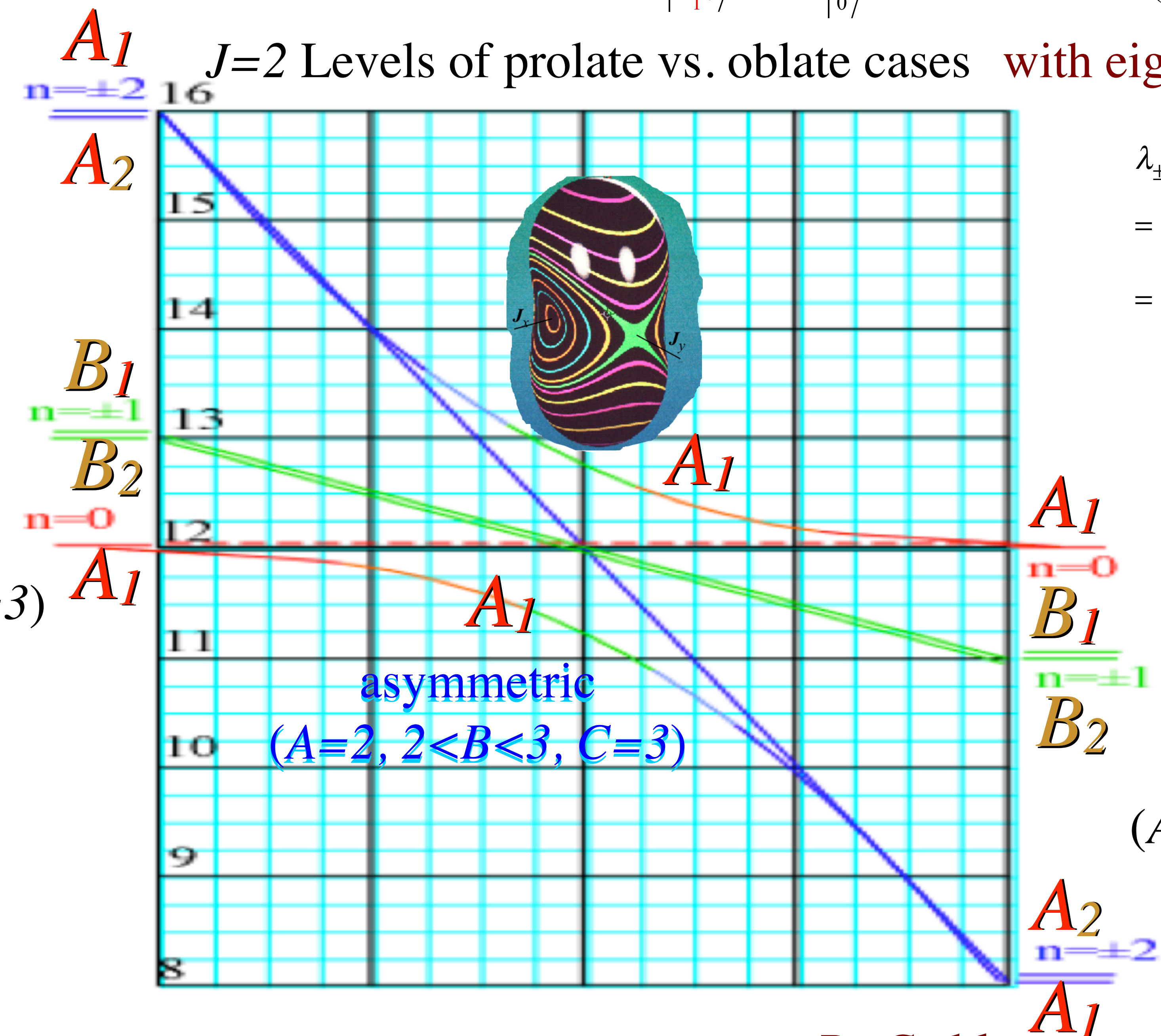
$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

with eigenvalues:

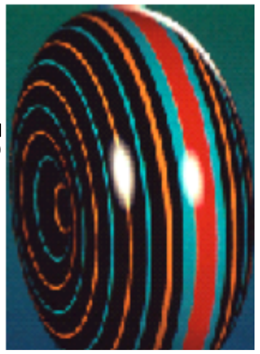
$$\lambda_\pm = 2C+2A+2B \pm \sqrt{(2C-A-B)^2+3(A-B)^2}$$
$$= 2(A+B+C) \pm 2\sqrt{C^2-(A+B)C+A^2-AB+B^2}$$
$$= 2C+4B \pm 2(C-B) = \begin{cases} 4C+2B \\ 6B \end{cases} \quad \text{if: } A=B$$

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

J=2 Levels of prolate vs. oblate cases



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+)

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

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

J=2 Levels of prolate vs. oblate cases

with eigenvalues:

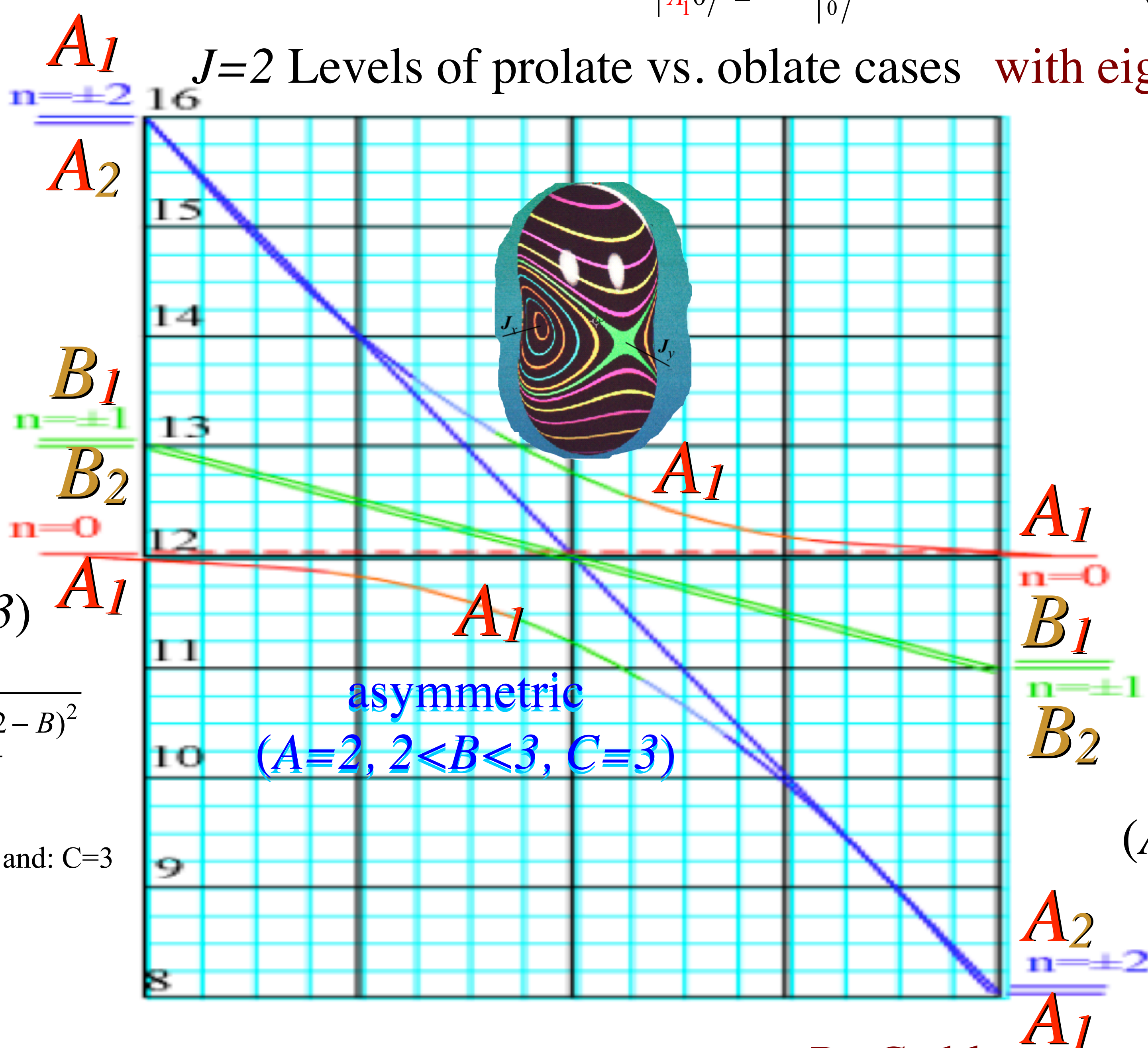
$$\begin{pmatrix} 14+B & \sqrt{3}(2-B) \\ \sqrt{3}(2-B) & 6+3B \end{pmatrix} =$$

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

prolate

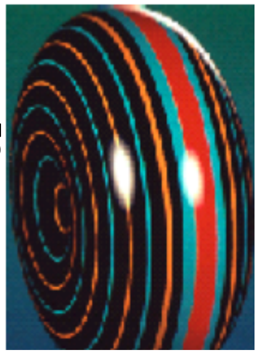
(*A*=2, *B*=2, *C*=3)

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



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=2*B*+4*C*=4+12=16 (*n*=±2)

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

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

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

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

Review of freshman Chemistry and Physics (contd)

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

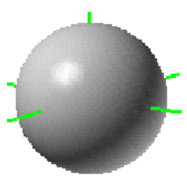
Energy 101 $E = \frac{1}{2} m\,v^2 = p^2/2m$ $E = \frac{1}{2} I\,\omega^2 = J^2/2I$ $BUCK$

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

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

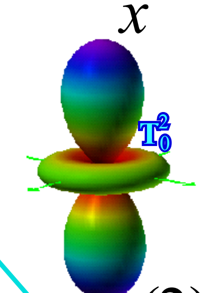
...and its multi-pole expansion...

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



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

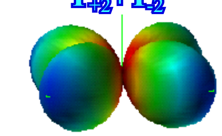
$$\mathbf{T}_0^{(0)} = \mathbf{J}^2$$



Symmetric Top *(A=B≠C)*

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

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



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

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…)

As of April 3, 2014

Links to the current Harter-Soft LearnIt web apps for Physics

Bold links have default redirect pages. *Italics* are not yet meant for production.Red: the final stages of testing.

List of *production* Harter-Soft Web Apps & Textbooks (For public)

Classical Mechanics with a Bang! - URL is "http://www.uark.edu/ua/modphys/markup/CMwBangWeb.html"
Quantum Theory for the Computer Age - URL is "http://www.uark.edu/ua/modphys/markup/QTCAWeb.html"
LearnIt Web Applications - URL is "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"

Individual web-apps for current classes:

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"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
MolVibes - Production; URL is "http://www.uark.edu/ua/modphys/markup/MolVibesWeb.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"

The old relativity website (2005):
Relativity - Pirelli Entrant - Production; URL is "**http://www.uark.edu/ua/pirelli**" or "http://www.uark.edu/ua/pirelli/html/default.html"

Newer relativity web-apps currently being developed (2013-)
RelativIt Production; URL is "http://www.uark.edu/ua/modphys/markup/RelativItWeb.html"
RelaWavity Production; URL is "http://www.uark.edu/ua/modphys/markup/RelaWavityWeb.html"

Additional classical wep-apps:
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"
WaveIt Production; URL is "http://www.uark.edu/ua/modphys/markup/WaveItWeb.html"

Link to master list of all Harter-Soft Web Apps & Textbooks (Prod, Testing, & Developement)

http://www.uark.edu/ua/modphys/testing/markup/Harter-SoftWebApps.html