Why it is worthwhile taking time for spherical harmonics?

1. it is a wave function — but, of what ?
2. rotational energy — $E = Bh\, J(J+1)$
3. angular momentum — J, K, Ka, Kc

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4. symmetry — $(-1)^J$
5. selection rule — $\Delta J = 0, \pm 1, 0 \nleftrightarrow 0$
6. (vanishing integral) — expansion

Let us have a close look at **spherical harmonics**

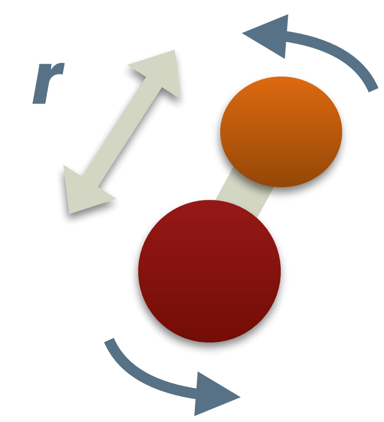
$$H\Psi = E\Psi$$

$$H\Psi(x, y, z) = E\Psi(x, y, z)$$

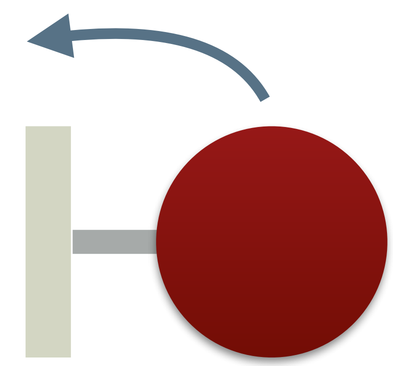
polar coordinate

$$H\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi)$$

rigid rotor



$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$



Laplacian

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

Legendrian angular part (θ, Φ) only

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Let us have a close look at **spherical harmonics**

$$H\Psi = E\Psi$$

$$H\Psi(x, y, z) = E\Psi(x, y, z)$$

$$H\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi)$$

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$

Laplacian

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

Legendrian angular part (θ, Φ) only

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

$$\Lambda^2 Y = [\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}]Y$$

$$\Lambda^2\Theta = -\frac{m^2}{\sin^2\theta}\Theta + [\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}]\Theta$$

$$\Lambda^2 Y = aY$$ scalar

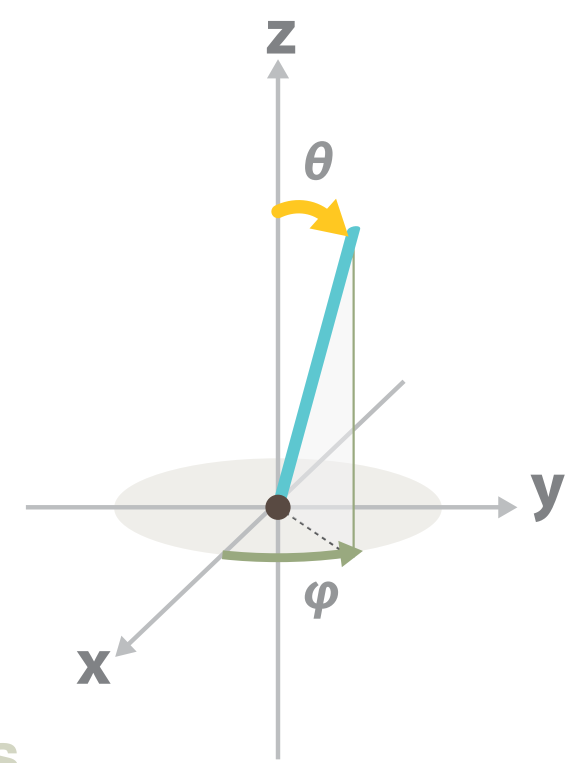
if such function exists

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

$$\frac{\partial^2\Phi}{\partial\phi^2} = b\Phi$$ scalar

if such function exists

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$



yes it does

$$\Phi(\phi) = e^{im\phi}$$

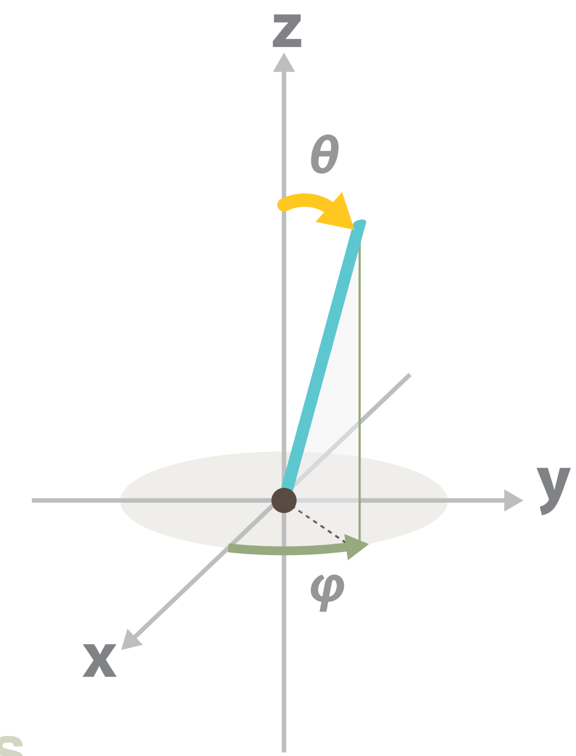
$$\frac{\partial^2\Phi}{\partial\phi^2} = -m^2\Phi$$

Let us have a close look at **spherical harmonics**

$$\Lambda^2 Y = aY$$ scalar

if such function exists

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$



solution of Associated Legendre

$$-\frac{m^2}{\sin^2\theta}\Theta + \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]\Theta = -J(J+1)\Theta$$

$$\frac{\partial^2\Phi}{\partial\phi^2} = b\Phi$$ scalar

if such function exists

satisfies

$$\Lambda^2\Theta = -J(J+1)\Theta$$

yes it does

$$\Phi(\phi) = e^{im\phi}$$

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$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

$$\Lambda^2 Y = \left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]Y$$

$$\Lambda^2\Theta = -\frac{m^2}{\sin^2\theta}\Theta + \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]\Theta$$

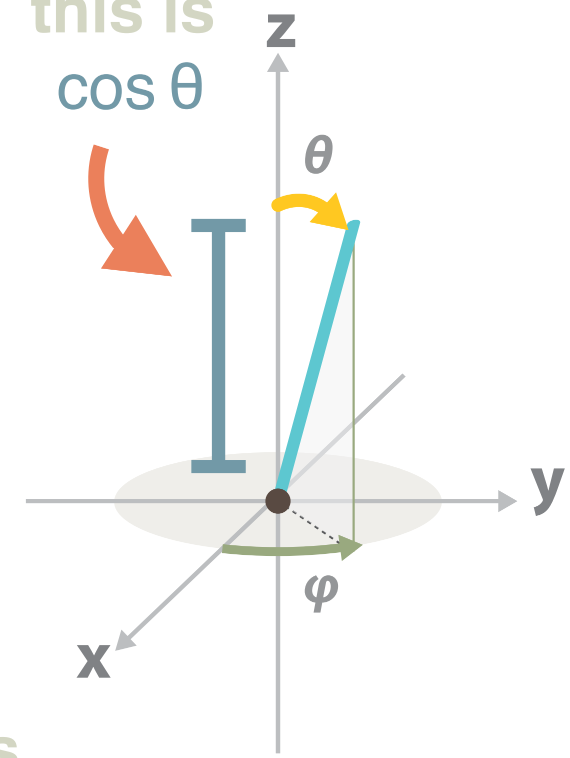
Let us have a close look at **spherical harmonics**

$\Lambda^2 Y = aY$ scalar

if such function exists

$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$

this is $\cos\theta$



solution of Associated Legendre

$$-\frac{m^2}{\sin^2\theta}\Theta + [\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}]\Theta = -J(J+1)\Theta$$

$$\frac{\partial^2\Phi}{\partial\phi^2} = b\Phi$$ scalar

if such function exists

satisfies

$$\Lambda^2\Theta = -J(J+1)\Theta$$

explicitly

$$\Theta(x) = \frac{1}{2^J J!}(1-x^2)^{\frac{m}{2}}\frac{d^{m+J}}{dx^{m+J}}[(x^2-1)^J]$$

$$x = \cos\theta$$

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

$$Y(x, \phi) = \Theta(x)\Phi(\phi)$$

$$= \frac{1}{2^J J!}(1-x^2)^{\frac{m}{2}}\frac{d^{m+J}}{dx^{m+J}}[(x^2-1)^J]e^{-im\phi}$$

$\Theta(x)$ function of **J**, **m**

$\Phi(\phi) = e^{im\phi}$ function of **m**

$$Y_{Jm}(x, \phi) = \Theta_{Jm}(x)\Phi_m(\phi)$$

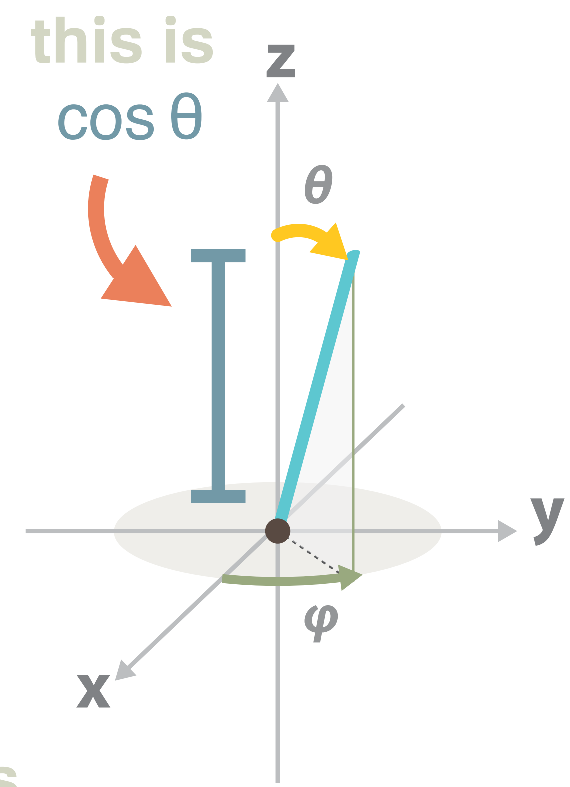
$$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

Let us have a close look at **spherical harmonics**

$\Lambda^2 Y = aY$ scalar

if such function exists

$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$



solution of Associated Legendre

$$-\frac{m^2}{\sin^2\theta}\Theta + \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]\Theta = -J(J+1)\Theta$$

$$\frac{\partial^2\Phi}{\partial\phi^2} = b\Phi$$ scalar

if such function exists

satisfies

$$\Lambda^2\Theta = -J(J+1)\Theta$$

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$$\Theta(x) = \frac{1}{2^J J!}(1-x^2)^{\frac{m}{2}}\frac{d^{m+J}}{dx^{m+J}}[(x^2-1)^J]$$

$$x = \cos\theta$$

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

$$Y(x, \phi) = \Theta(x)\Phi(\phi)$$ spherical harmonics

$\Theta(x)$ function of **J**, **m**

$\Phi(\phi) = e^{im\phi}$ function of **m**

$$Y(z, \phi) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]e^{-im\phi}$$

$$Y_{Jm}(x, \phi) = \Theta_{Jm}(x)\Phi_m(\phi)$$

$$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

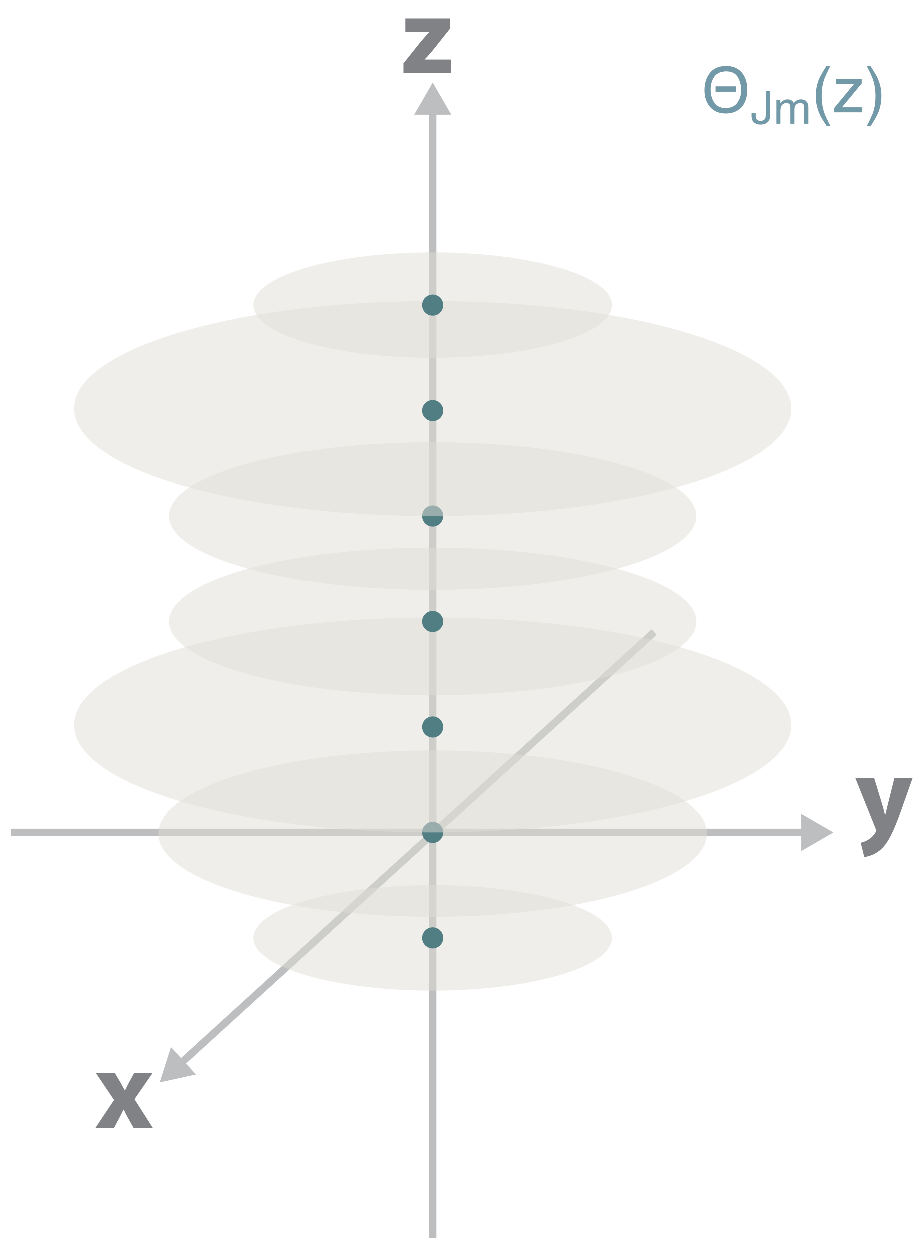
$$Y_{lm}(z, \phi) = \Theta_{lm}(z)\Phi_m(\phi)$$

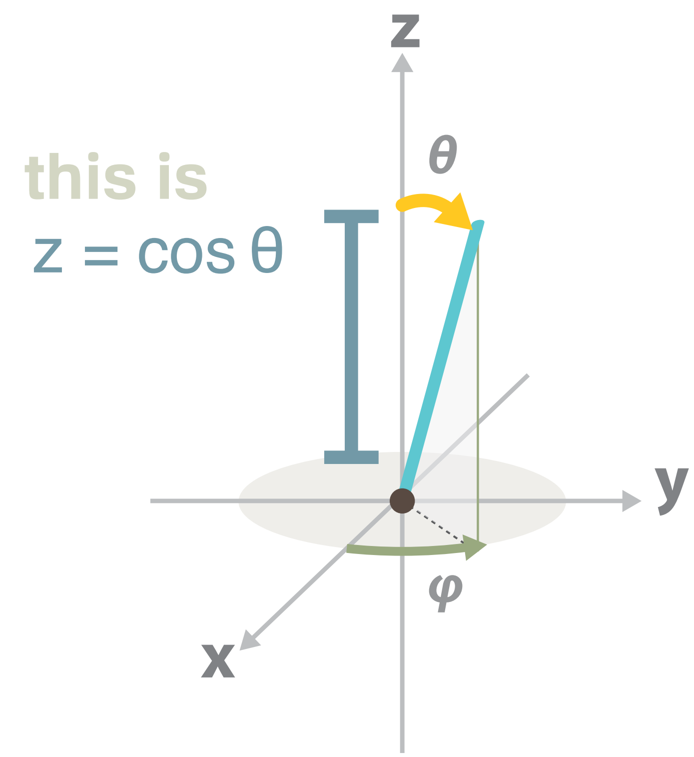
$$\Theta(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$$

$0 < \theta < \pi$

$1 > z > -1$

$$\Phi(\phi) = e^{im\phi}$$





1. function of z only
2. function of θ only
3. no dependence on ϕ
4. azimuthally symmetric
5. horizontal cross-section always circular

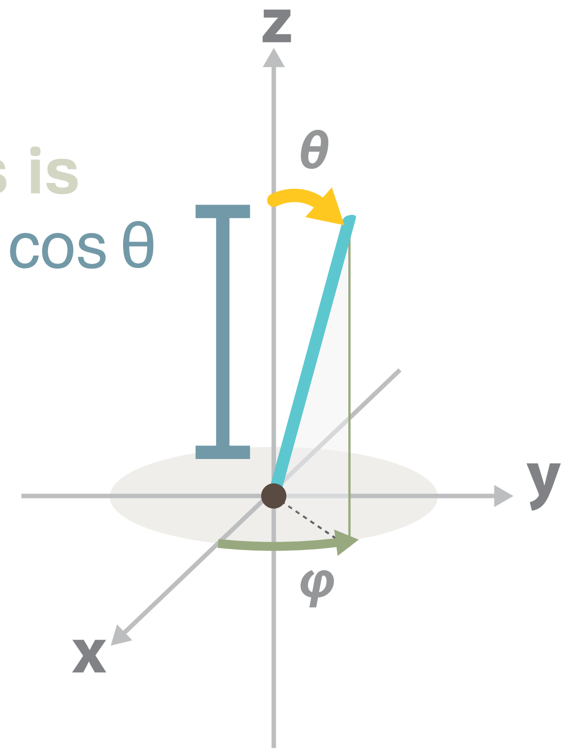
It is a function on a sphere

$$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$$

this is

$z = \cos\theta$



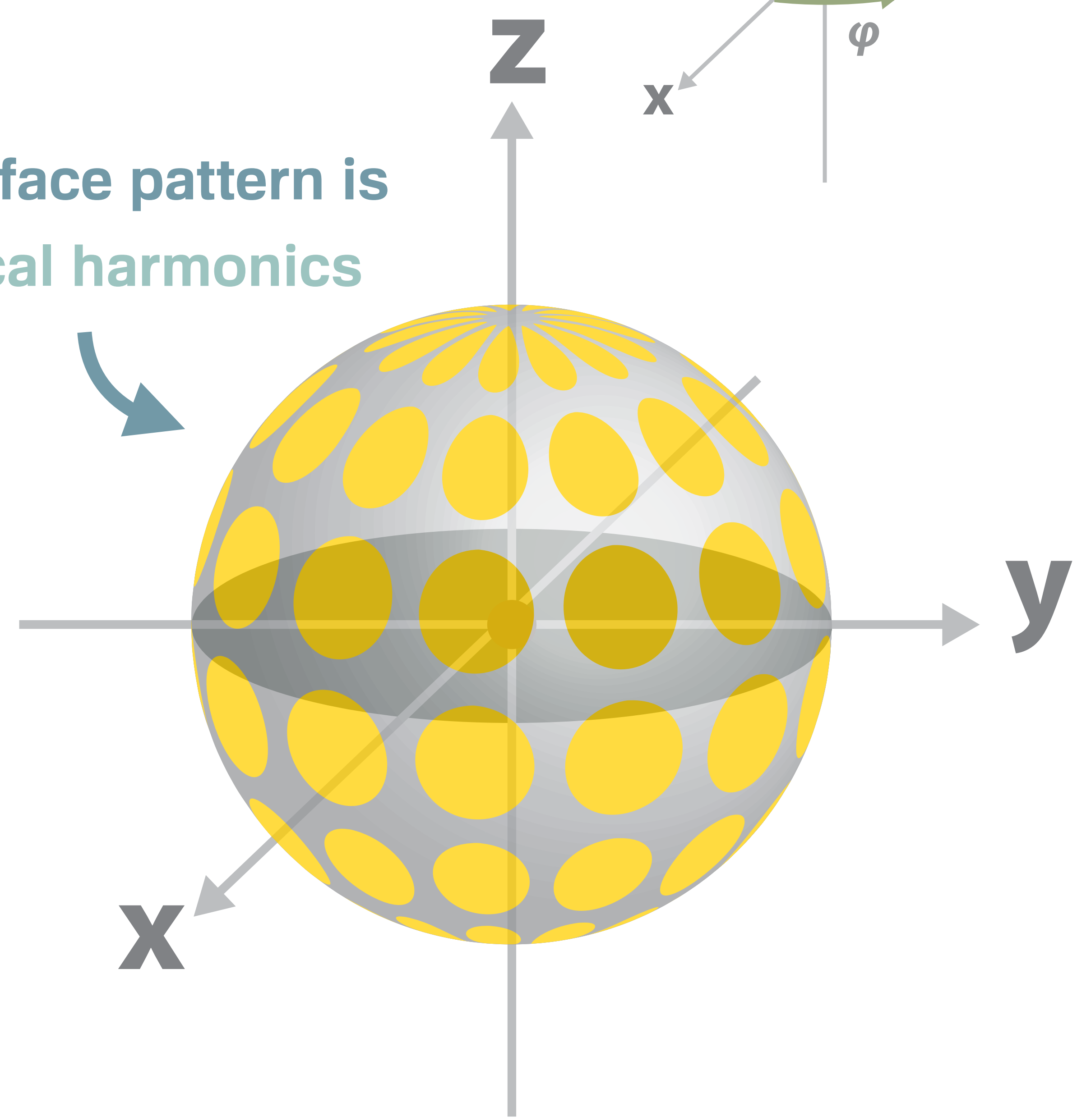
$0 < \theta < \pi$

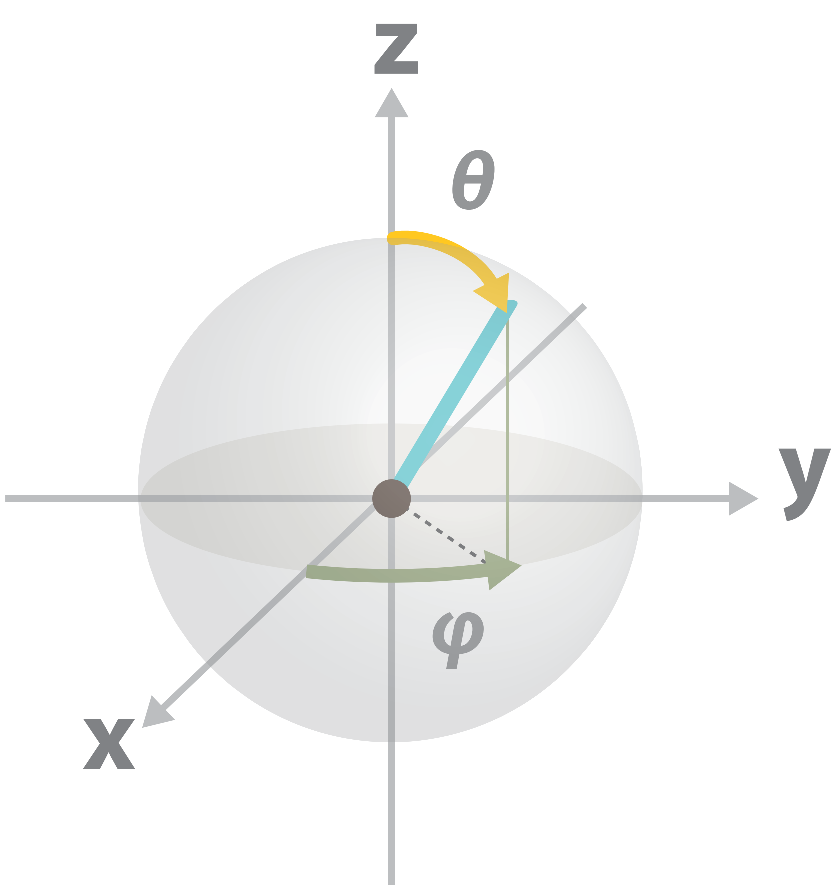
$1 > z > -1$

$$\Phi(\phi) = e^{im\phi}$$

this surface pattern is

Spherical harmonics





unit sphere

$x^2 + y^2 + z^2 = 1$

$x = \sin\theta\cos\phi$

$y = \sin\theta\sin\phi$

$z = \cos\phi$

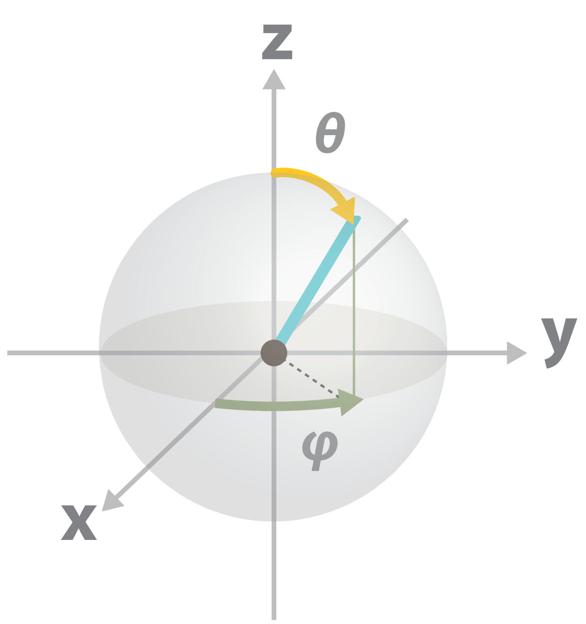
Let us take a look one by one

$$Y_{Jm}(z,\phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

$$0 < \theta < \pi$$
$$-1 < z < 1$$

$$\Phi_m(\phi) = e^{im\phi}$$



J = 0, m=0

$\Theta_{00}(z) = 1 \quad \Phi_0(\phi) = 1 \quad \Rightarrow \quad Y_{00} = 1$

normalization factor $\frac{1}{2\sqrt{\pi}}$ why?

Let us take a look one by one

$$Y_{Jm}(z,\phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

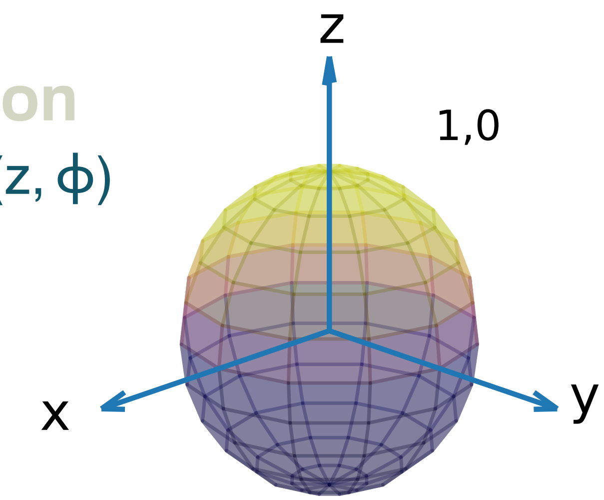
$$\Phi(\phi) = e^{im\phi}$$

$0 < \theta < \pi$

$-1 < z < 1$

wavefunction

$Y_{Jm}(z,\phi)$



J = 1, m=0

$$\Theta_{10}(z) = \frac{1}{2}\frac{d}{dz}(z^2-1) \qquad \Phi_0(\phi) = 1$$

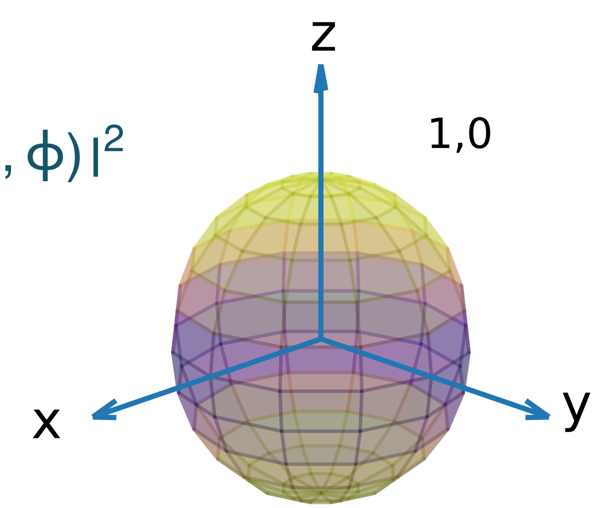
$$= \frac{1}{2}\cdot 2z$$

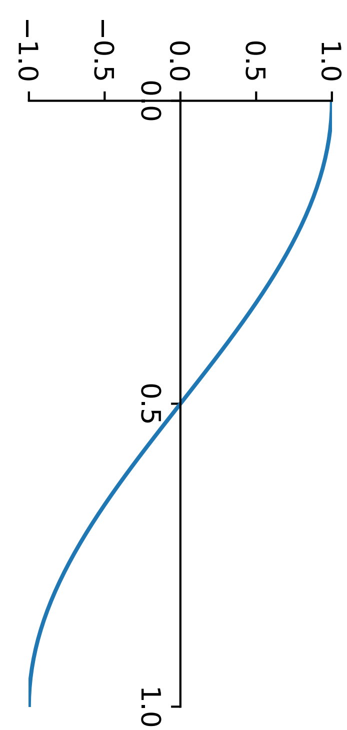
$$= z$$

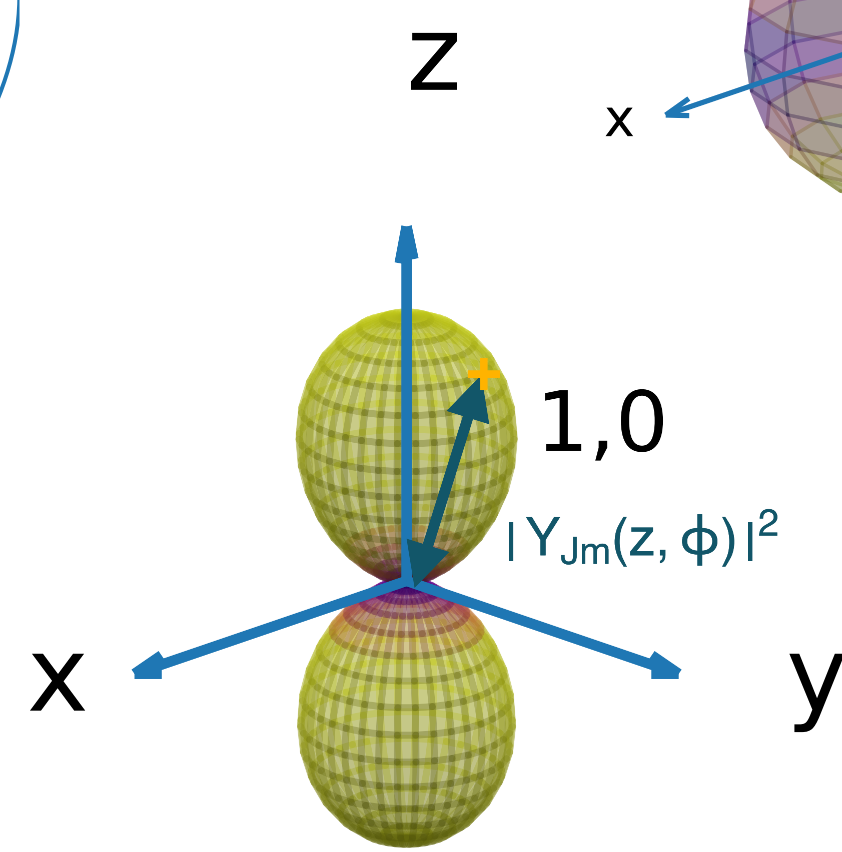
$$= \cos\theta$$

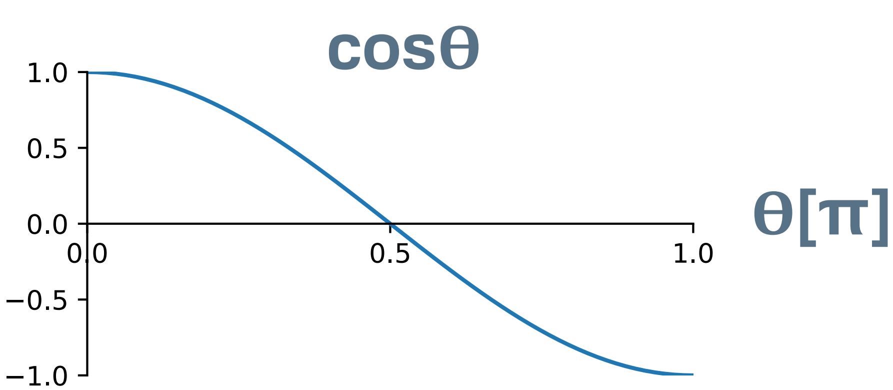
probability distribution

$|Y_{Jm}(z,\phi)|^2$









Let us take a look one by one

$$Y_{Jm}(z,\phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

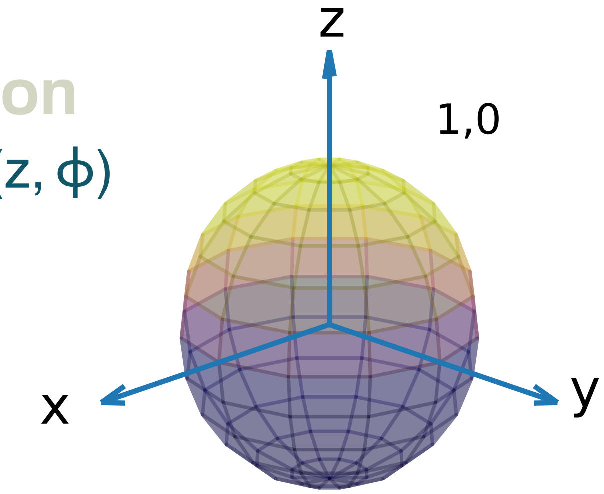
$$\Phi(\phi) = e^{im\phi}$$

$0 < \theta < \pi$

$-1 < z < 1$

wavefunction

$Y_{Jm}(z,\phi)$



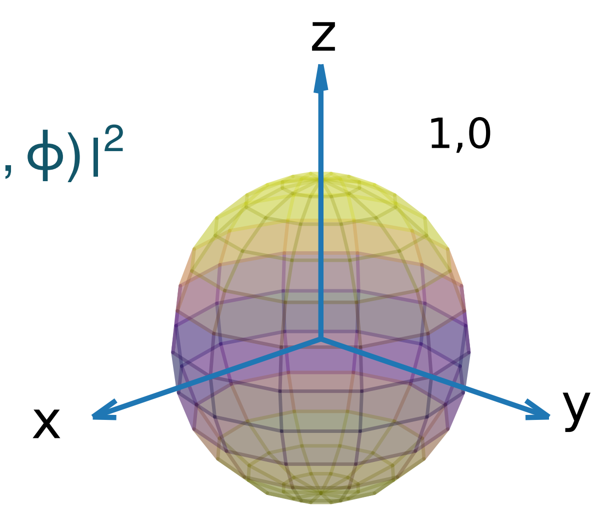
J = 1, m=0

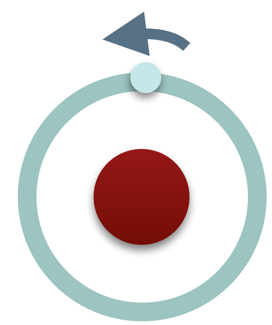
$$\Theta_{10}(z) = \frac{1}{2}\frac{d}{dz}(z^2-1) \qquad \Phi_0(\phi) = 1$$

$$= \cos\theta$$

probability distribution

$|Y_{Jm}(z,\phi)|^2$

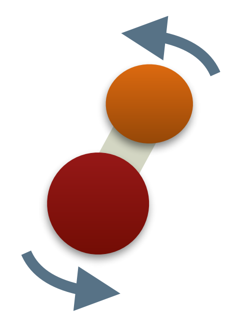


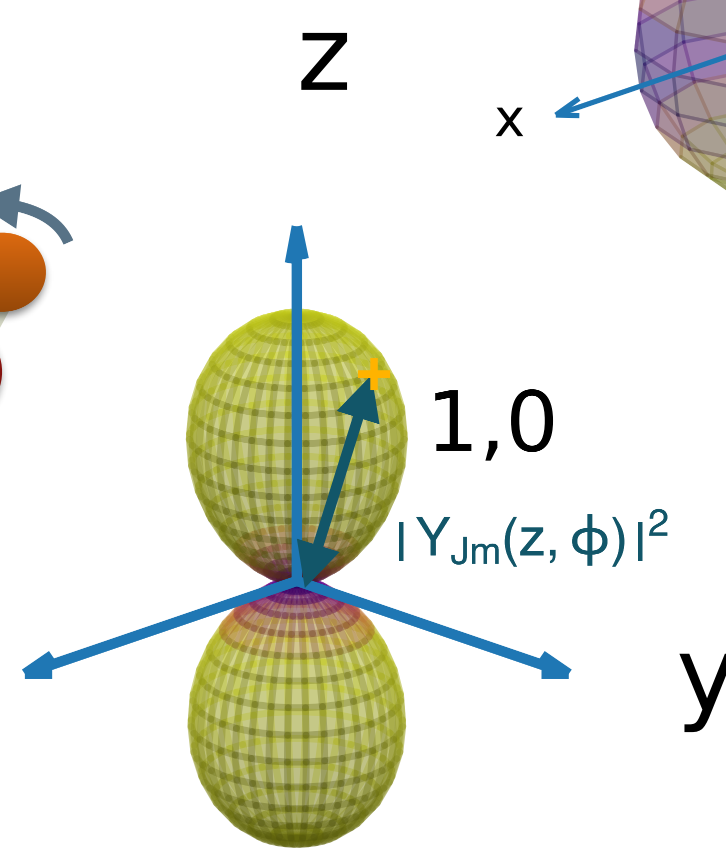


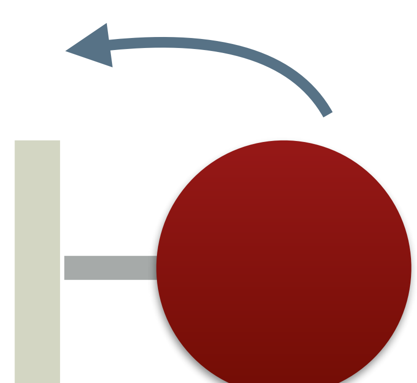
but the distribution of **what**?

$$H\Psi = -\frac{\hbar^2}{2\mu}\nabla^2\Psi$$

of **this**







Let us take a look one by one

$$Y_{Jm}(z,\phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

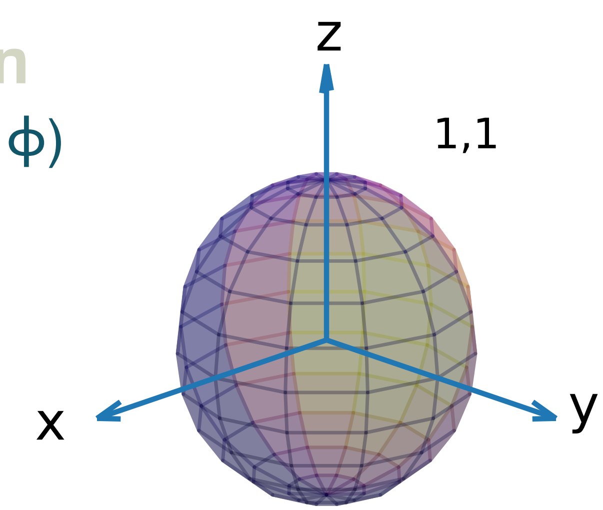
$$\Phi(\phi) = e^{im\phi}$$

$0 < \theta < \pi$

$-1 < z < 1$

wavefunction

$Y_{Jm}(z,\phi)$



J = 1, m=1

$$\Theta_{11}(z) = \frac{1}{2}(1-z^2)^{\frac{1}{2}}\frac{d^2}{dz^2}(z^2-1)$$

$$= \frac{1}{2}(1-z^2)^{\frac{1}{2}} \cdot 2$$

$$= (1-z^2)^{\frac{1}{2}}$$

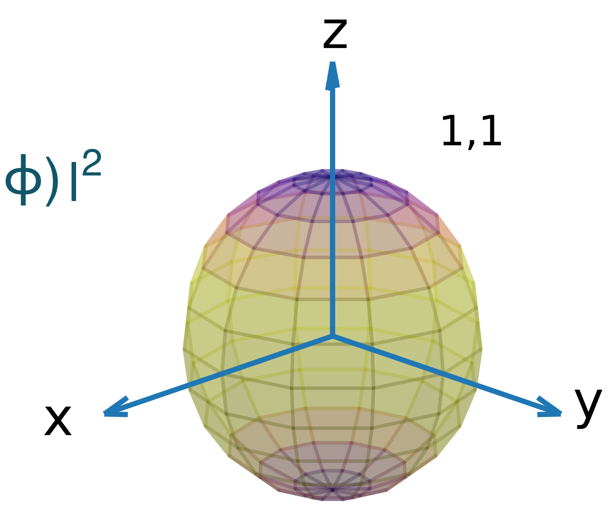
$$= \sin\theta$$

$\Phi_1(\phi) = e^{i\phi}$

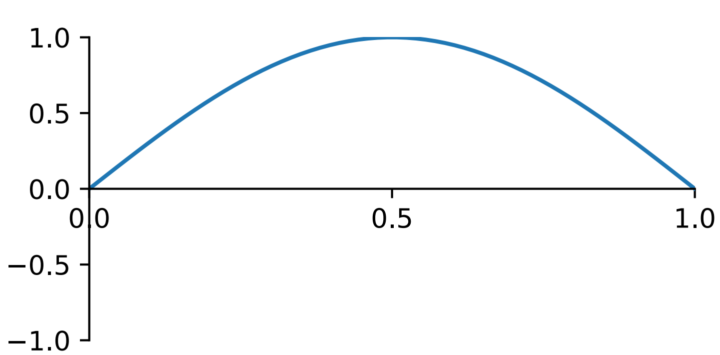
$0 < \phi < 2\pi$

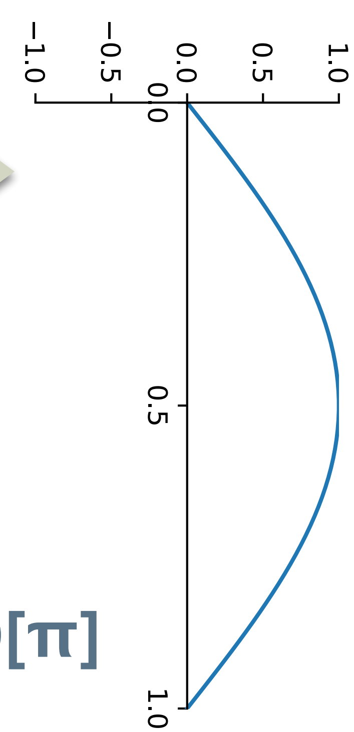
probability distribution

$|Y_{Jm}(z,\phi)|^2$

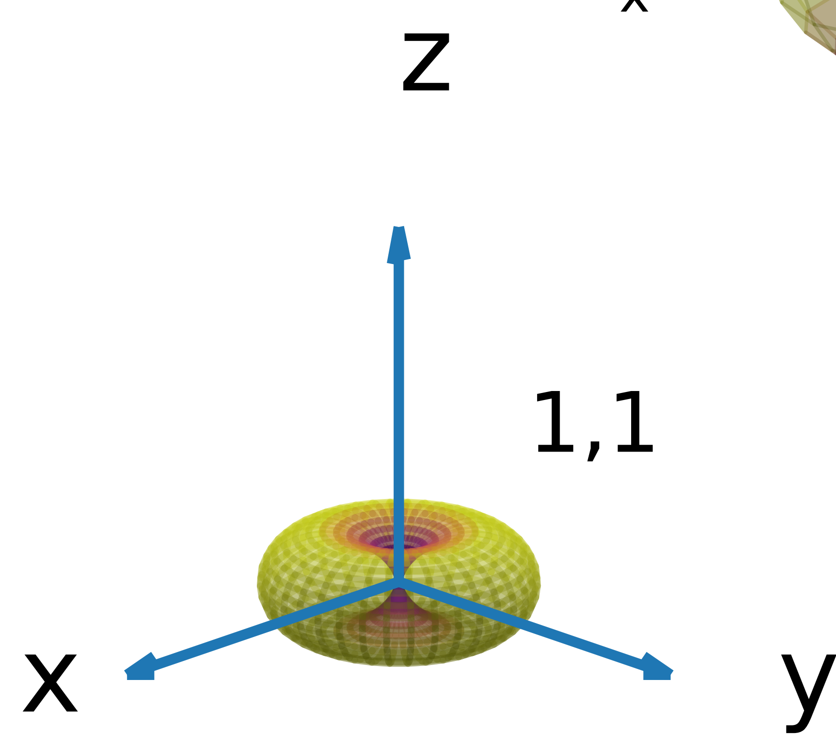


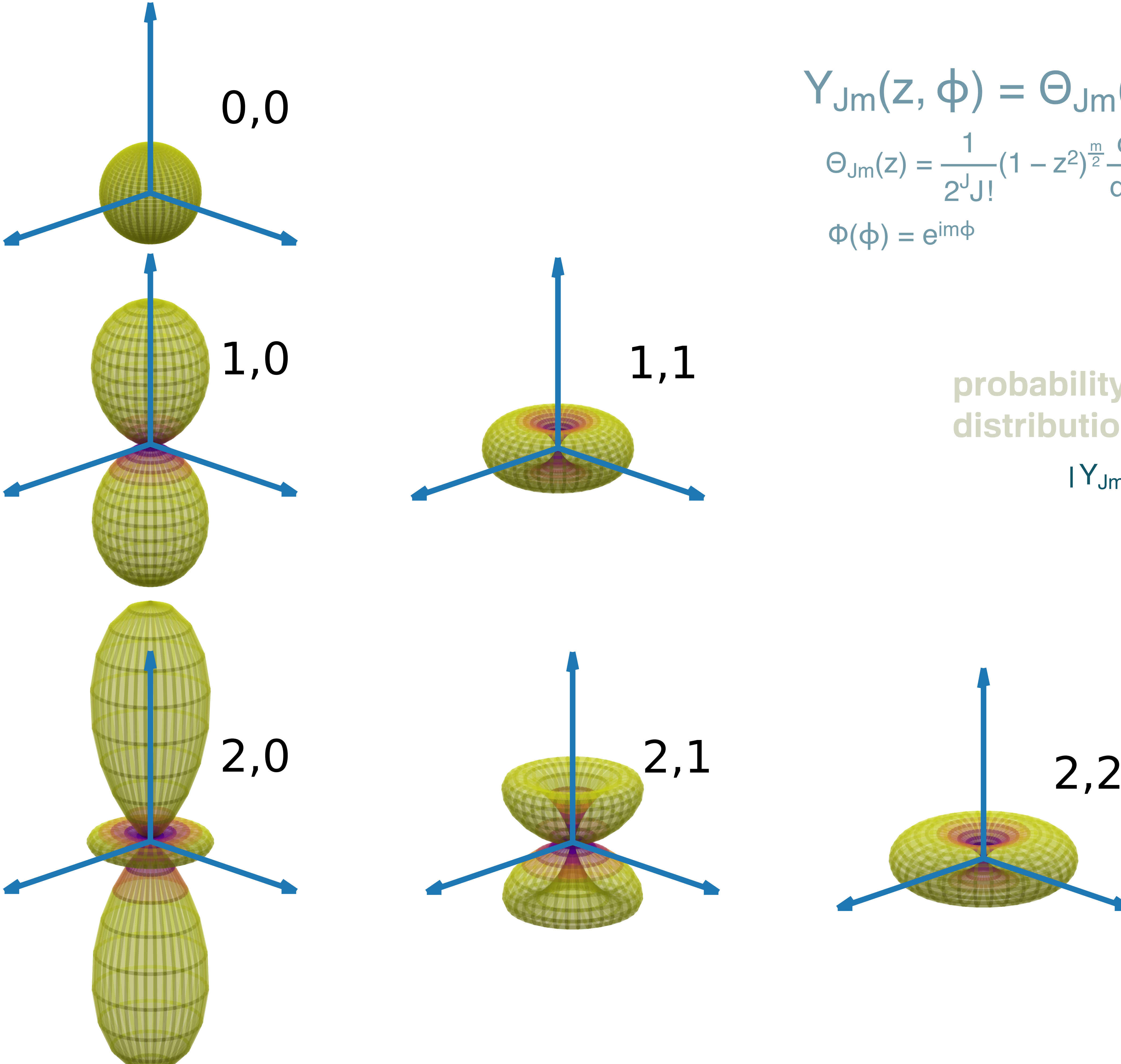
sinθ





θ[π]





$$Y_{Jm}(z,\phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

$$\Phi(\phi) = e^{im\phi}$$

probability distribution

$$|Y_{Jm}(z,\phi)|^2$$

let us have a close look

$z = \cos\theta$

$z^2 - 1 = -\sin^2\theta$

$\sin^m\theta$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}} \frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$$

order of **z** 2 * m/2 - (J + m) + 2 * J **= J**

J-m

odd function + continuous

node at 0

m is minimum -J

m = J, J-1, …, 0, …, -J+1, -J

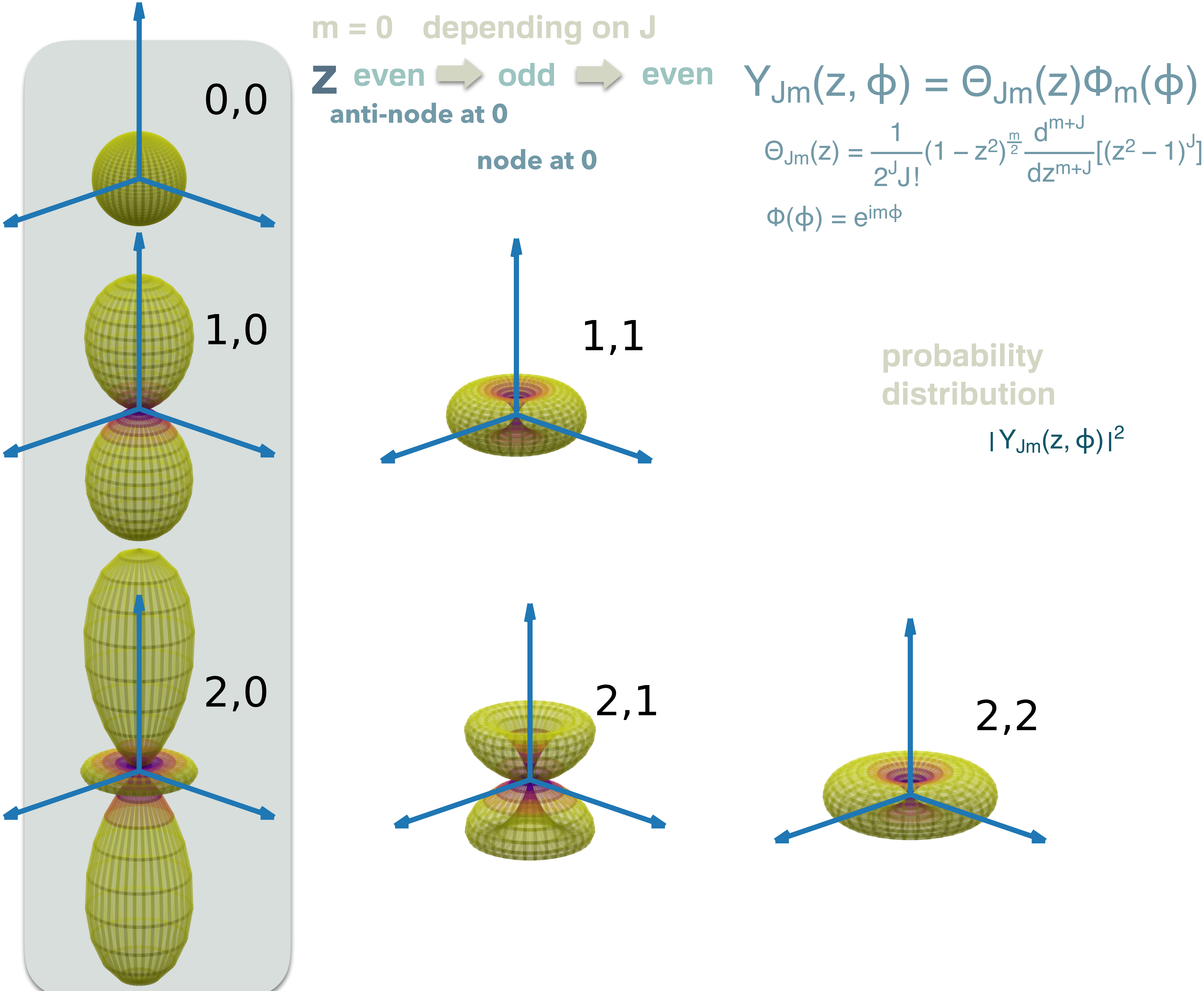
m = 0

depending only on J

node at 0

z even → odd → even →

anti-node at 0 **anti-node at 0**


m = 0 depending on J
z even odd even
anti-node at 0
node at 0
$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$
$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}} \frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$
$\Phi(\phi) = e^{im\phi}$
probability distribution
$|Y_{Jm}(z, \phi)|^2$
0,0
1,0
2,0
1,1
2,1
2,2

let us have a close look

$z = \cos\theta$

$z^2 - 1 = -\sin^2\theta$

$\sin^m\theta$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}} \frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

order of **z**

2 * m/2

- (J + m)

+ 2 * J

= J

J-m

m is minimum -J

m = J, J-1, …, 0, …, -J+1, -J

always

anti-node at z=0

$z = 0$

$\theta = \frac{\pi}{2}$

m = J

J-m = 0

$\Theta_{Jm}(z) = \sin^m\theta$

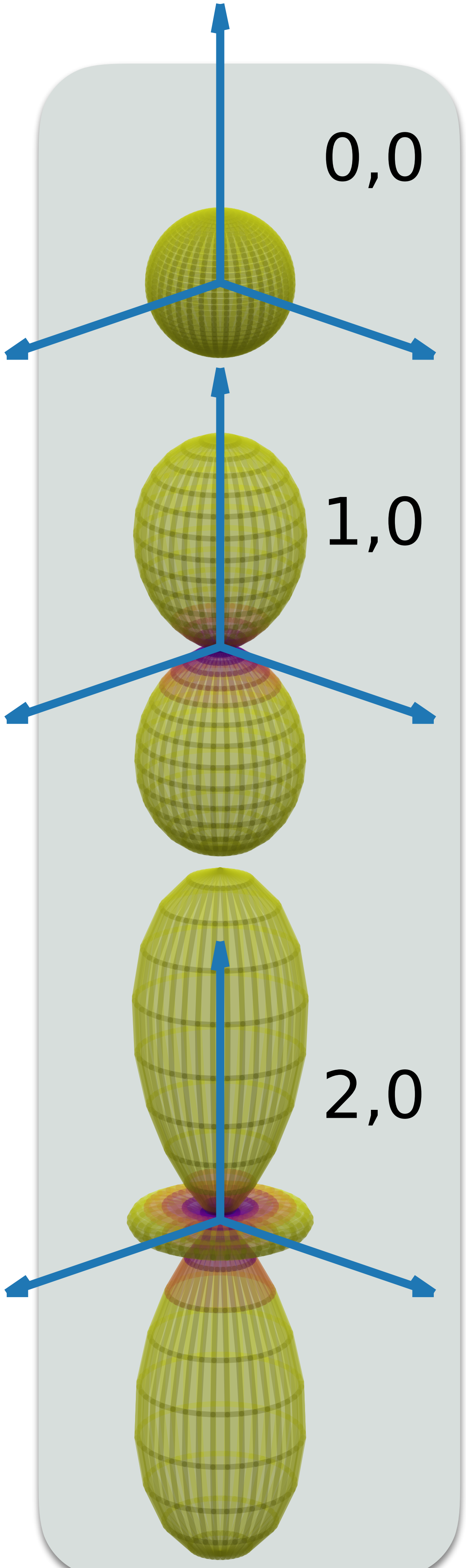
m is minimum -J

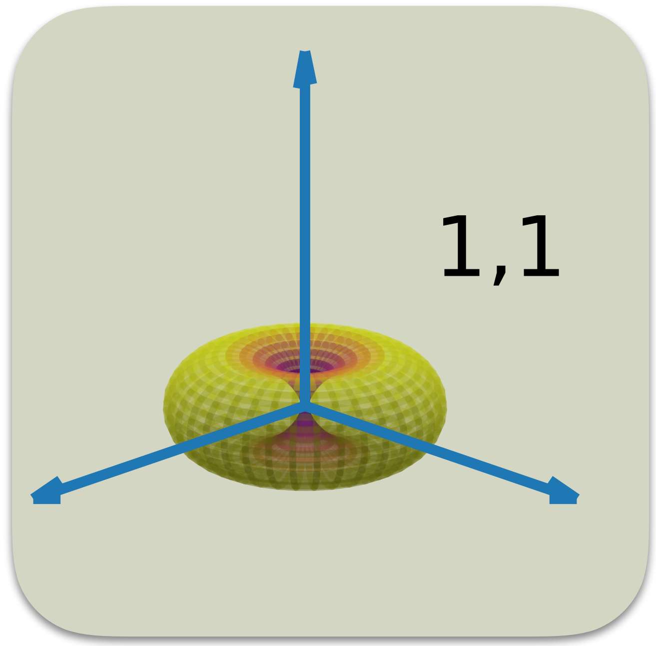
m = J, J-1, ..., 0, ..., -J+1, -J

$$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}} \frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$$

$$\Phi(\phi) = e^{im\phi}$$





always

anti-node at z=0

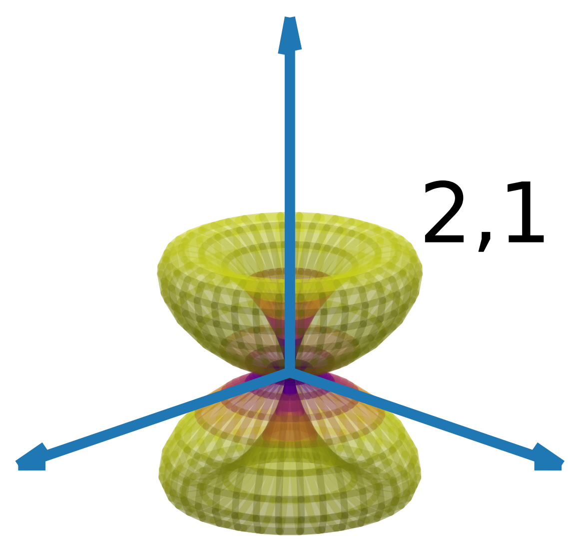
$$z = 0$$

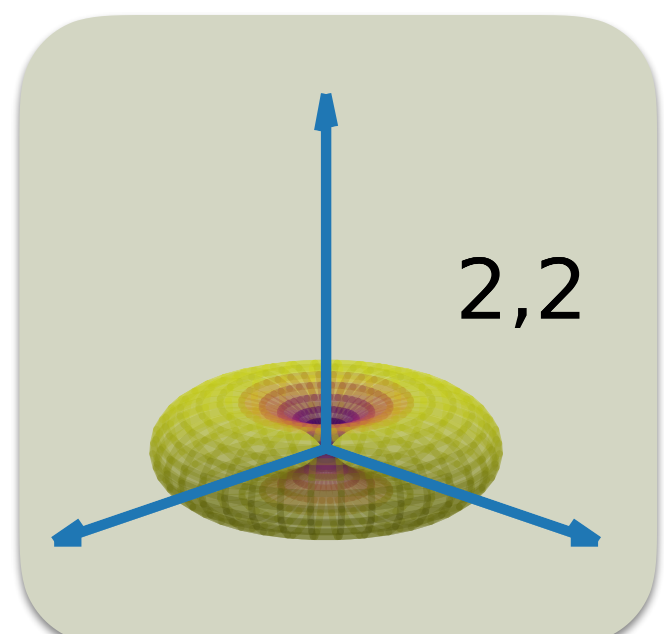
$$\theta = \frac{\pi}{2}$$

m = J

J-m = 0

$$\Theta_{Jm}(z) = \sin^m \theta$$





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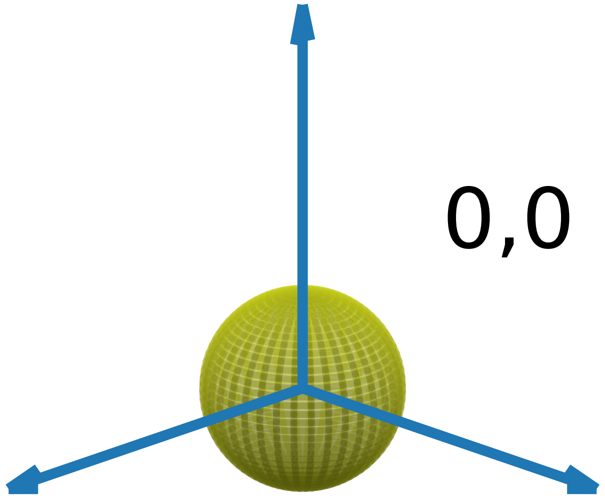
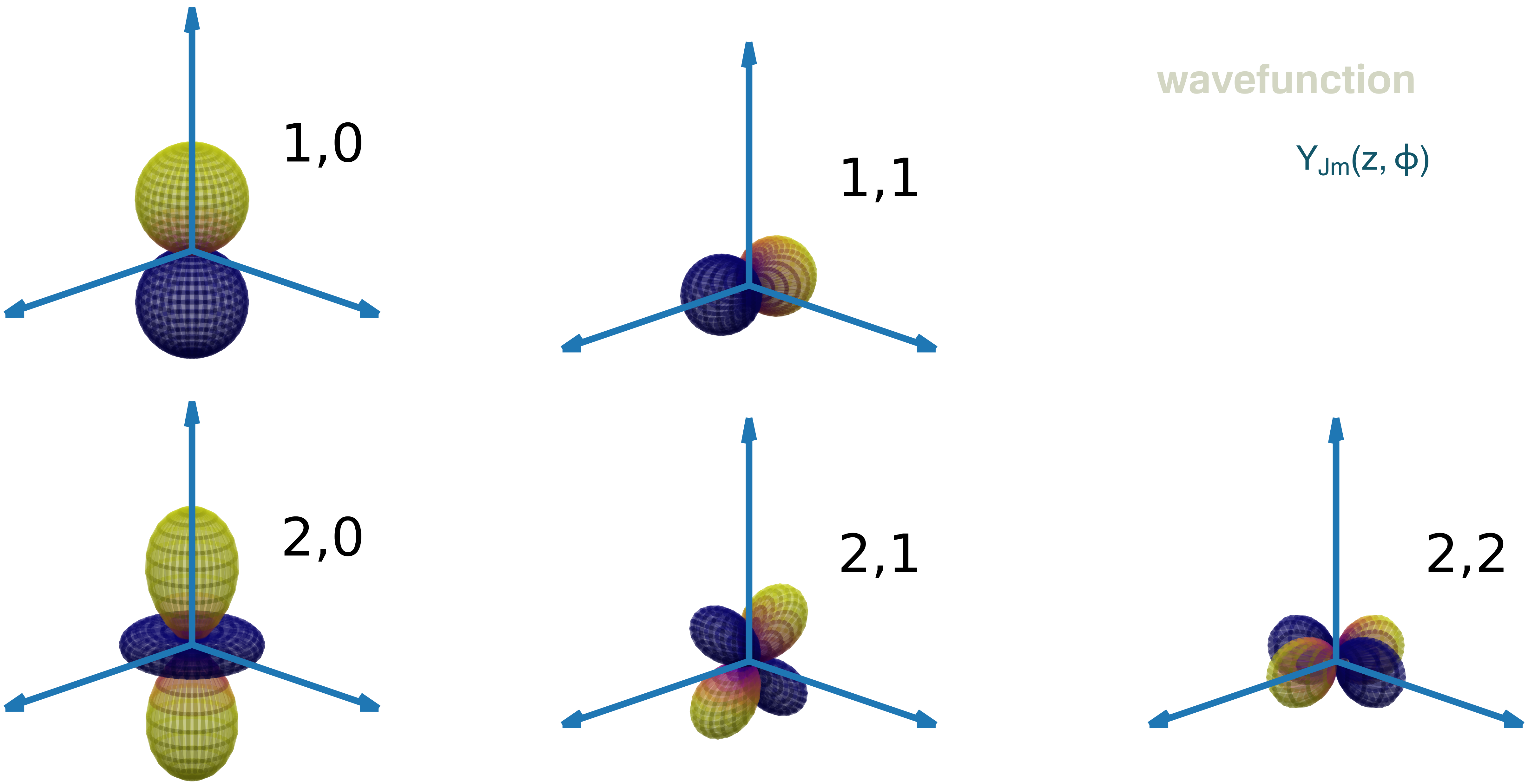
$$\Phi(\phi) = e^{im\phi}$$



wavefunction

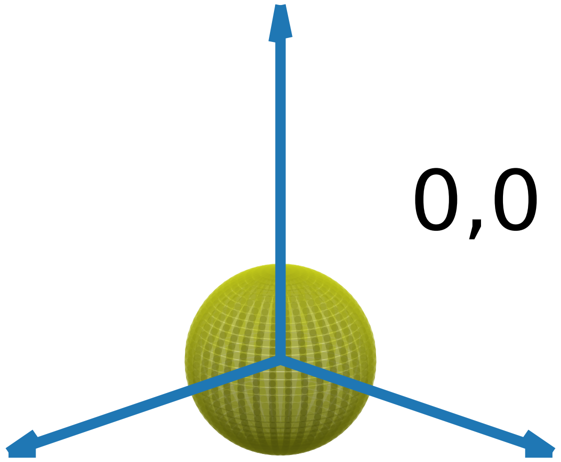
$Y_{Jm}(z, \phi)$

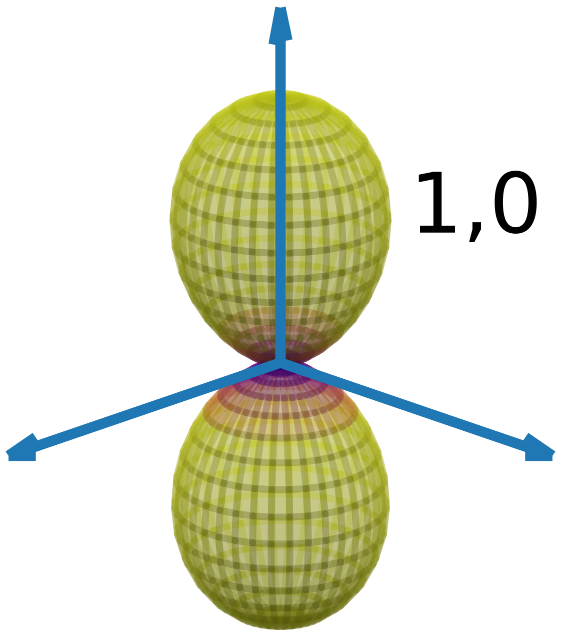


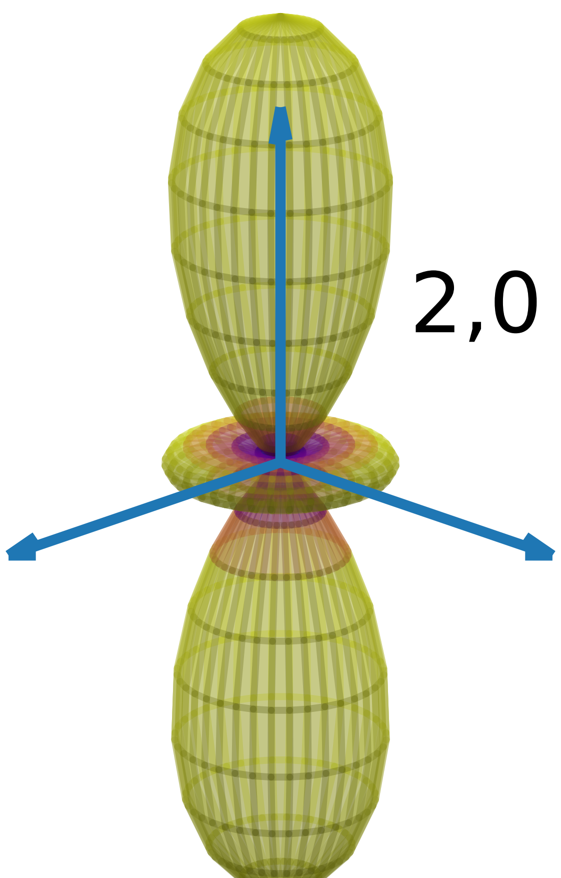
$$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

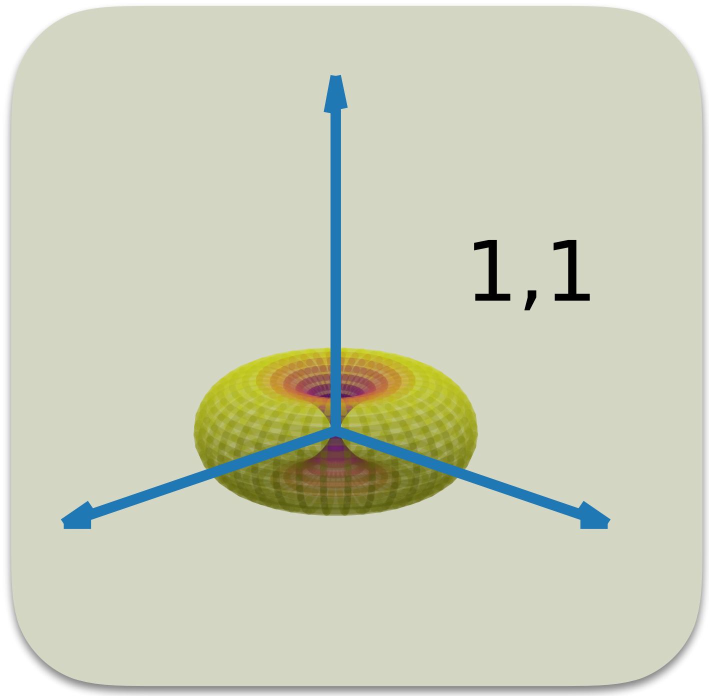
$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$$

$$\Phi(\phi) = e^{im\phi}$$



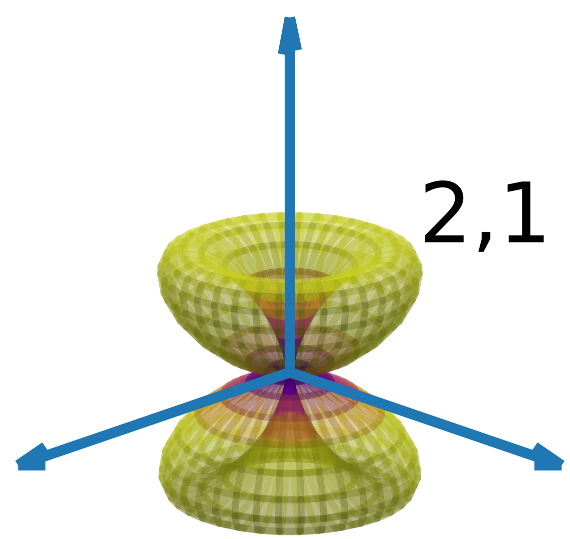


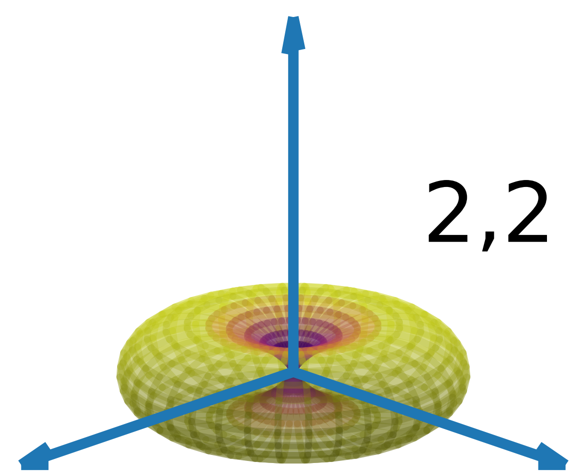




probability distribution

$$|Y_{Jm}(z, \phi)|^2$$





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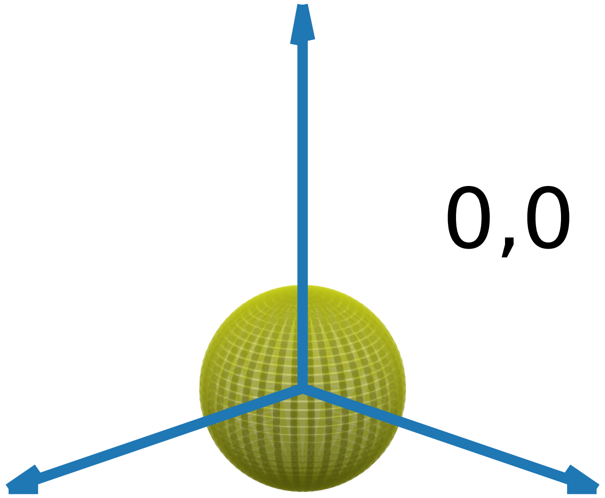
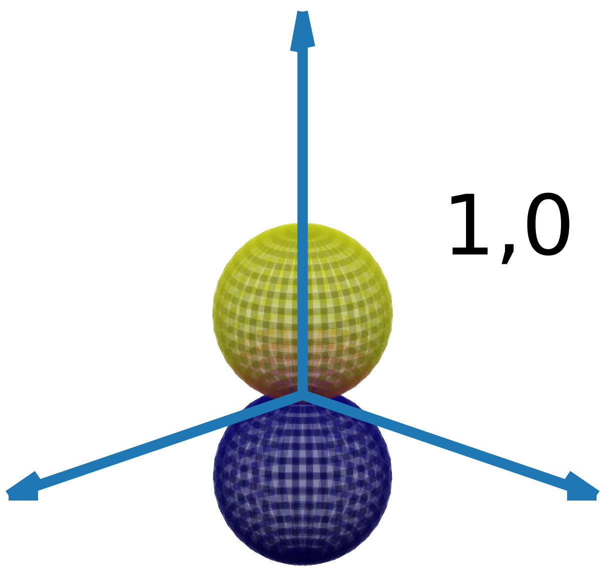
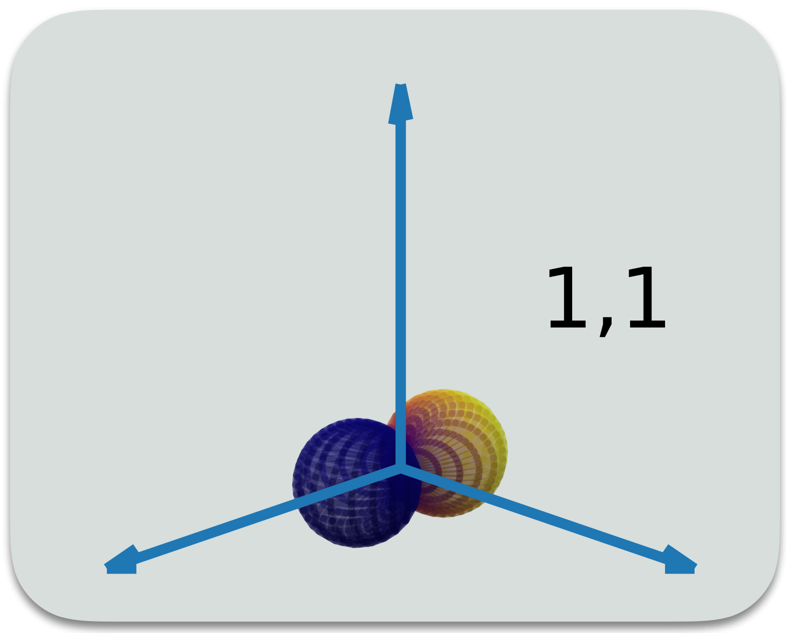
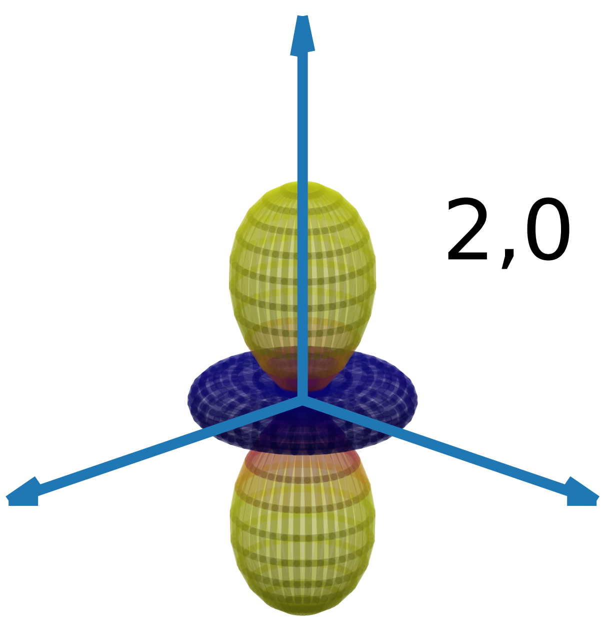


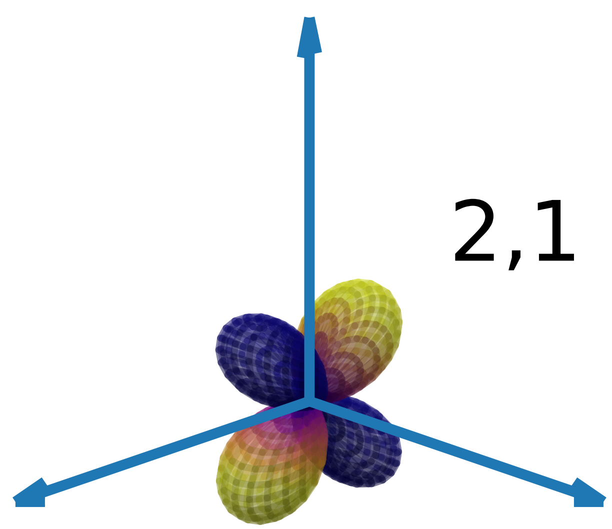


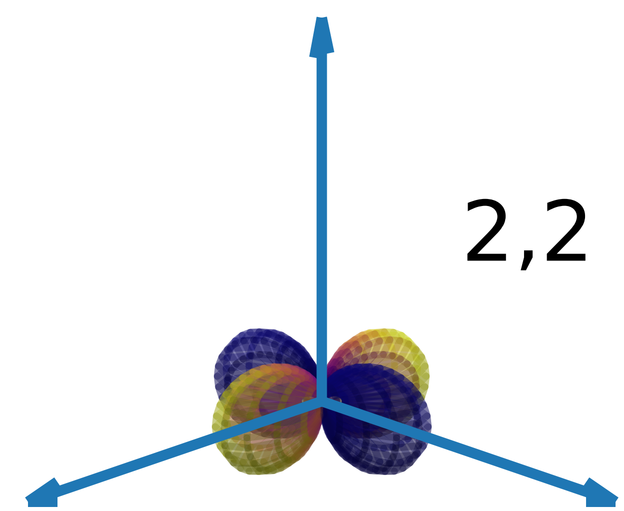


wavefunction

$Y_{Jm}(z, \phi)$







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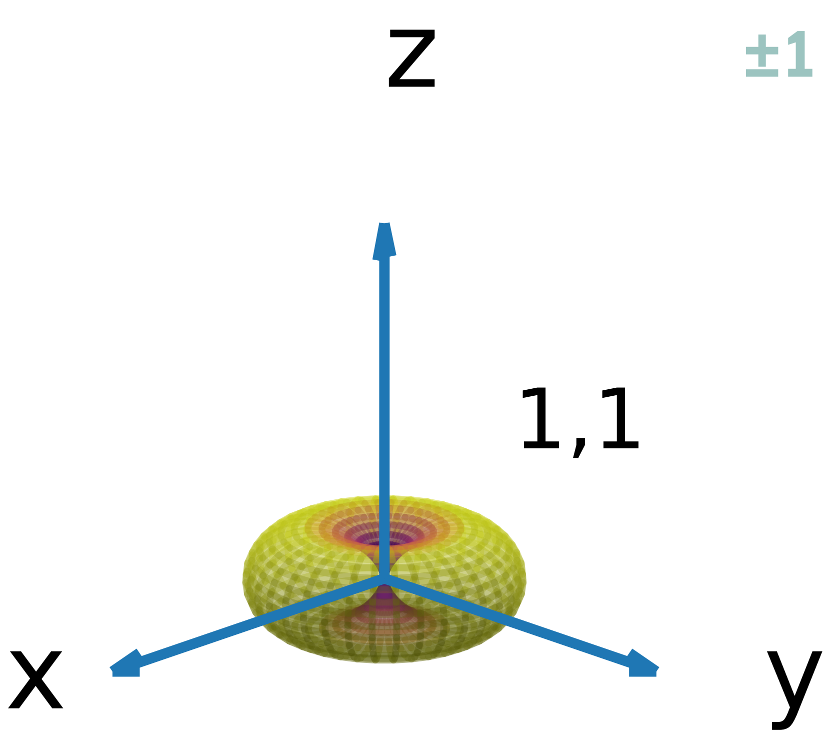
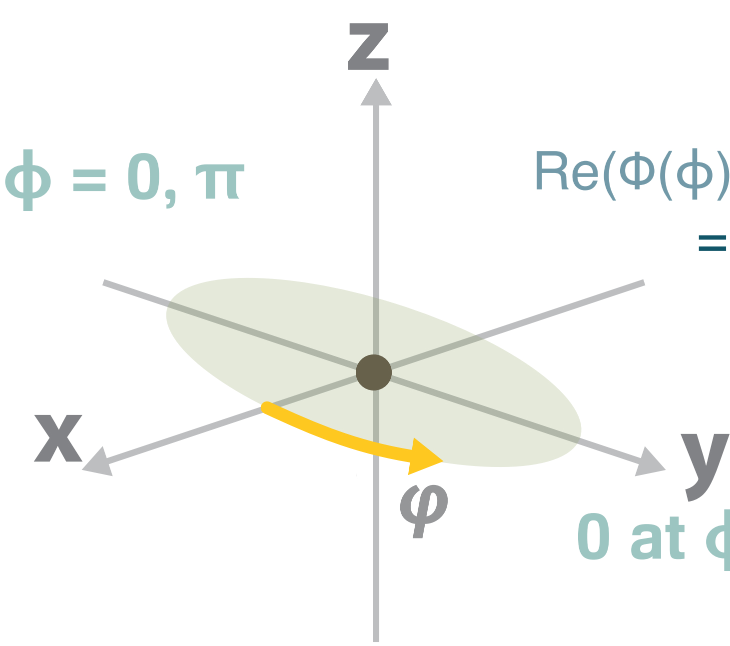


± 1 at $\phi = 0, \pi$

$Re(\Phi(\phi))$

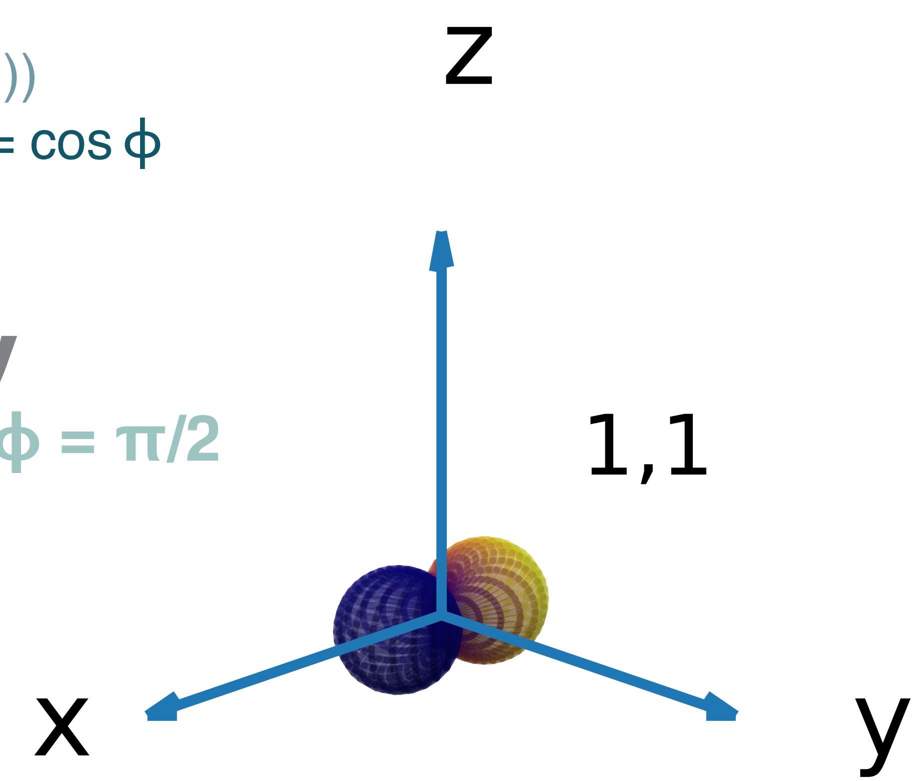
$= \cos\phi$



0 at $\phi = \pi/2$

wavefunction

$Y_{Jm}(z, \phi)$



when we discuss bonding always come back to wavefunction

let us have a close look

$z = \cos\theta$

$z^2 - 1 = -\sin^2\theta$

$\sin^m\theta$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1 - z^2)^{\frac{m}{2}} \frac{d^{m+J}}{dz^{m+J}}[(z^2 - 1)^J]$$

order of z 2 * m/2 - (J + m) + 2 * J = J

J-m

function of z

of the order J

m is minimum -J

m = J, J-1, …, 0, …, -J+1, -J

$$\Phi_m(\phi) = e^{im\phi}$$

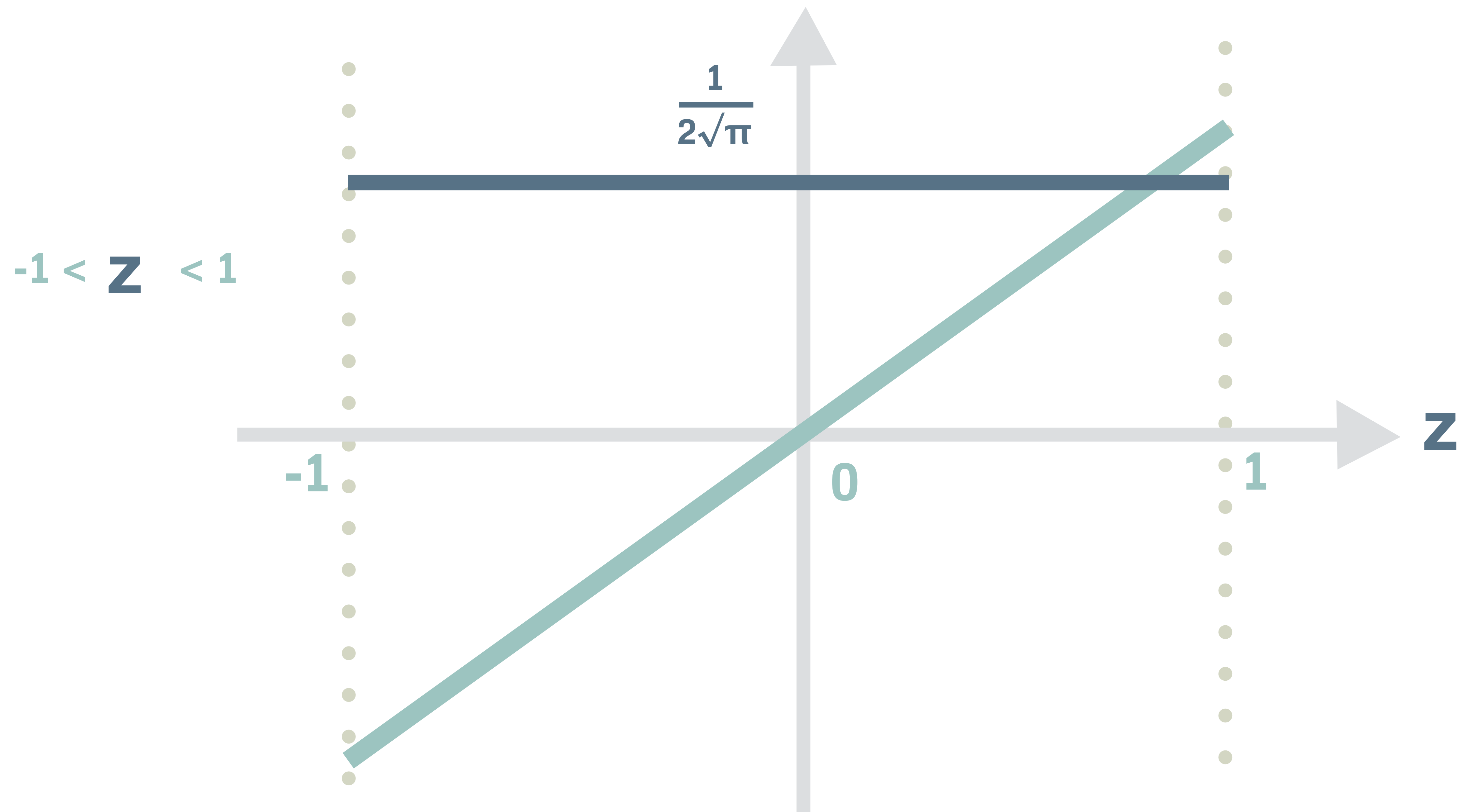
$$\mathrm{Re}(\Phi_m(\phi)) = \cos m\phi$$

$$Y_{J,m}(z,\phi) = \frac{1}{2^J\, J!}(1 - z^2)^{\frac{m}{2}} \frac{d^{J+m}}{dz^{J+m}}\left[(z^2 - 1)^J\right] \qquad z = \cos\theta$$

m   - (J + m)   2J   = J

function of **Z**

of the order **J**



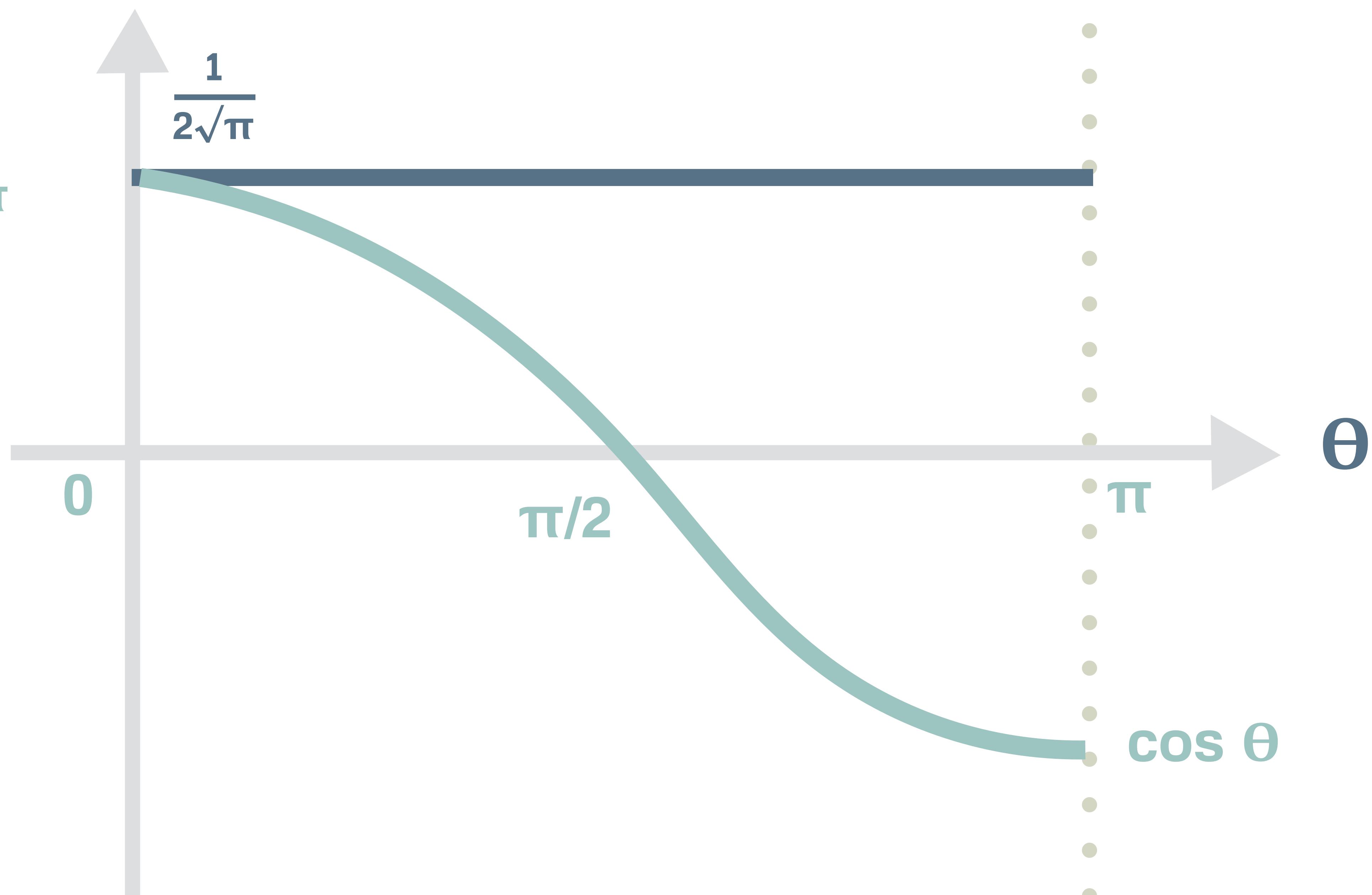
spherical harmonics are orthogonal

$$Y_{J,m}(z,\phi) = \frac{1}{2^J\, J!}(1-z^2)^{\frac{m}{2}}\,\frac{d^{J+m}}{dz^{J+m}}\left[(z^2-1)^J\right] \qquad z = \cos\theta$$

function of z m - (J + m) 2J = J

of the order J

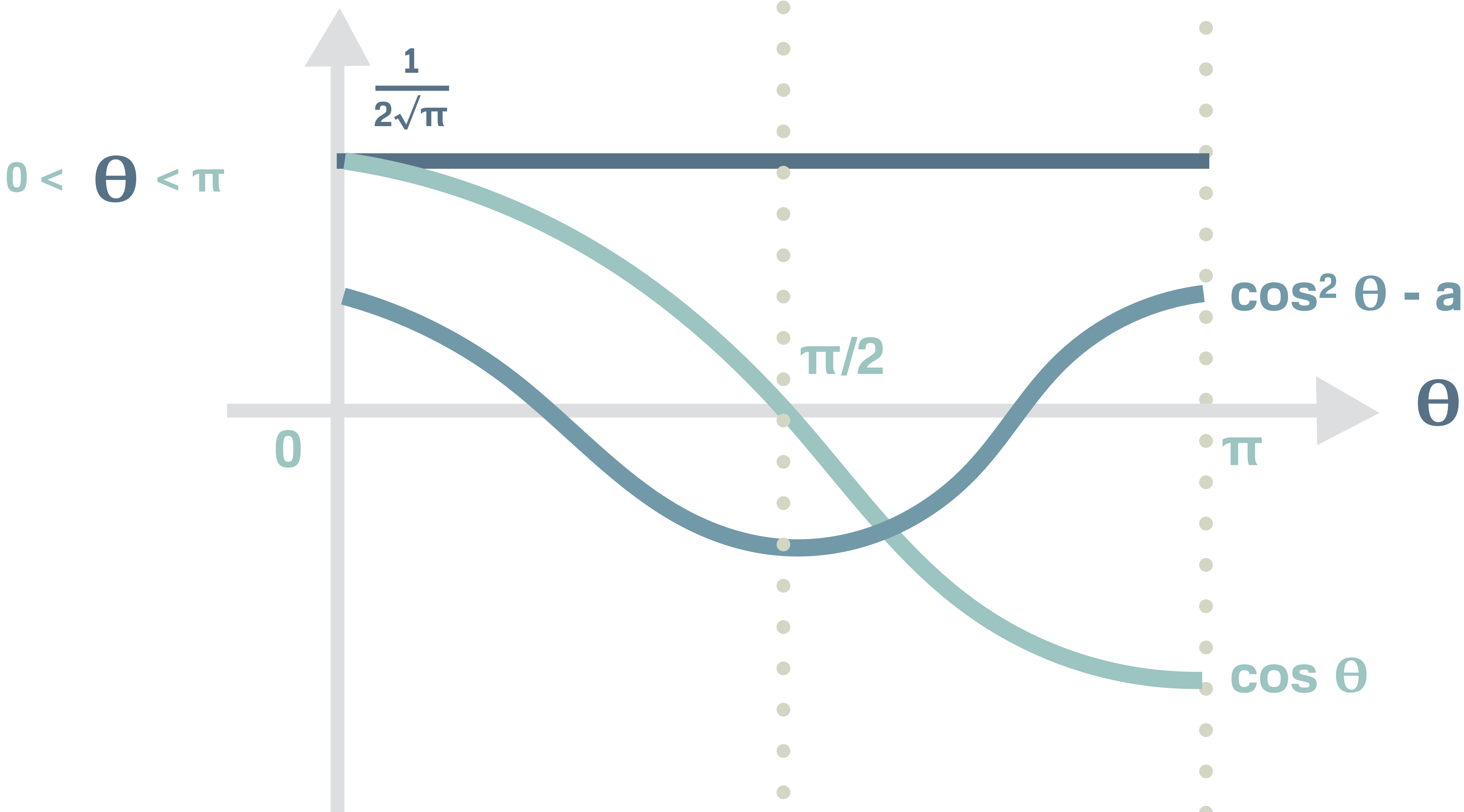
0 < θ < π



$$Y_{J,m}(z,\phi) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}} \frac{d^{J+m}}{dz^{J+m}}\left[(z^2-1)^J\right] \qquad z = \cos\theta$$

function of **z** m - (J + m) 2J = J

of the order **J**



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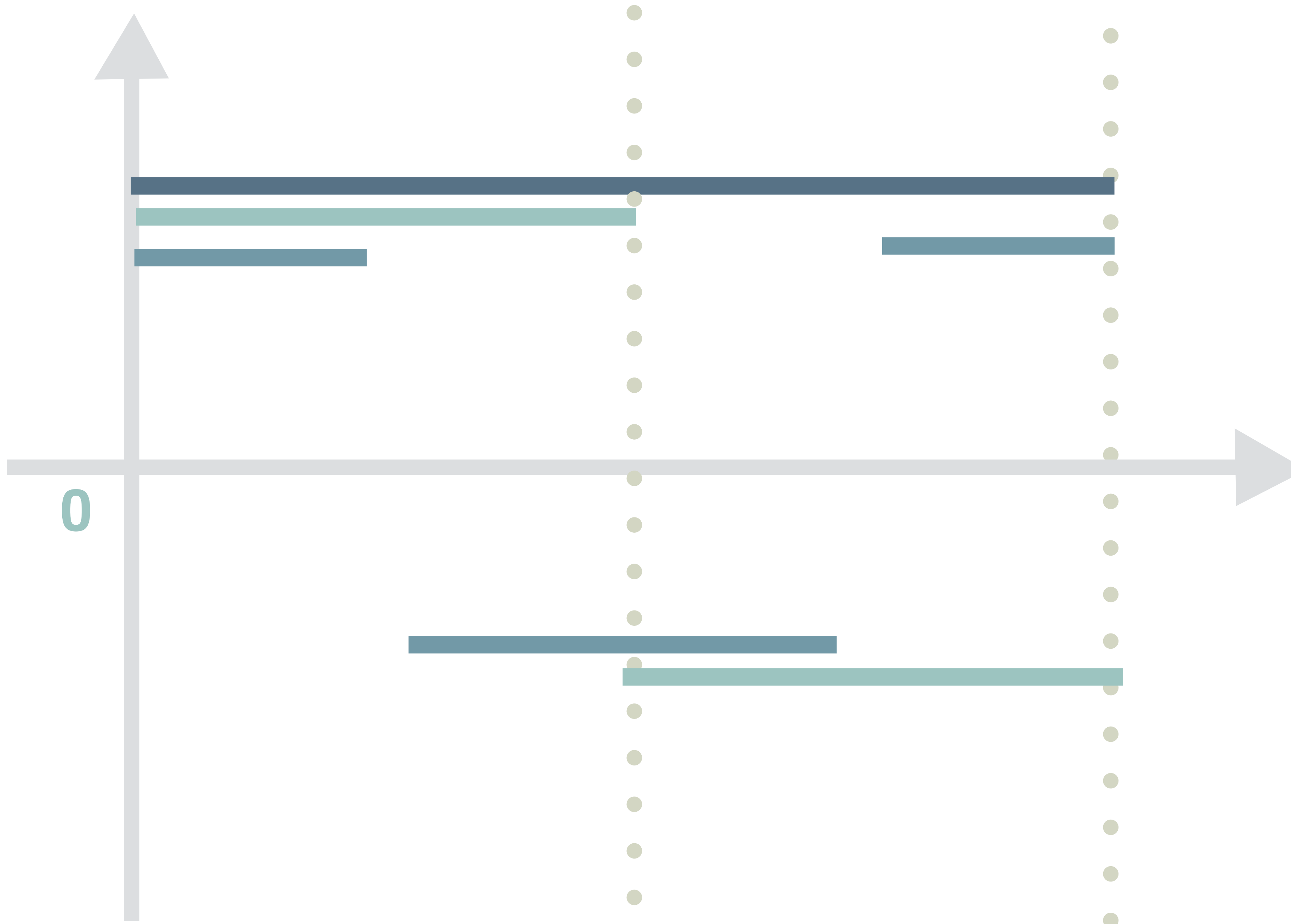
m **- (J + m)** **2J** **= J**

function of Z

of the order J



Why it is worthwhile taking time for spherical harmonics?

✓ 1 it is a wave function — but, of what ?

2 rotational energy — $E = Bh\,J(J+1)$

3 angular momentum — J, K, Ka, Kc

4 symmetry — $(-1)^J$

5 selection rule — $\Delta J = 0, \pm 1, 0 \nleftrightarrow 0$

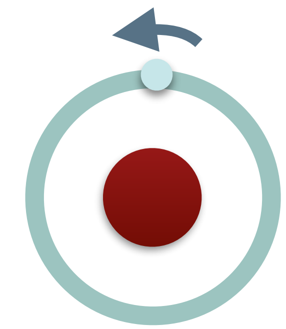
6 (vanishing integral) — expansion

Rotational energy

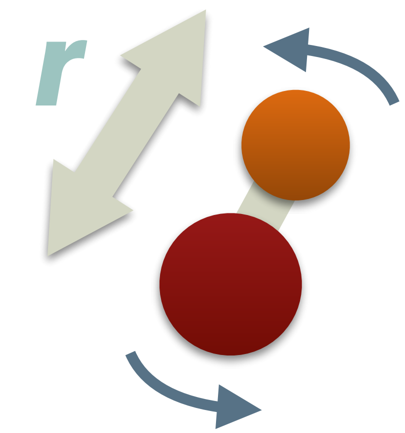
$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2$$

1. Rigid rotor. **r** is fixed.
2. central field is not explicit.



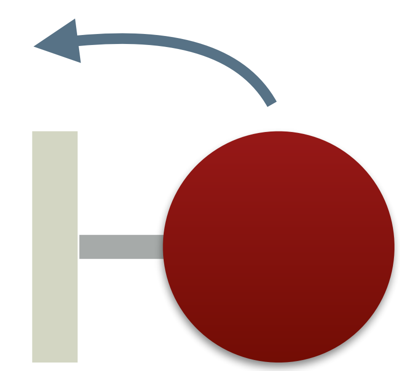
Rigid rotor



$$\left[-\frac{\hbar}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2\right] - \frac{Ze^2}{r}\right]\Psi = E\Psi$$

think only about rotation

both of them are



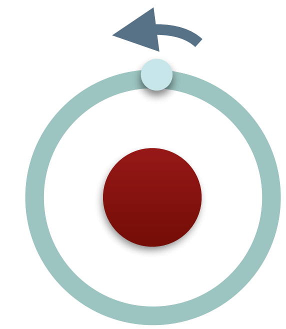
$$-\frac{\hbar}{2\mu}\left[\frac{1}{r^2}\Lambda^2\right]\Psi = E\Psi$$

$$\frac{\hbar}{2\mu}\left[\frac{1}{r^2}\cdot J(J+1)\right]\Psi = E\Psi$$

$$\frac{\hbar}{2\mu r^2}\cdot J(J+1)\Psi = E\Psi$$

$$E = \frac{\hbar}{2\mu r^2}\cdot J(J+1)$$

Rotational energy



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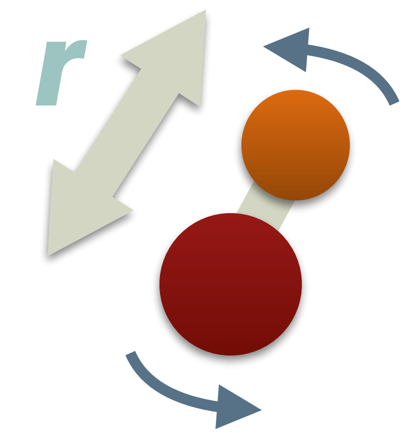
Rigid rotor



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think only about rotation

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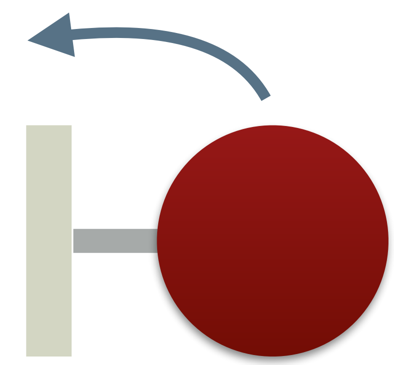

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$$\frac{\hbar}{2\mu r^2}\cdot J(J+1)\Psi = E\Psi$$

$$E = \frac{\hbar}{2\mu r^2}\cdot J(J+1)$$

$$I = \mu r^2$$ moment of inertia

$$B = \frac{1}{2I}$$ rotational constant

$$E = B\hbar J(J+1)$$ rotation energy

classically

$$J = mrv$$

$$I = mr^2$$

$$E = \frac{1}{2}mv^2$$

$$= \frac{1}{2}\frac{(mrv)^2}{mr^2}$$

$$= \frac{J^2}{2I}$$

J : total angular momentum

Angular momentum

we need again

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

~mrv

$$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

angular momentum
in polar coordinate

$$\hat{\mathbf{l}} = \mathbf{x} \times \mathbf{p}$$

$$= \begin{bmatrix} x \\ y \\ z \end{bmatrix} \times \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial x} \\ \frac{\hbar}{i}\frac{\partial}{\partial y} \\ \frac{\hbar}{i}\frac{\partial}{\partial z} \end{bmatrix}$$

$$f_x = g_r \sin\theta\cos\phi + \frac{g_\theta}{r}\cos\theta\cos\phi - \frac{g_\phi \sin\phi}{r\sin\theta} \quad (4)$$

$$f_y = g_r \sin\theta\sin\phi + \frac{g_\theta}{r}\cos\theta\sin\phi + \frac{g_\phi \cos\phi}{r\sin\theta} \quad (5)$$

Angular momentum

we need again

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \quad \sim mrv$$

$$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

angular momentum in polar coordinate

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$$\mathbf{x}\cdot(5) - \mathbf{y}\cdot(4)$$

$$= r\sin\theta\left[\frac{g_\phi\cos^2\phi}{r\sin\theta} + \frac{g_\phi\sin^2\phi}{r\sin\theta}\right] = g_\phi$$

angular momentum operator

along **z** axis

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

was derivative around **ϕ**

$$\hat{l}_z\Phi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi$$

in whole angular wavefunction only **ϕ** is dependent on **ϕ**

$$= \frac{\hbar}{i}\cdot(im)\Phi \quad = m\hbar\Phi$$

Angular momentum

m is defined by

$$Y_{Jm}(z,\phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

$$\Theta_{Jm}(z) = \frac{1}{2^J J!}(1-z^2)^{\frac{m}{2}}\frac{d^{m+J}}{dz^{m+J}}[(z^2-1)^J]$$

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$$|\Phi(\phi)|^2 = e^{im\phi} \cdot e^{-im\phi} = 1$$

$$\frac{\partial^2\Phi}{\partial\phi^2} = -m^2\Phi$$

we need again

angular momentum in polar coordinate

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$$f_y = g_r \sin\theta\sin\phi + \frac{g_\theta}{r}\cos\theta\sin\phi + \frac{g_\phi \cos\phi}{r\sin\theta} \quad (5)$$

$$x \cdot (5) - y \cdot (4)$$

$$= r\sin\theta\left[\frac{g_\phi\cos^2\phi}{r\sin\theta} + \frac{g_\phi\sin^2\phi}{r\sin\theta}\right] = g_\phi$$

angular momentum operator along **z** axis

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was derivative around **ϕ**

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m : angular momentum

along z

in laboratory frame

angular momentum operator

along **z** axis

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

was derivative around **ϕ**

$$\hat{l}_z\Phi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi$$

in whole angular wavefunction only ϕ is dependent on ϕ

$$= \frac{\hbar}{i} \cdot (im)\Phi$$

$$= m\hbar\,\Phi$$

Rotational energy   what was m and J?

$$\frac{d}{dx}\left[(1-x^2)\frac{dy}{dx}\right] + n(n+1)\,y = 0$$

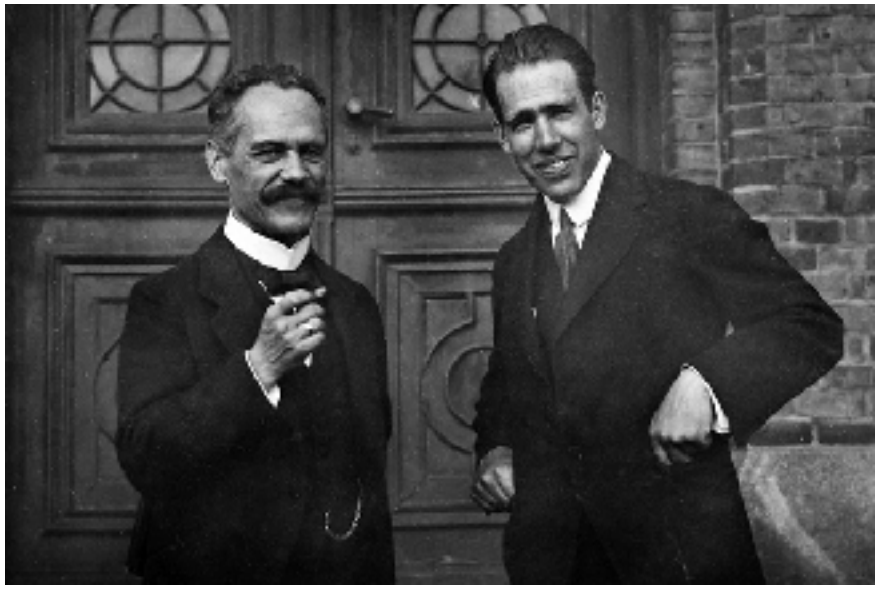
$$\frac{d}{dx}\left[(1-x^2)\frac{dv}{dx}\right] + \left[n(n+1) - \frac{m^2}{1-x^2}\right] v = 0$$

Adrien-Marie Legendre

1752-1833

$$E = B\hbar J(J+1)$$

quantized rotational energy



Bohr-Sommerfeld quantum condition
1916

quantized angular momentum on z

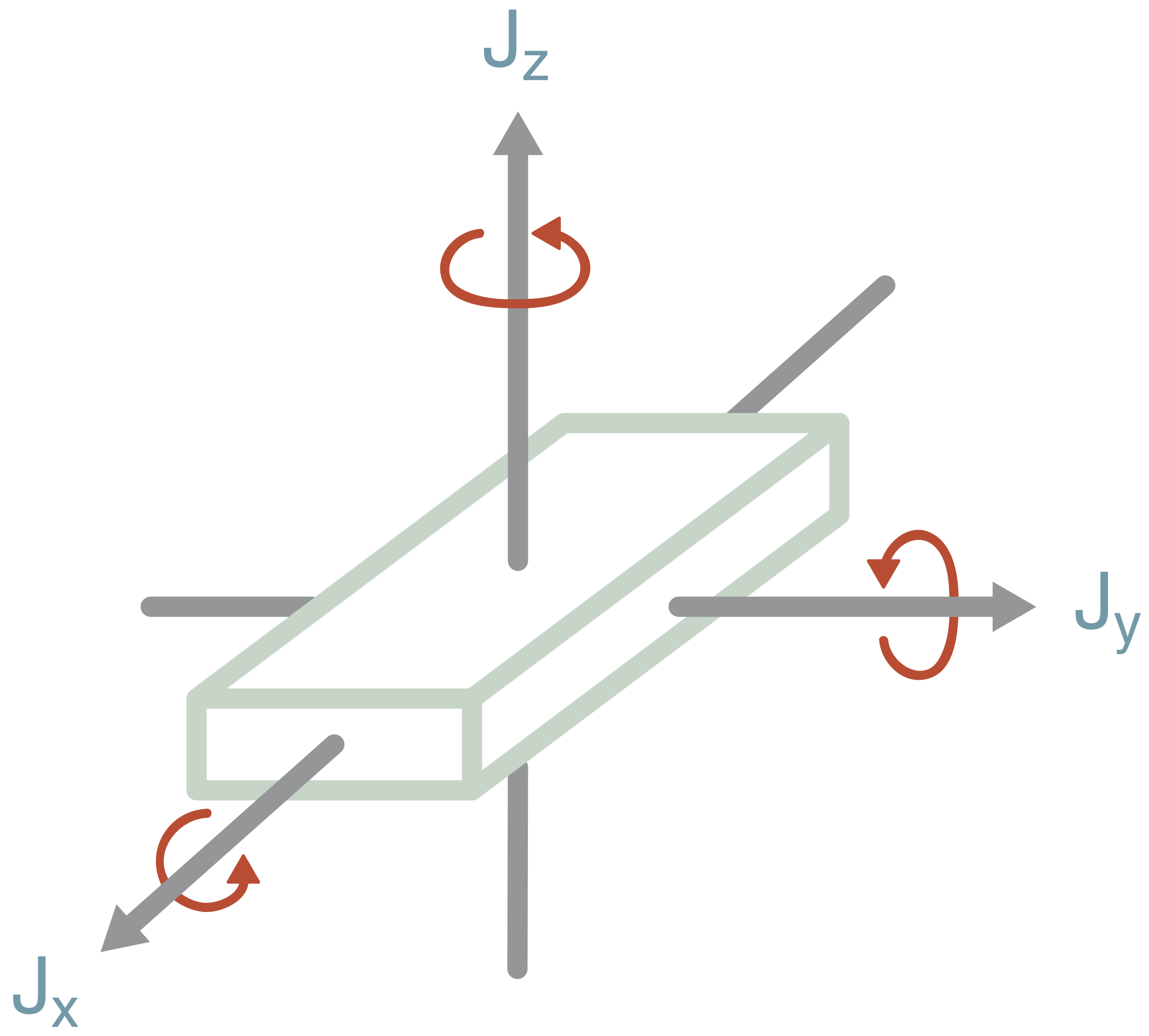
$$\frac{\partial^2\Phi}{\partial\phi^2} = b\Phi$$

how did he know that?

Why it is worthwhile taking time for spherical harmonics?

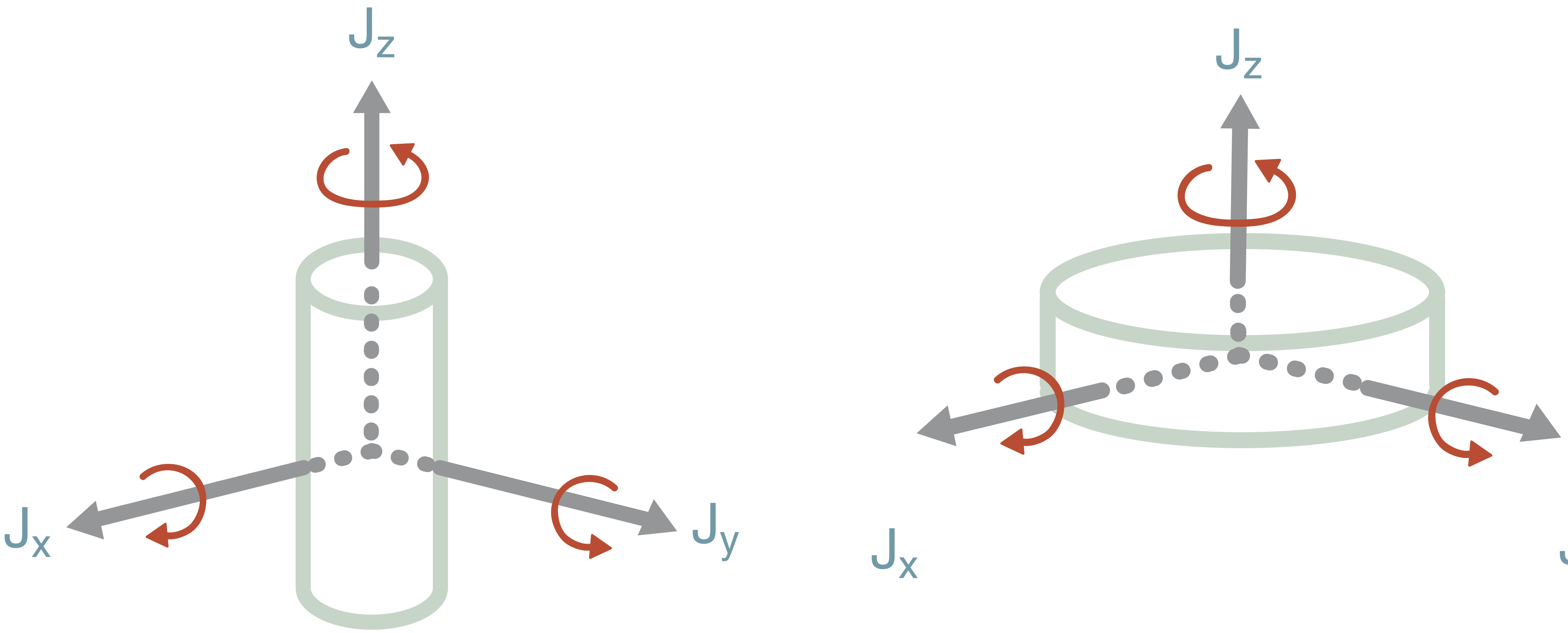
✓	1	it is a wave function	but, of what ?
✓	2	rotational energy	$E = Bh\,J(J+1)$
✓	3	angular momentum	J, K, Ka, Kc
	4	symmetry	$(-1)^J$
	5	selection rule	$\Delta J = 0, \pm 1, 0 \nleftrightarrow 0$
	6	(vanishing integral)	expansion

3 rotating axes



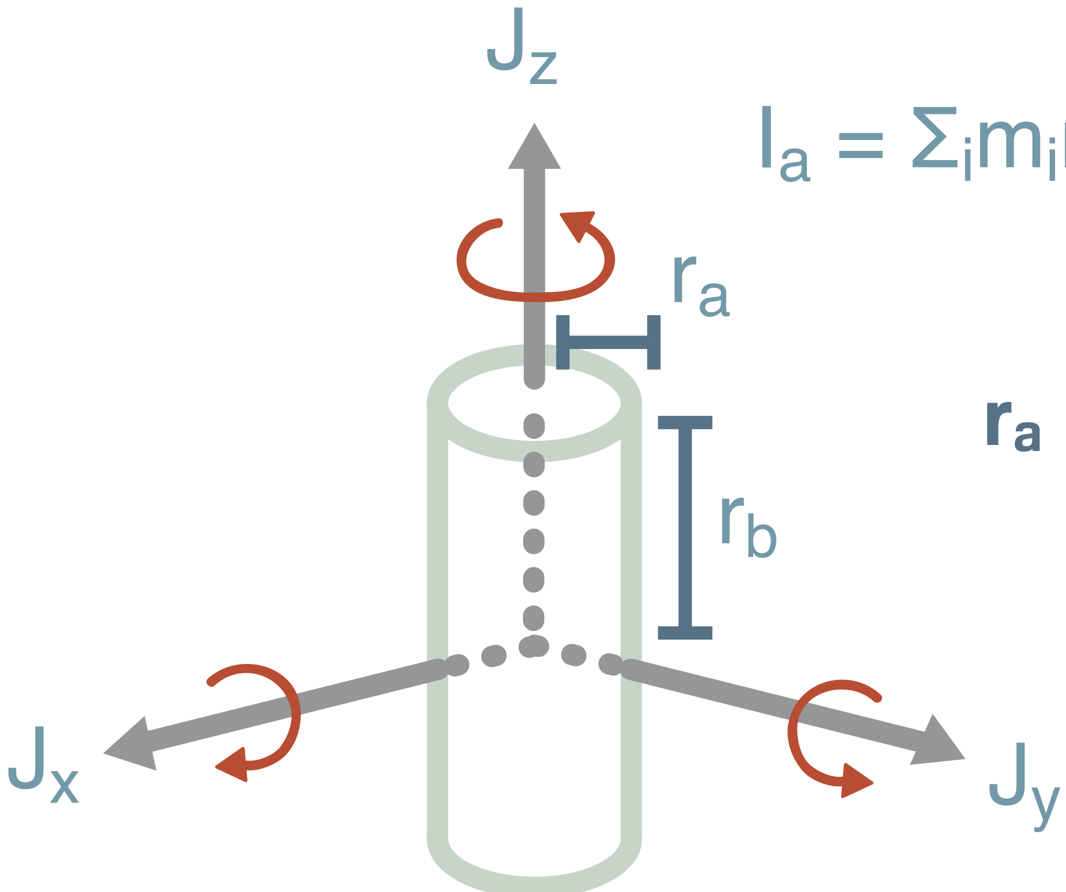
2 ways to increase symmetry

symmetric top

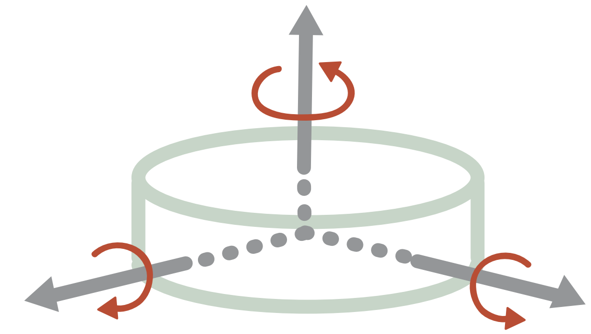


prolate

oblate



$$I_a = \Sigma_i m_i r_a^2$$



oblate

r_a close to rotation axis

r_b, r_c far from rotation axis

$$I_a < I_b = I_c \qquad A > B = C$$

$$A = \frac{1}{2I_a}$$

$$H = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

$$I_b = \Sigma_i m_i r_b^2$$

$$B = \frac{1}{2I_b}$$

$$I_c = \Sigma_i m_i r_c^2$$

$$C = \frac{1}{2I_c}$$

classically

$J = mrv$

$I = mr^2$

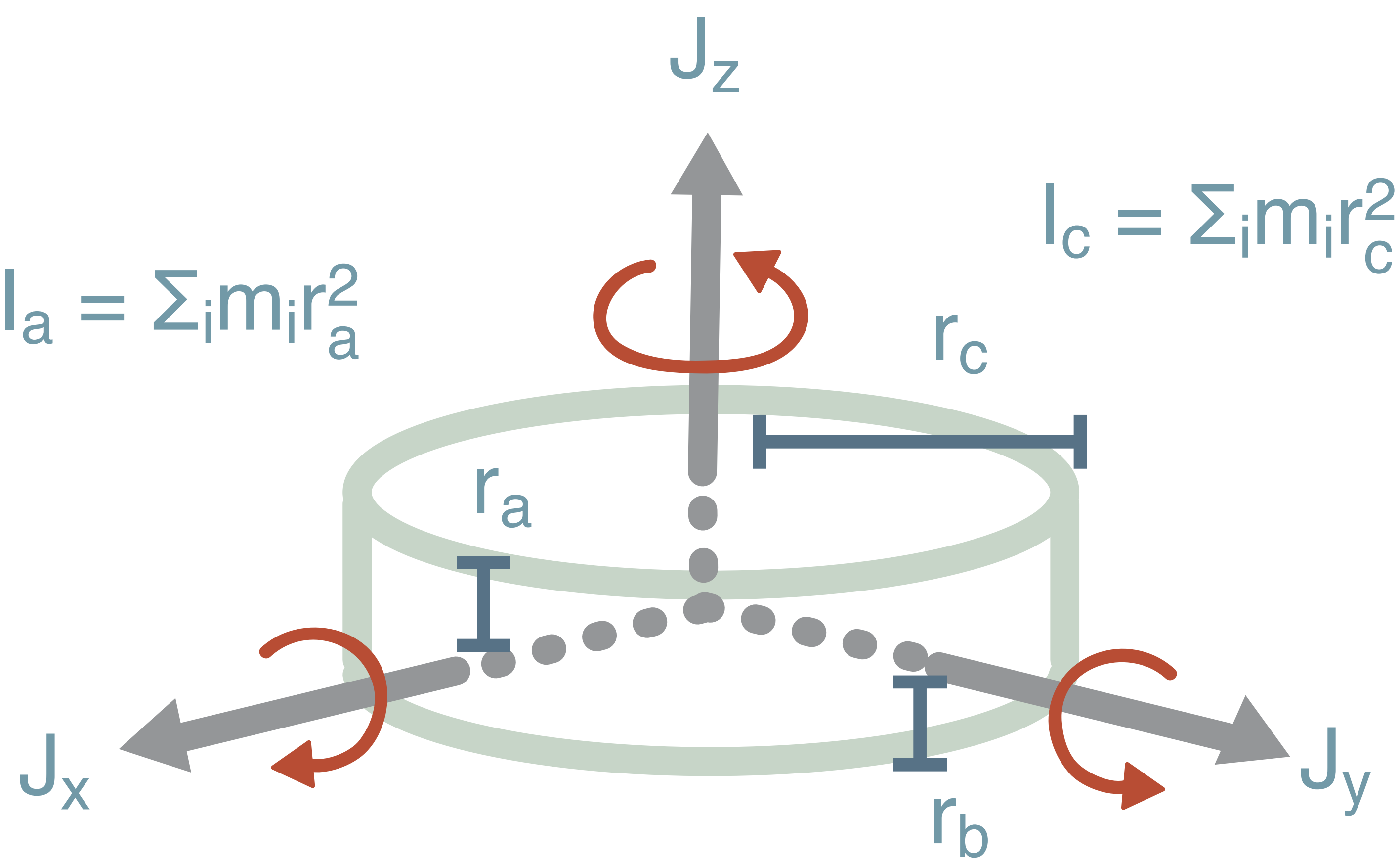
$$E = \frac{1}{2}mv^2$$

$$= \frac{1}{2}(mrv)^2/(mr^2) = \frac{J^2}{2I}$$

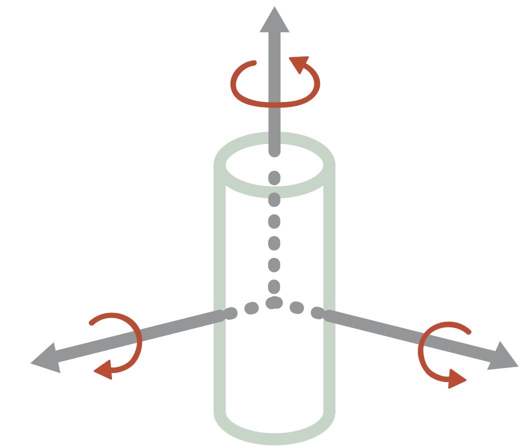
rotational constant

$I_a = \Sigma_i m_i r_a^2$

$I_c = \Sigma_i m_i r_c^2$



$I_b = \Sigma_i m_i r_b^2$



prolate

$A > B = C$

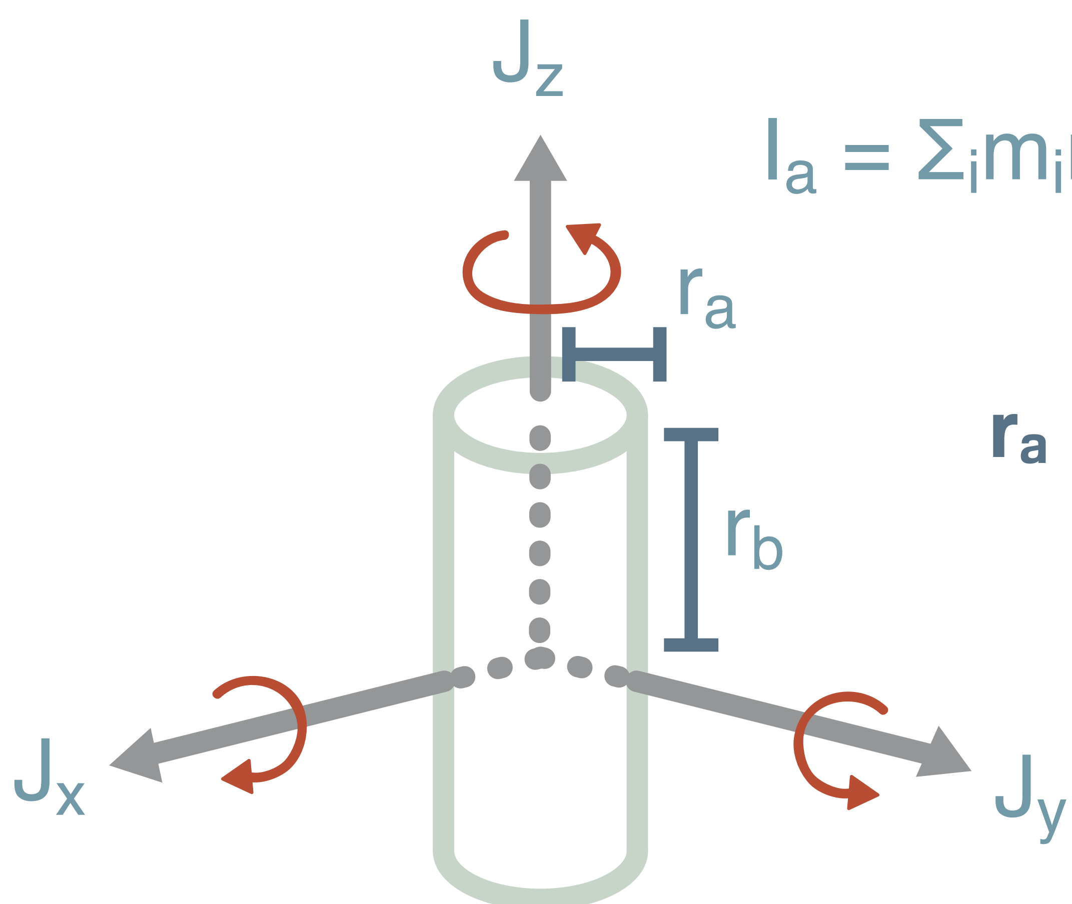
r_a, r_b close to rotation axes

r_c far from rotation axis

$I_a = I_b < I_c$

$A = B > C$

$$A = \frac{1}{2I_a} \qquad B = \frac{1}{2I_b} \qquad C = \frac{1}{2I_c}$$



$$I_a = \Sigma_i m_i r_a^2$$

$$H = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

$$A = \frac{1}{2I_a} \quad B = \frac{1}{2I_b} \quad C = \frac{1}{2I_c}$$

r_a **close to rotation axis**

r_b, r_c **far from rotation axis**

$$I_a < I_b = I_c \qquad A > B = C$$

$$H = AJ_z^2 + BJ_x^2 + CJ_y^2$$

$$J = J_x^2 + J_y^2 + J_z^2$$

$$J_z^2 = J^2 - (J_x^2 + J_y^2)$$

total angular momentum

this is J

$$H = AJ_z^2 + B(J_x^2 + J_y^2)$$

$$= AJ_z^2 + B(J^2 - J_z^2)$$

$$= BJ^2 + (A - B)J_z^2$$

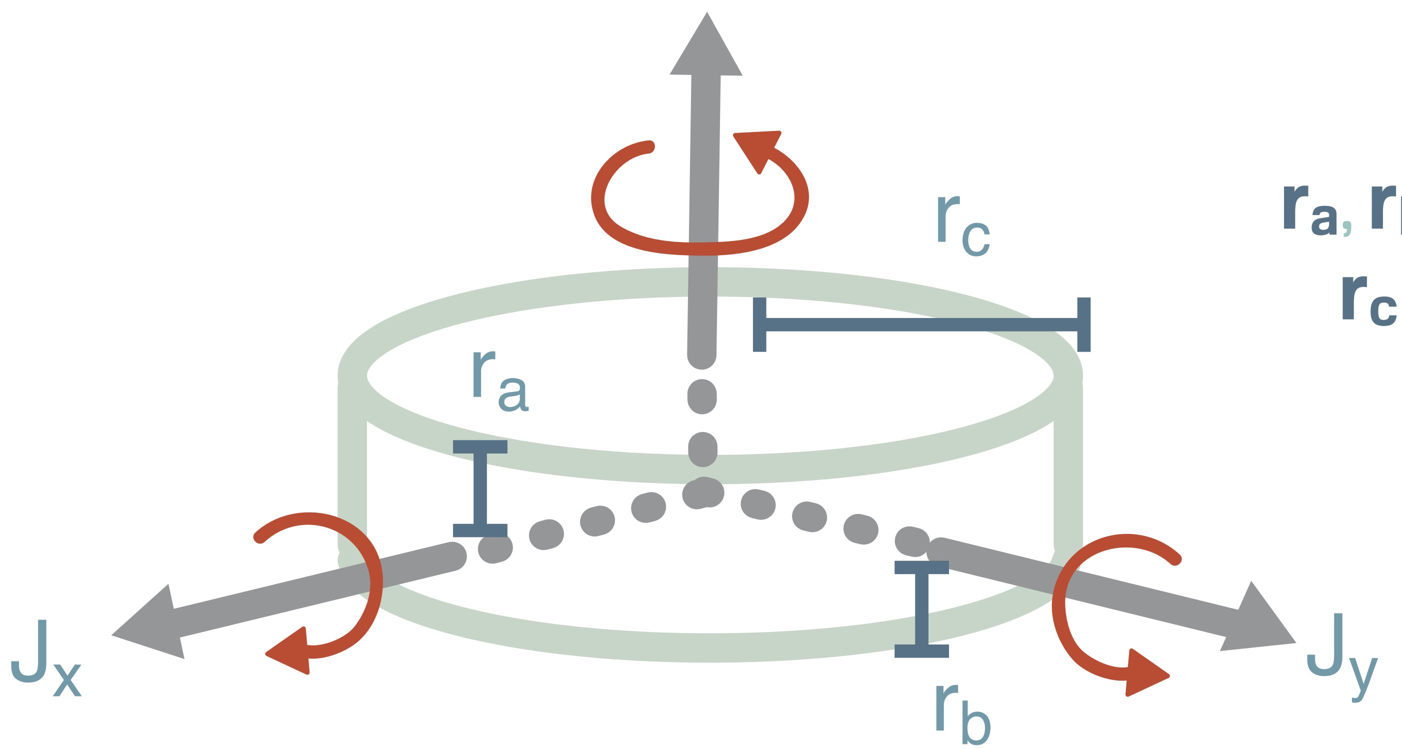
angular momentum along z

in molecular frame

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

$$H = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

$$A = \frac{1}{2I_a} \quad B = \frac{1}{2I_b} \quad C = \frac{1}{2I_c}$$



r_a, r_b close to rotation axes

r_c far from rotation axis

$$I_a = I_b < I_c \qquad A = B > C$$

$$H = AJ_x^2 + BJ_y^2 + CJ_z^2$$
$$= B(J_x^2 + J_Y^2) + CJ_z^2$$
$$= B(J^2 - J_z^2) + CJ_z^2$$
$$= BJ^2 - (B - C)J_z^2$$

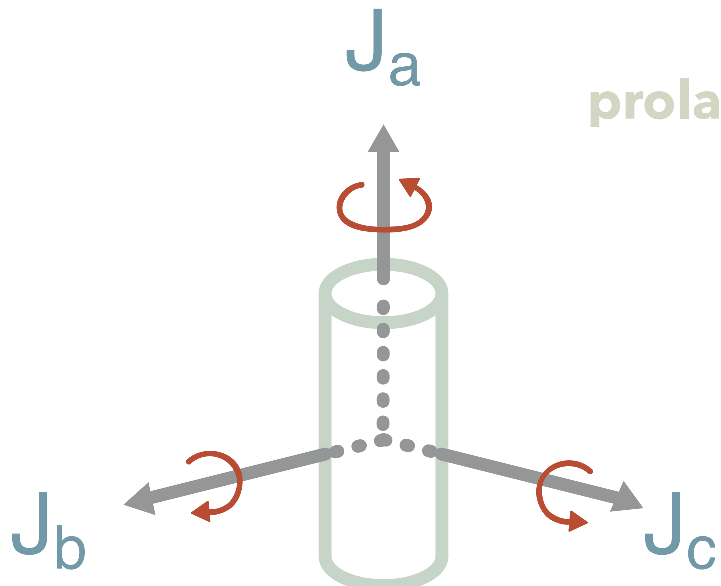
angular momentum along **z**

in molecular frame

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

this is **J** total angular momentum

prolate



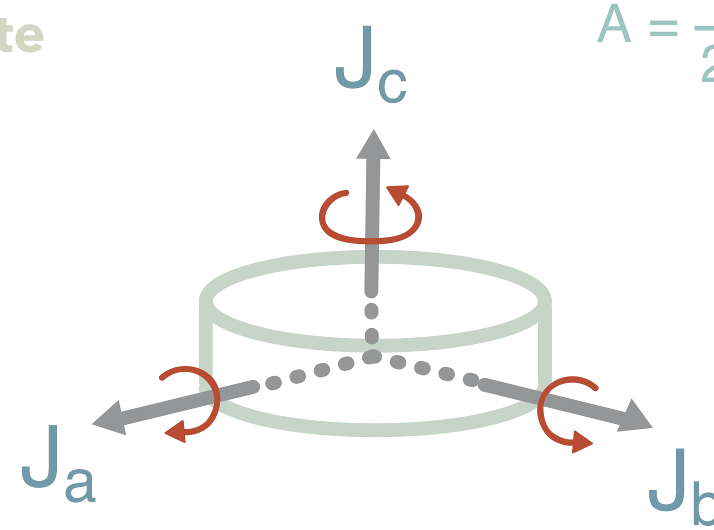
$$I_a < I_b = I_c$$

$$A > B = C$$

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

oblate

$$A = \frac{1}{2I_a}$$



$$I_a = I_b < I_c$$

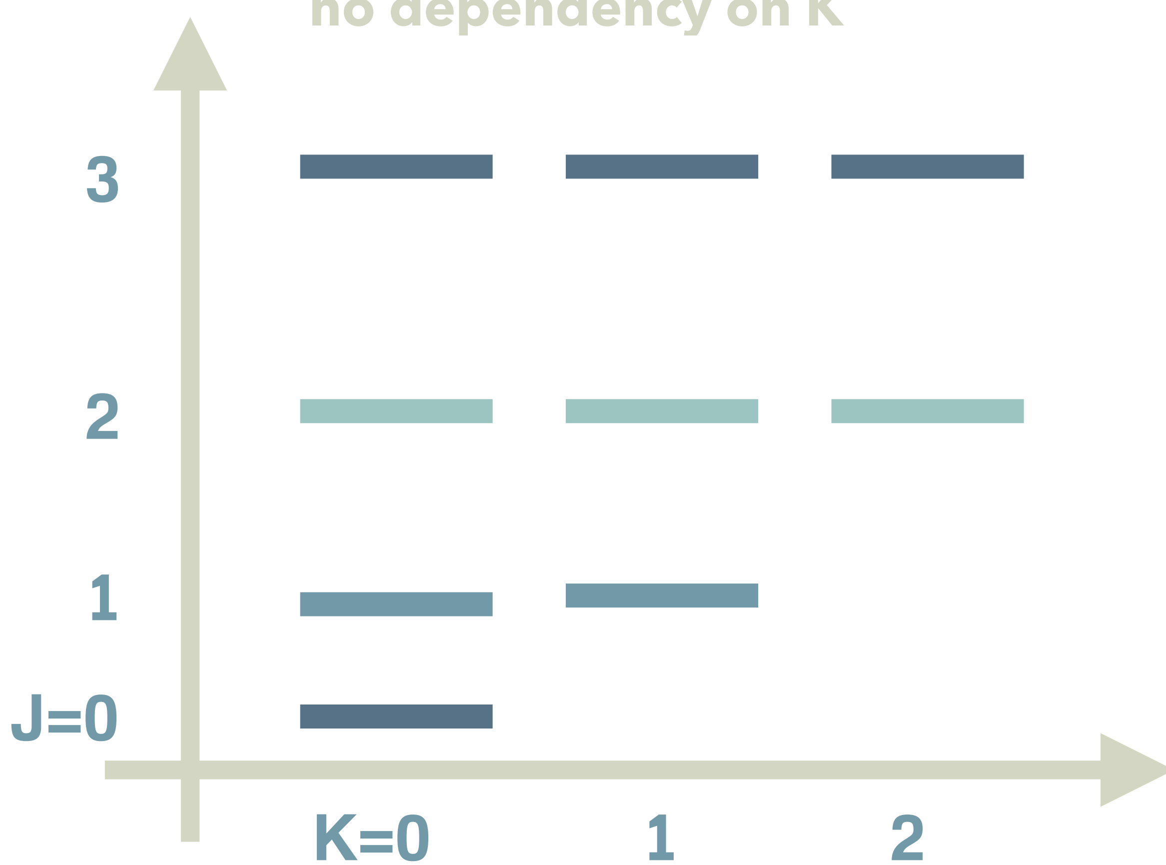
$$A = B > C$$

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

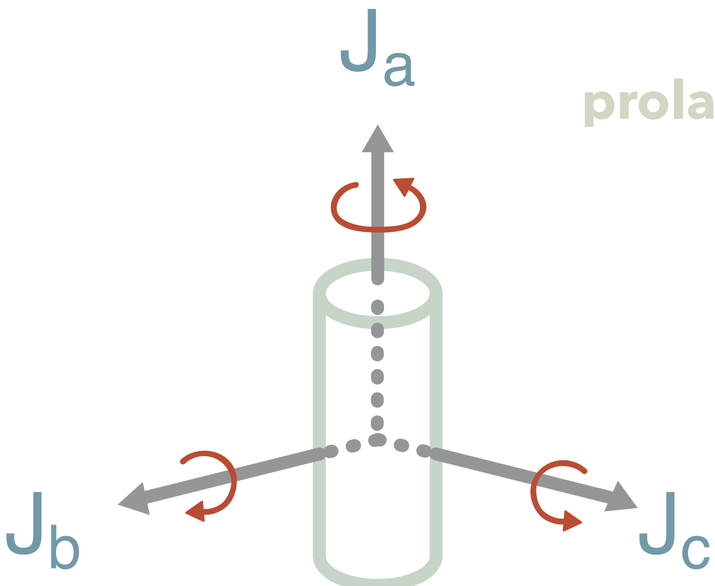
E

if A=B

no dependency on K



prolate



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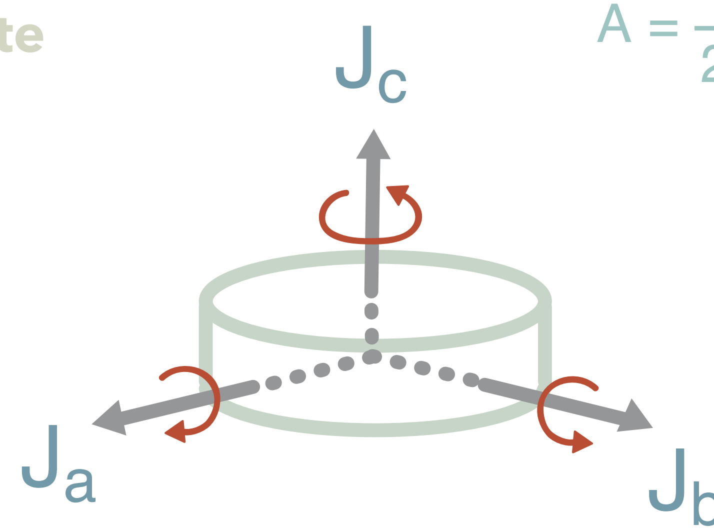

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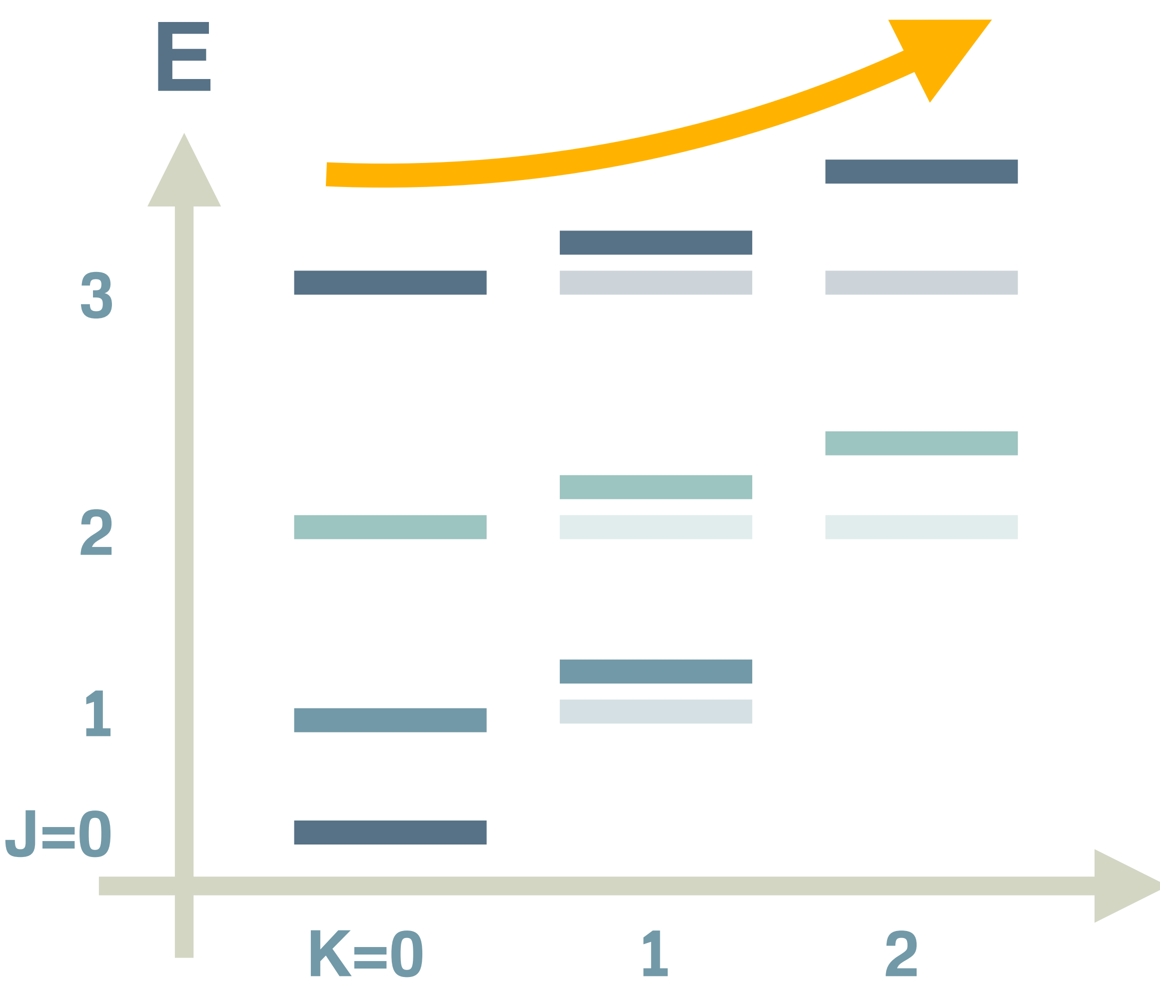
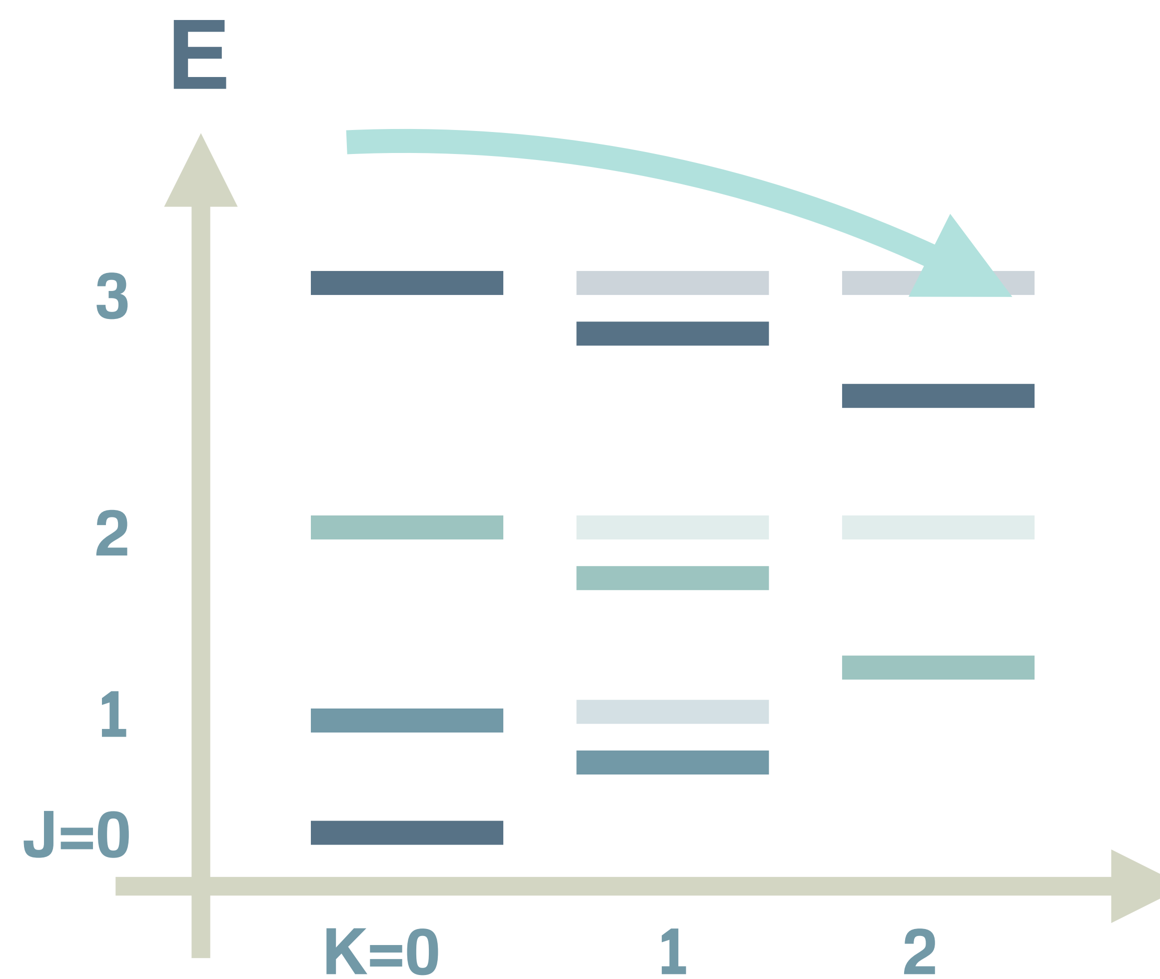
$A = B > C$

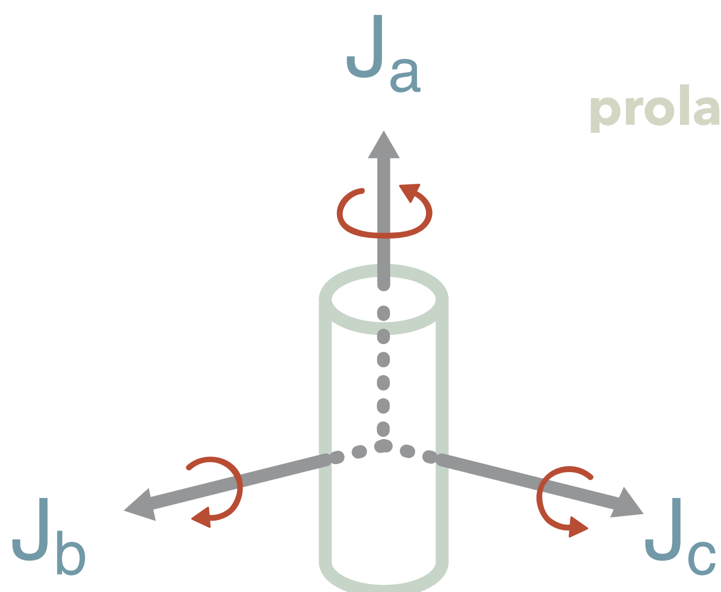
$$E = BJ(J+1) - (B - C)K^2$$

if you look at rotational levels can see shape of molecule





prolate



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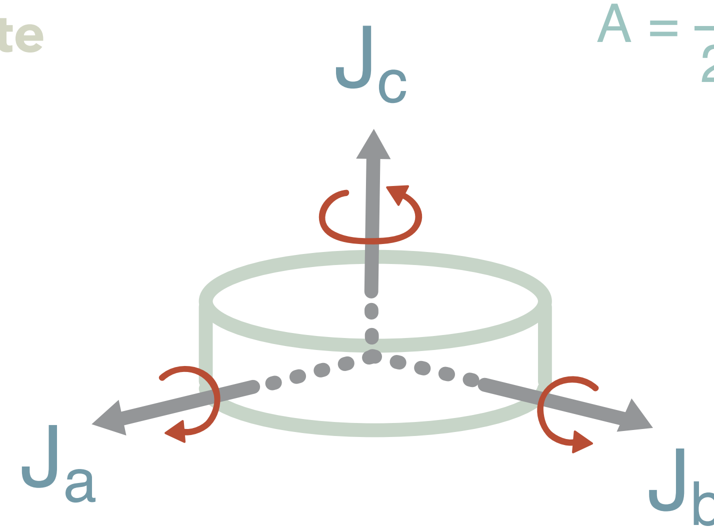

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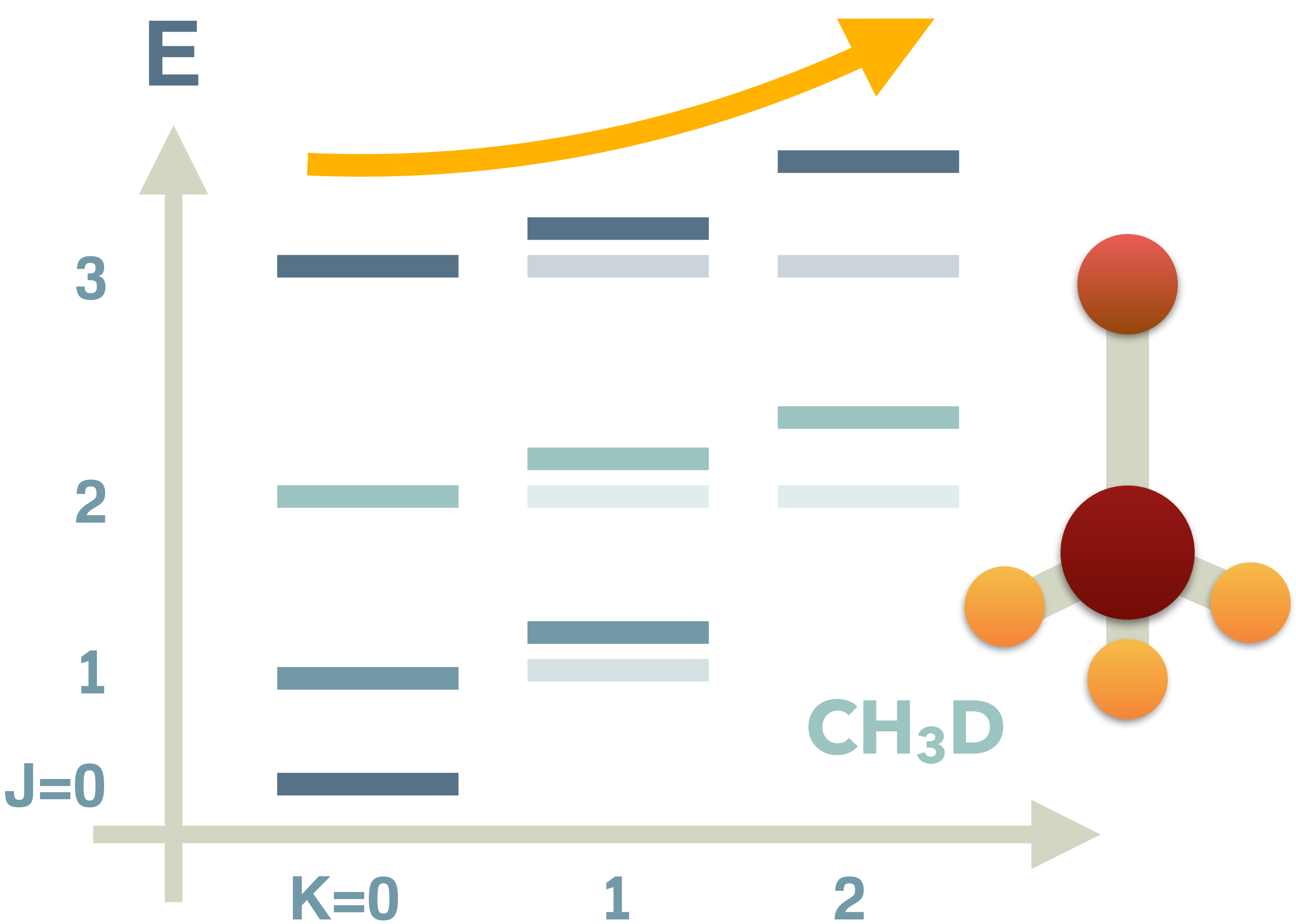
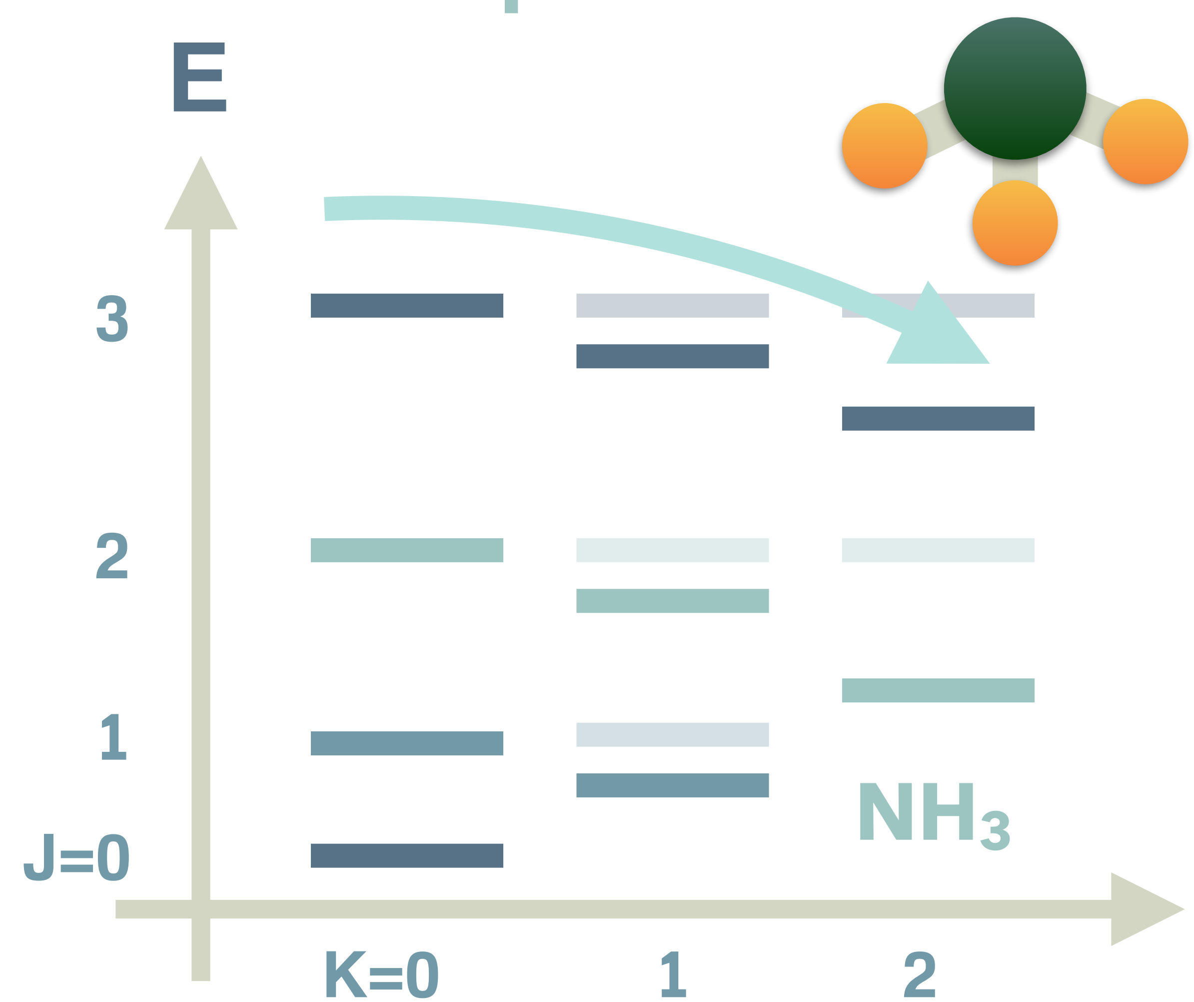
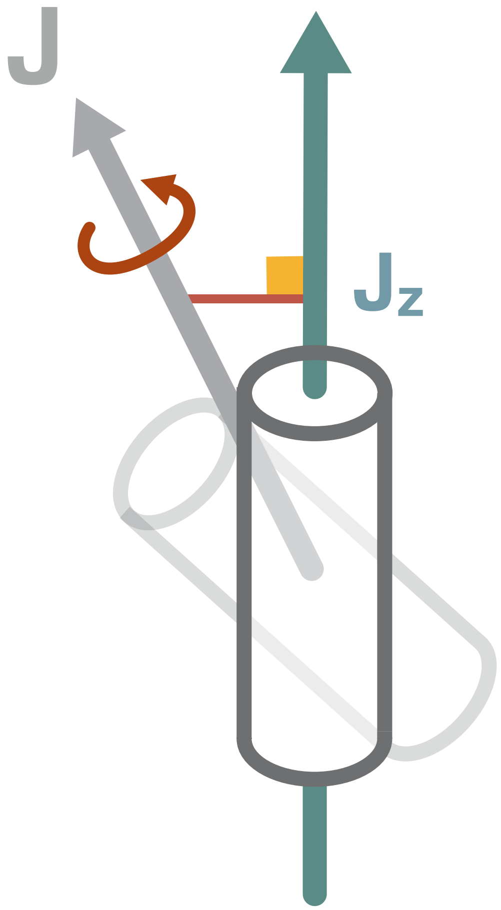
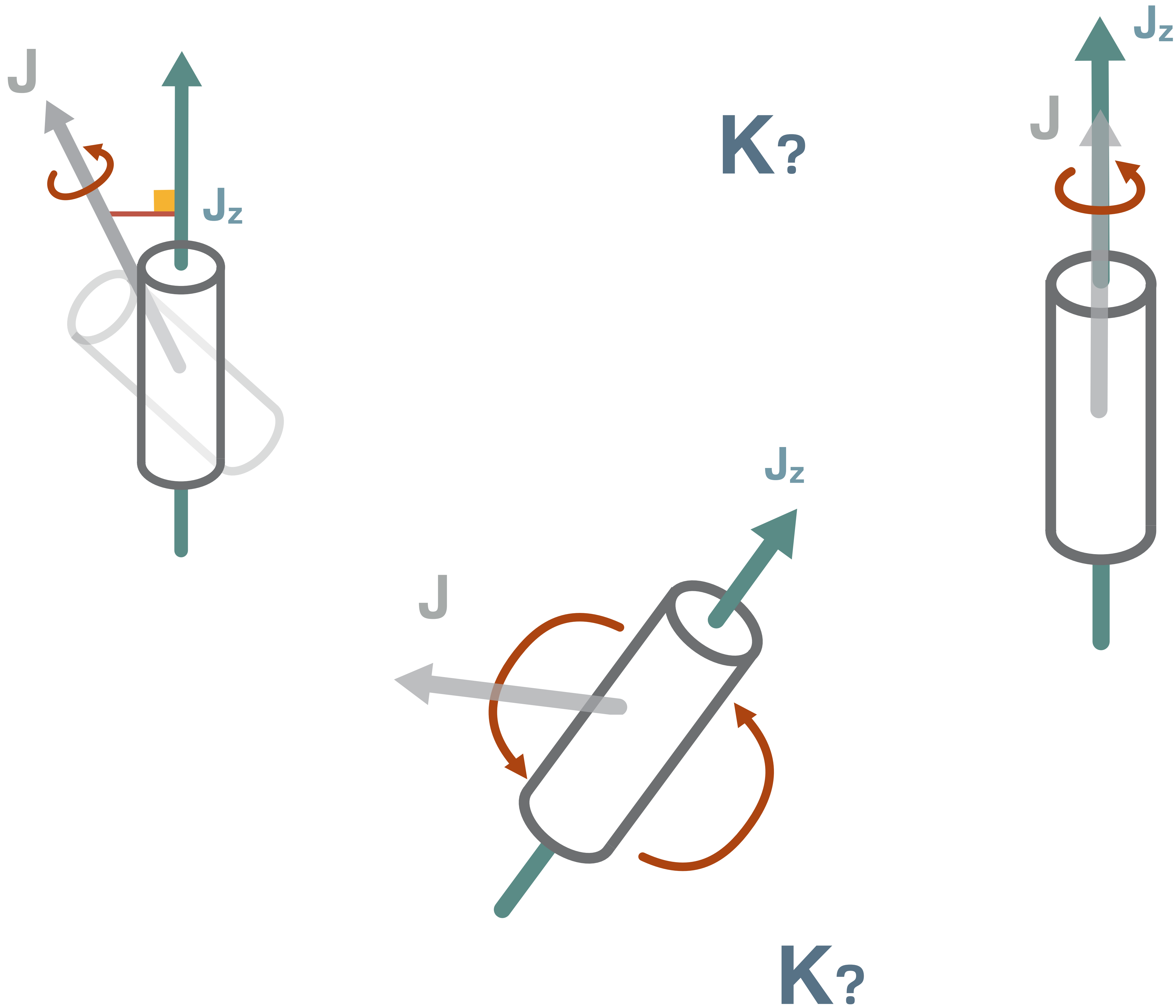


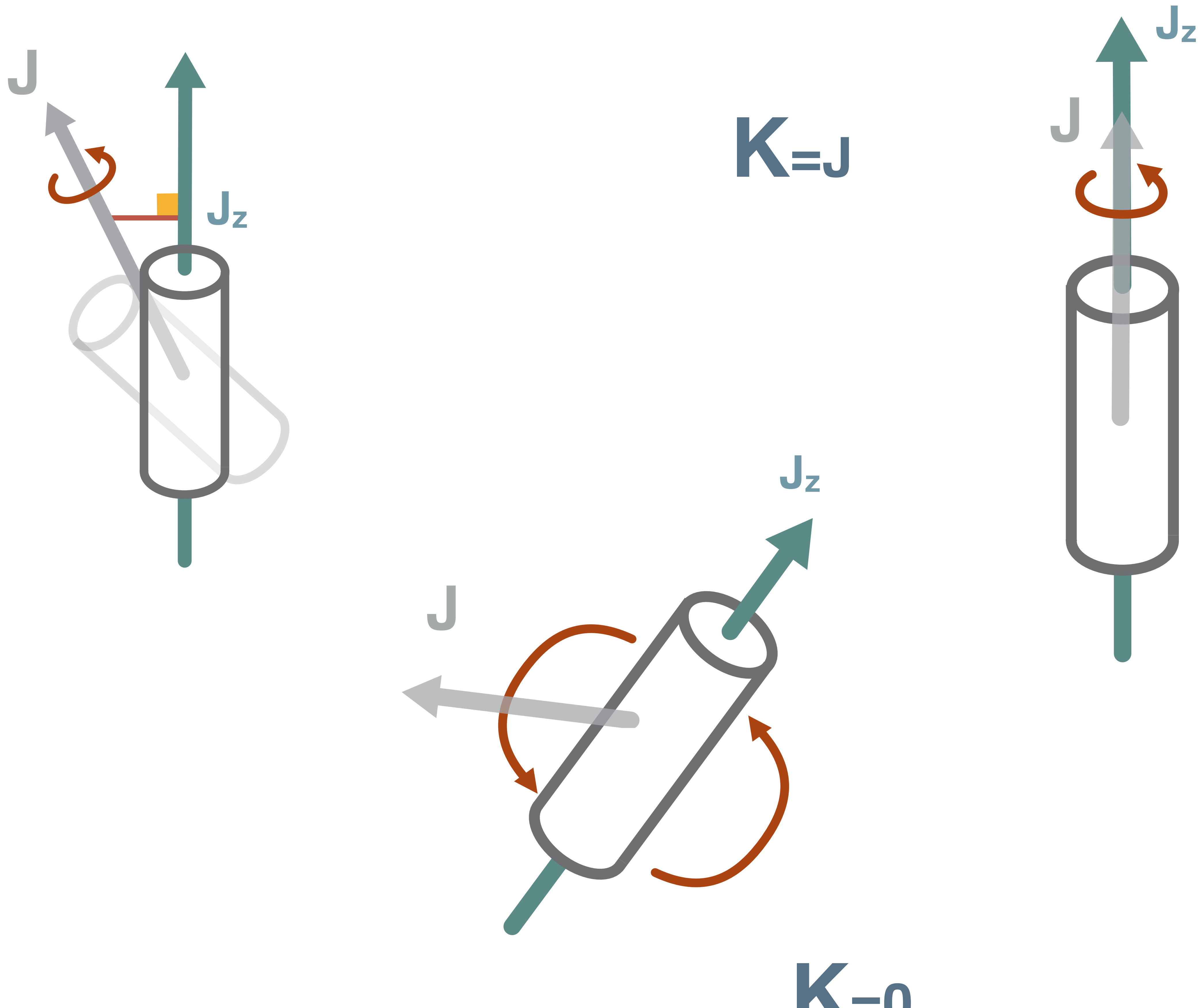



J
Jz

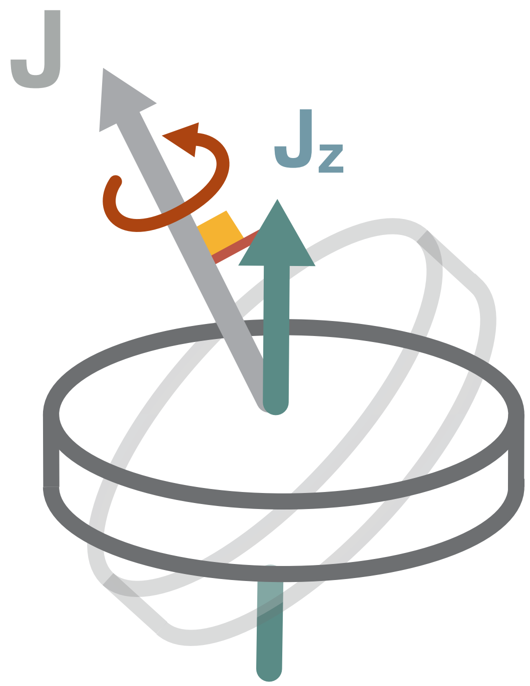

J
J_z



J
Jz
K?
Jz
J
Jz
J
K?



J
Jz
K=J
J
Jz
Jz
J
K=0



1

how it rotates when

$K_{=0}$

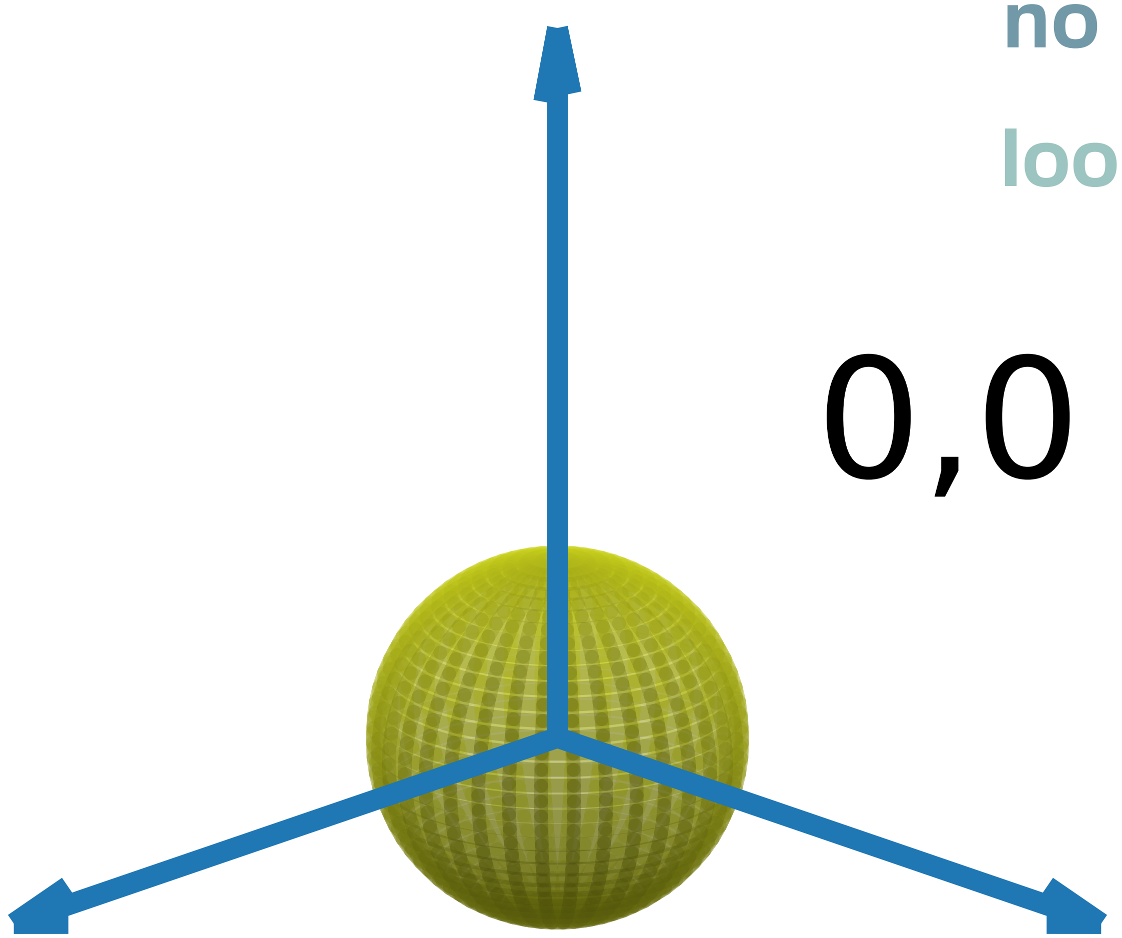
$K_{=J}$

This is wave function but of what?

J = 0

no angular momentum

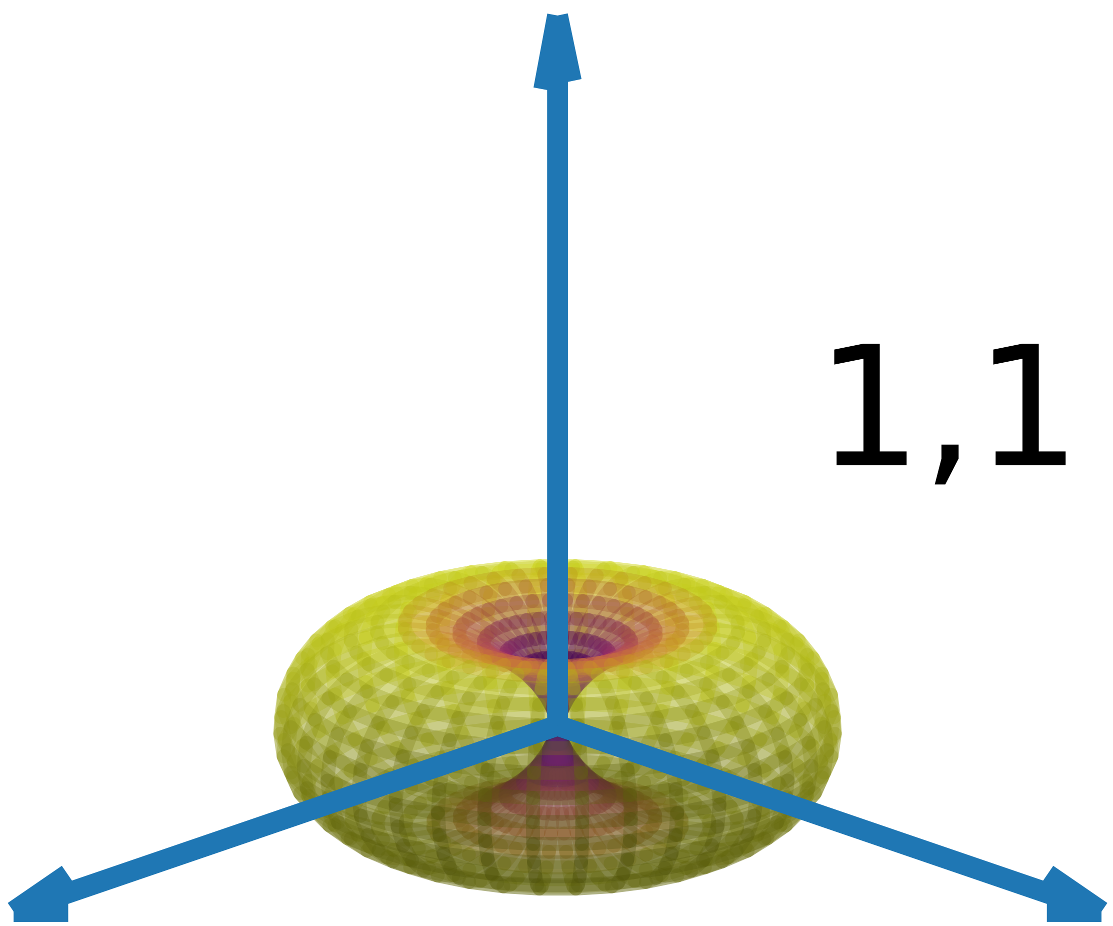
looking at no particular direction



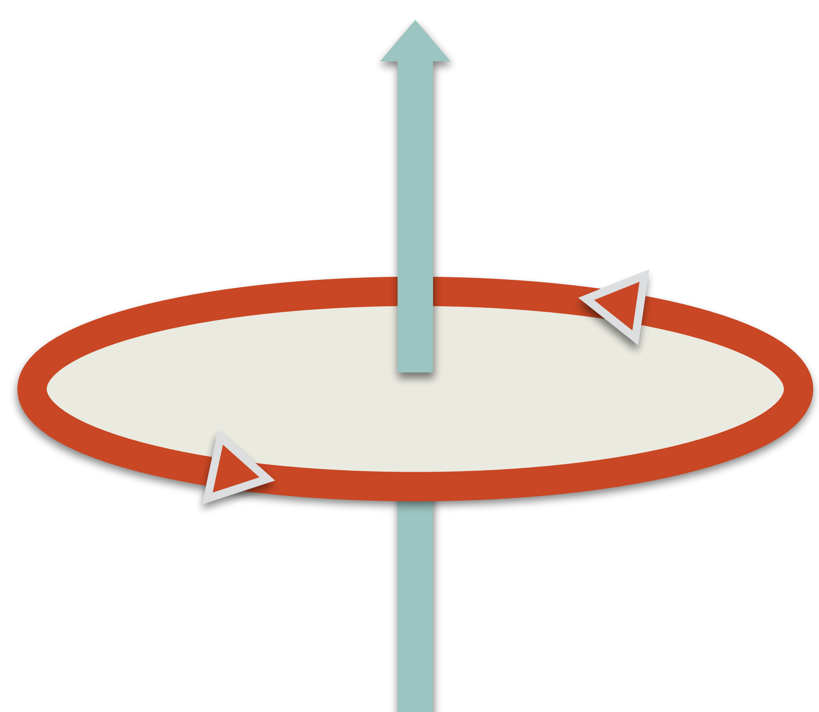
This is wave function but of what?

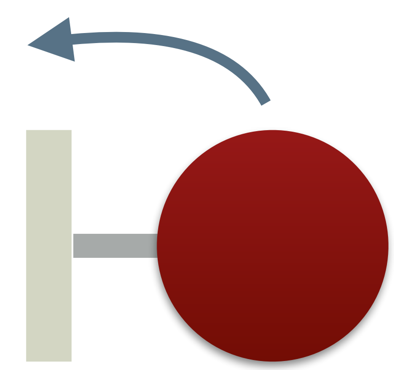
$J = 1$ $|m| = 1$

whole angular momentum along z



$J_z = J$

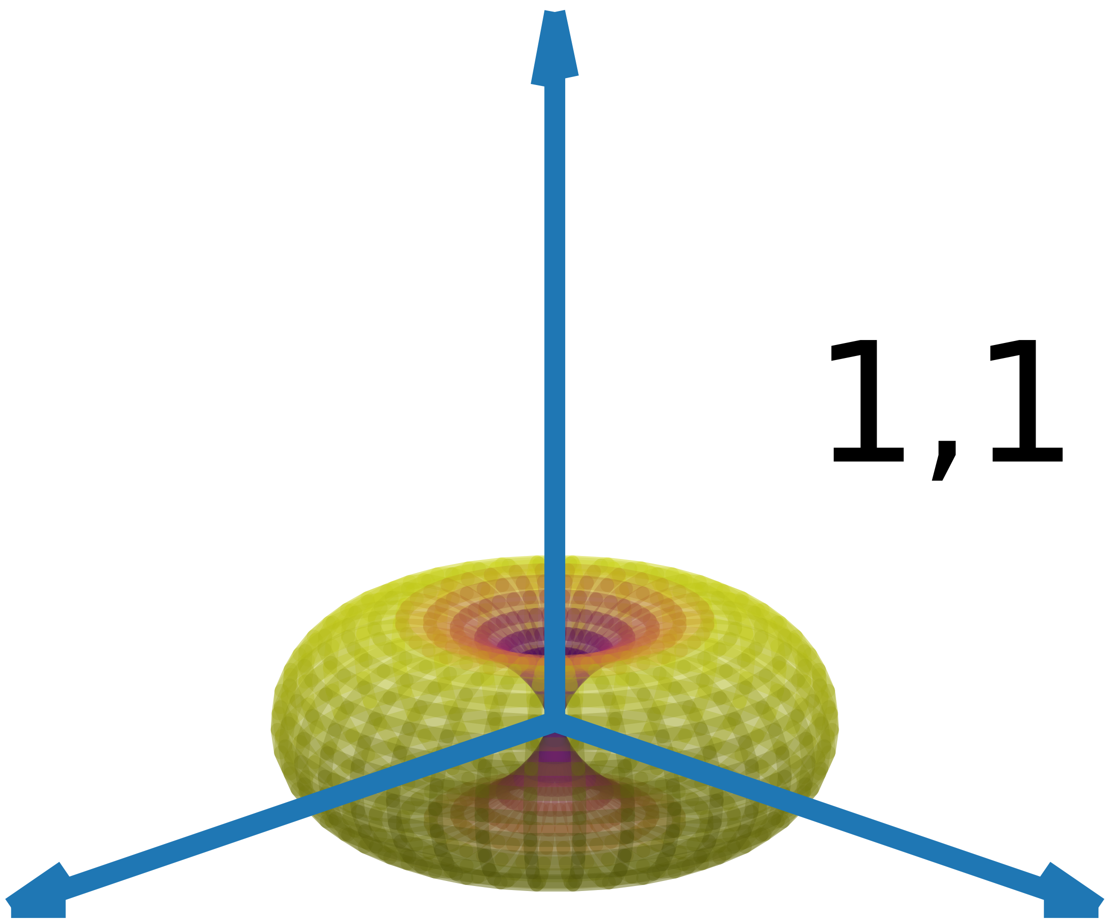




This is wave function but of what?

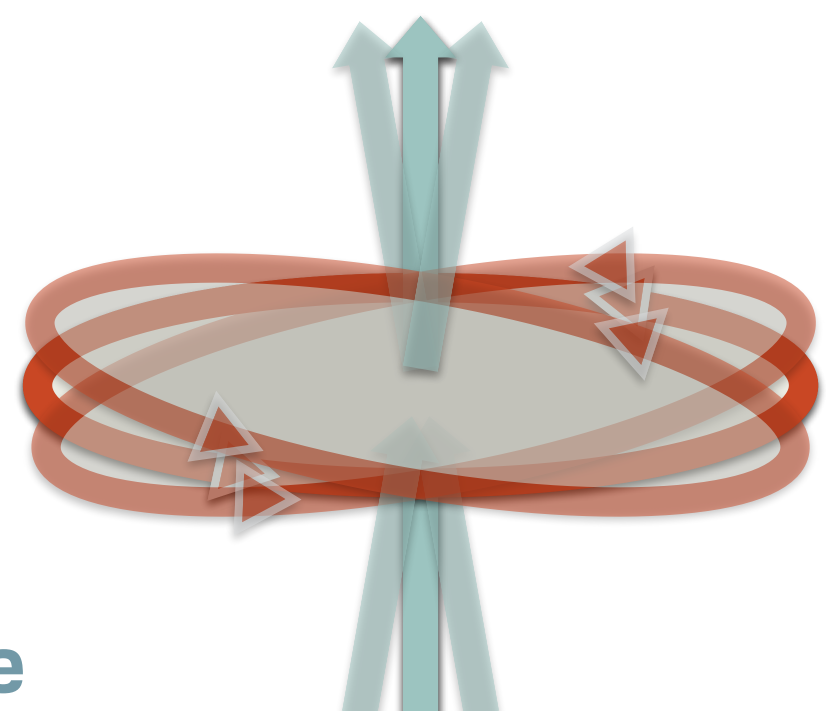
J = 1 |m| = 1

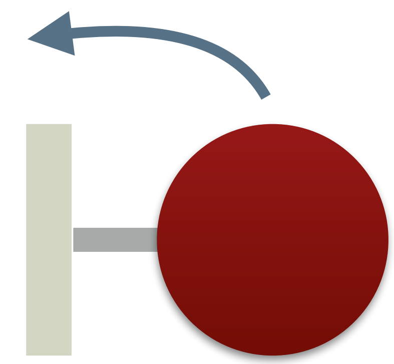
whole angular momentum along z



1,1

Jz = J

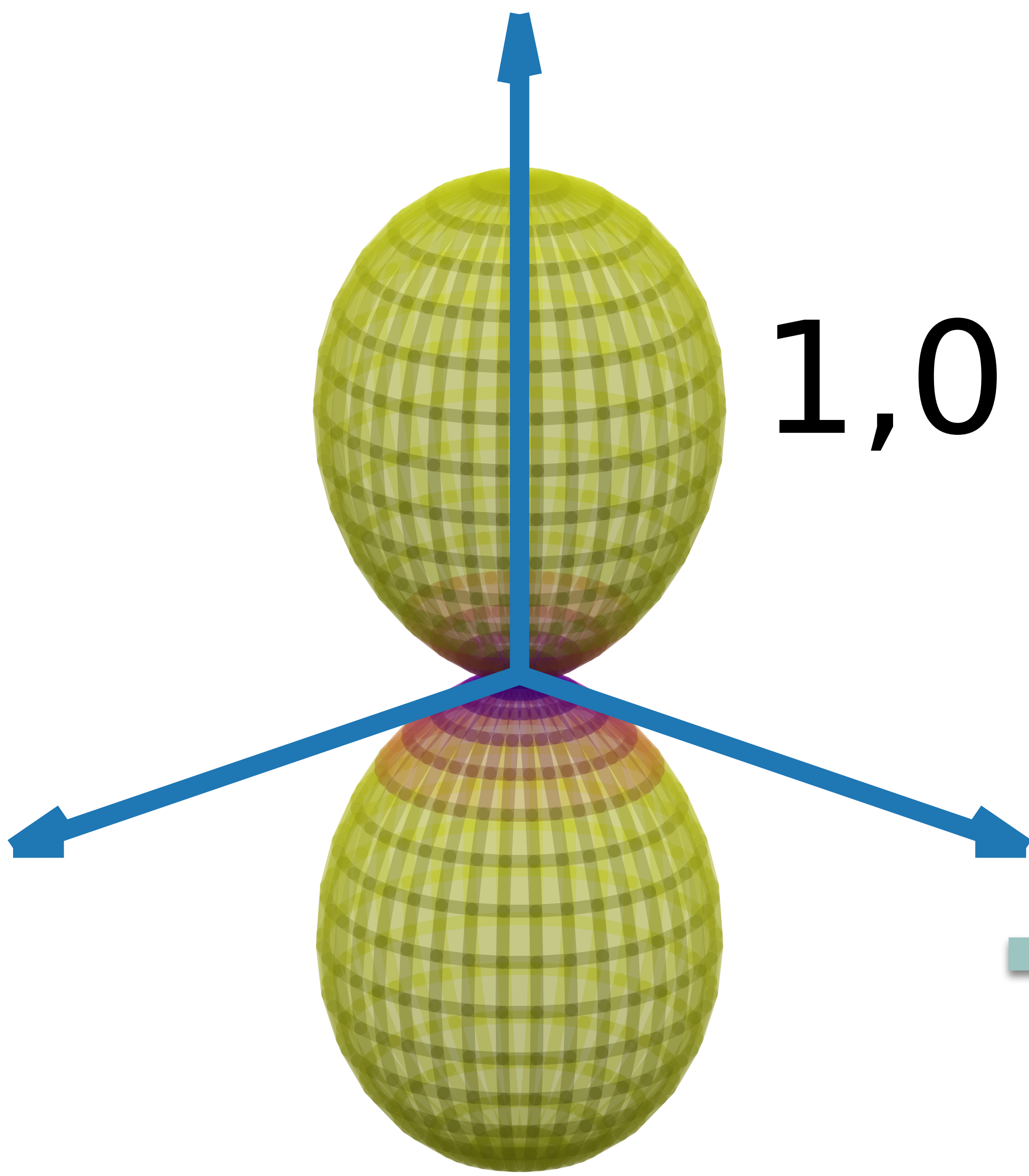




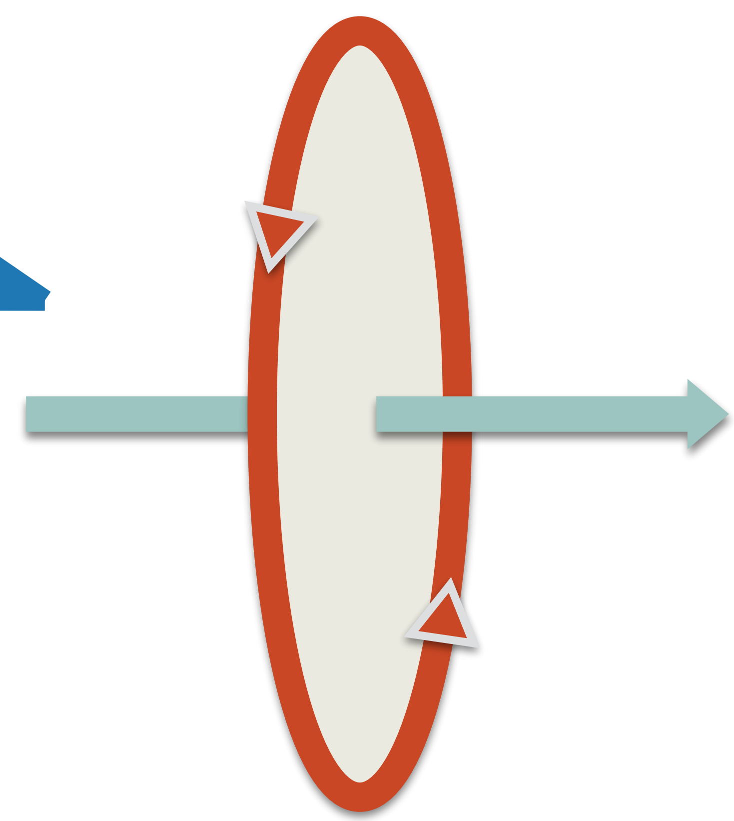
uncertain principle

J = 1 |m| = 0

0 angular momentum along z



Jz = 0

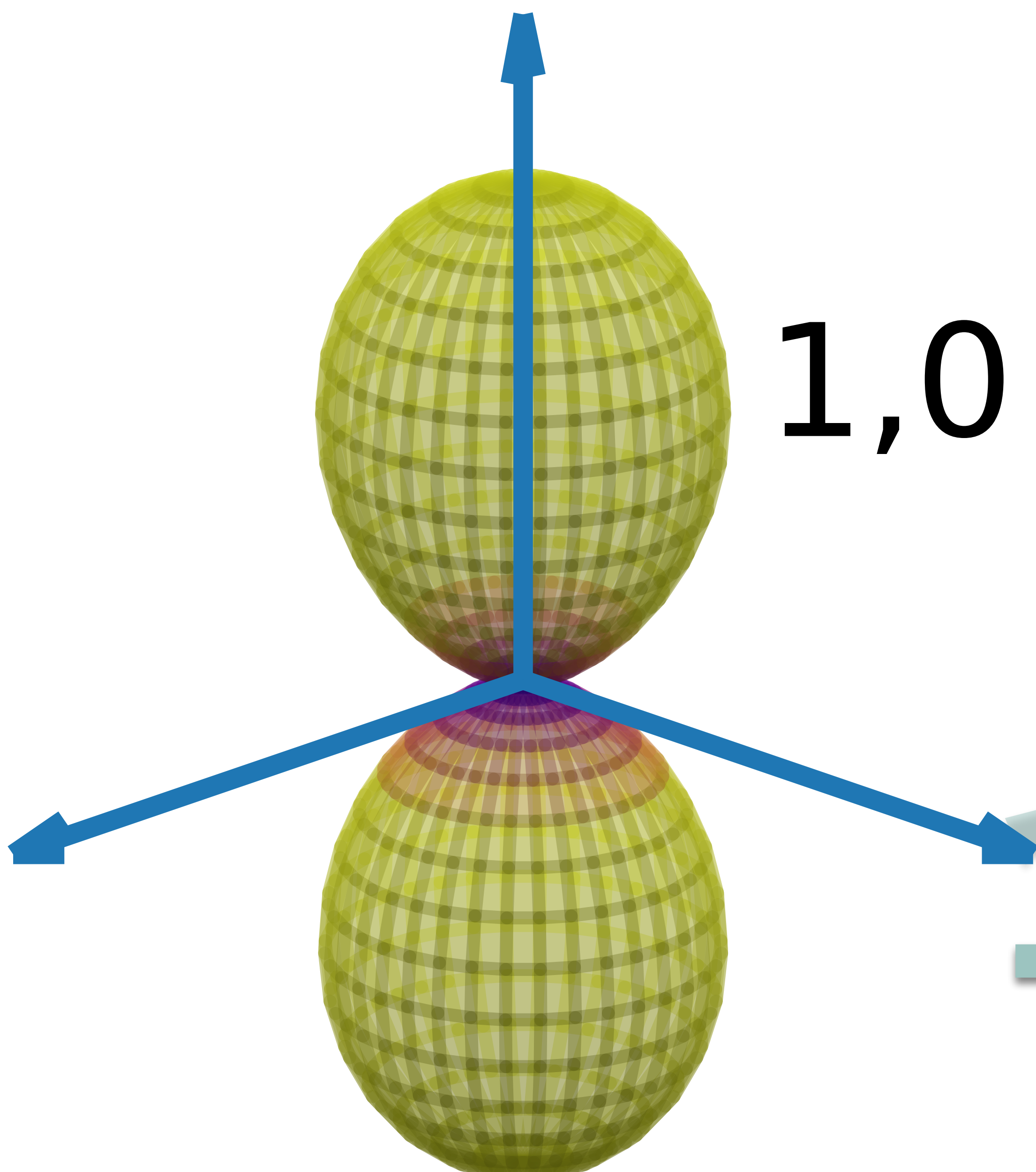


J = 1 |m| = 0

0 angular momentum along z

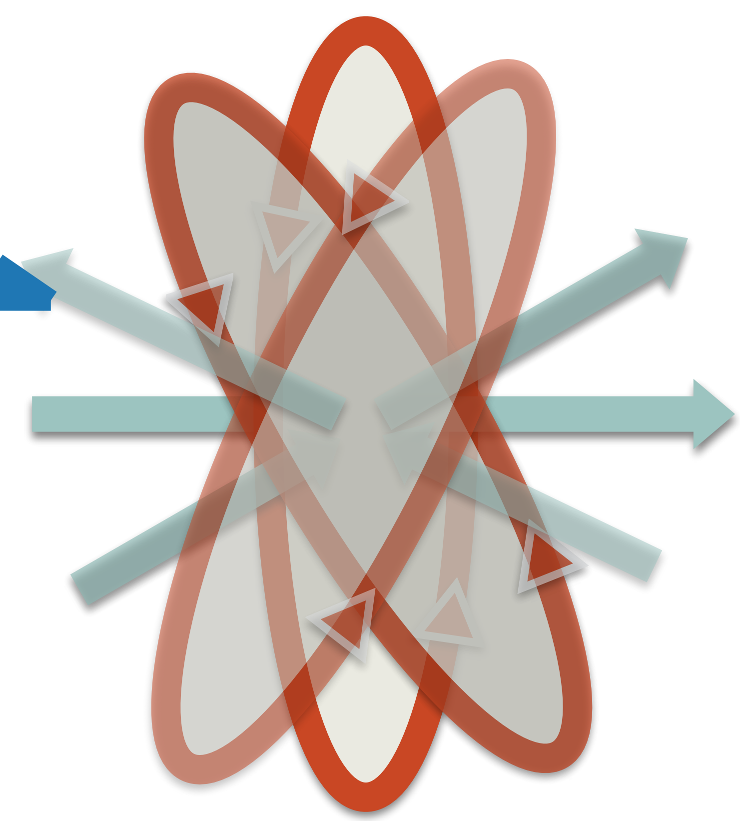
axis in x-y plane

probability highest at poles

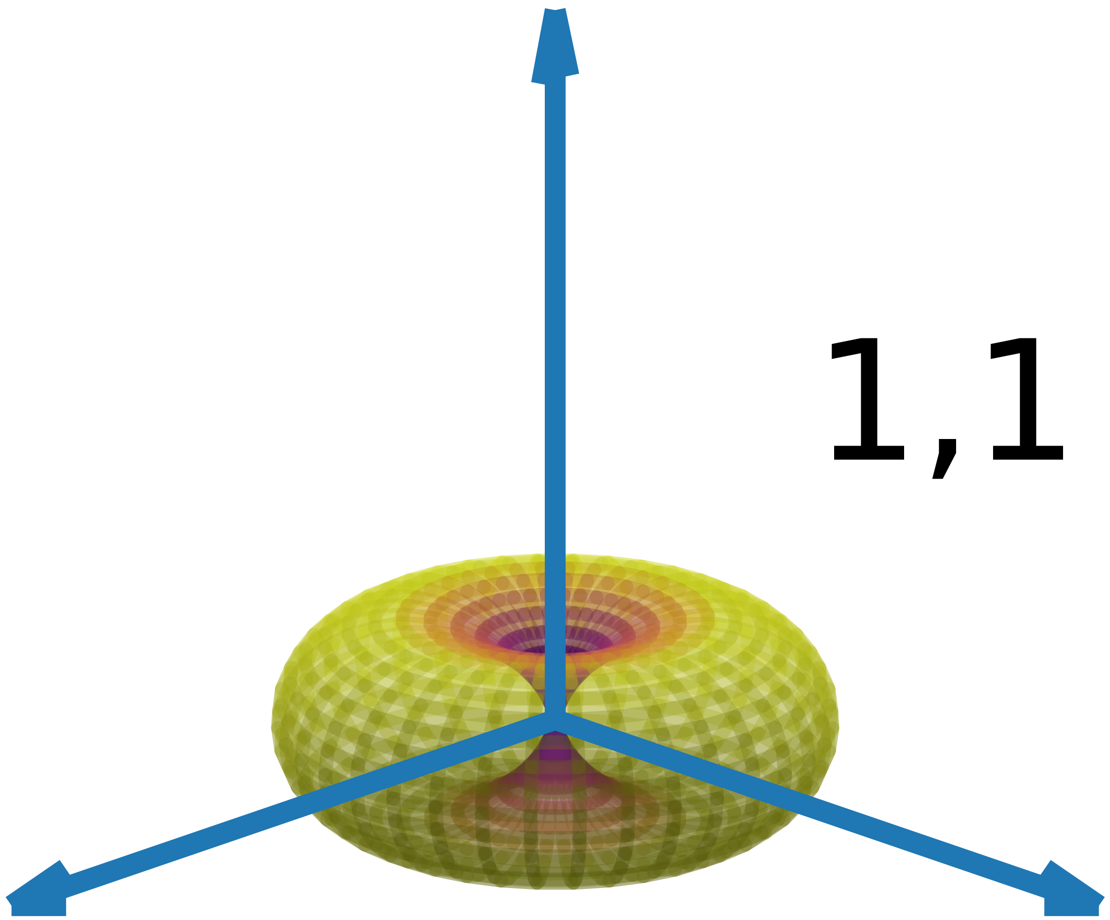


1,0

Jz = 0



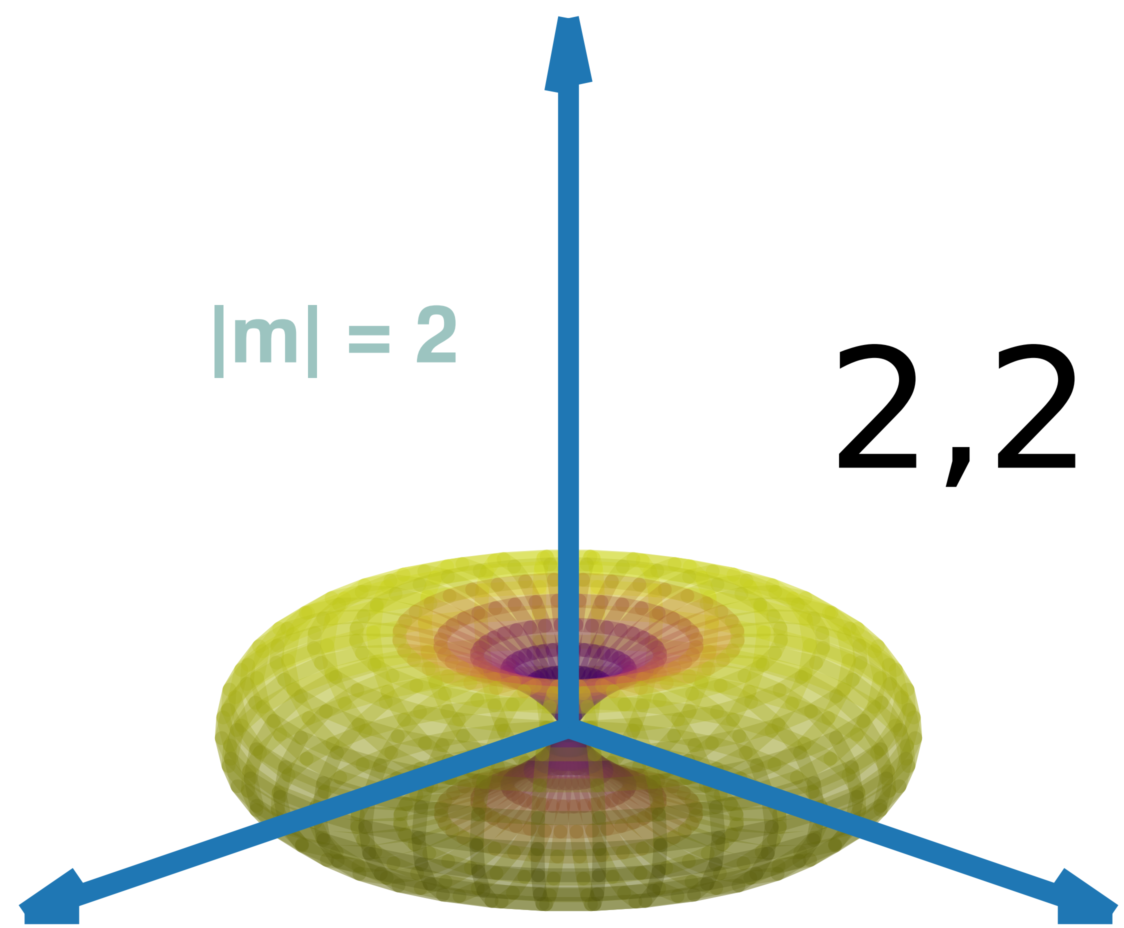
J = 1 |m| = 1



larger angular momentum

becomes flatter

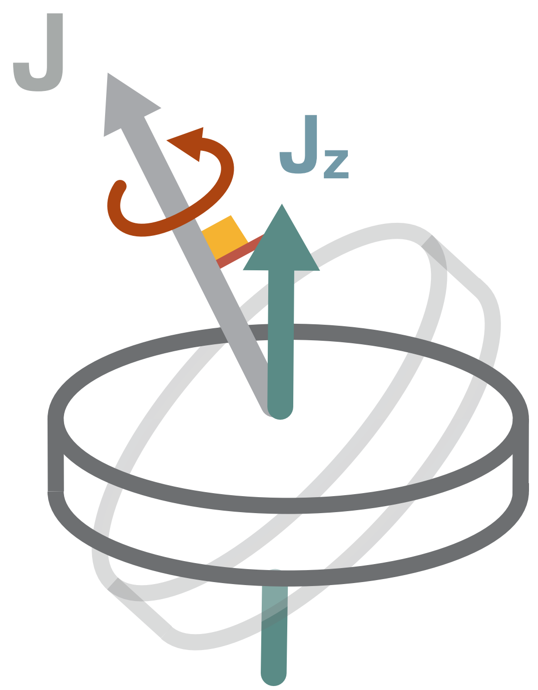
J = 2 |m| = 2



Why it is worthwhile taking time for spherical harmonics?

✓ 1	it is a wave function	but, of what ?
✓ 2	rotational energy	$E = Bh\,J(J+1)$
✓ 3	angular momentum	J, K, Ka, Kc
4	symmetry	$(-1)^J$
5	statistic degeneracy	$g_J = 2J + 1$
6	selection rule	expansion $\Delta J = 0, \pm 1, 0 \leftrightarrow 0$

Exercise today



1 how it rotates when

K=0

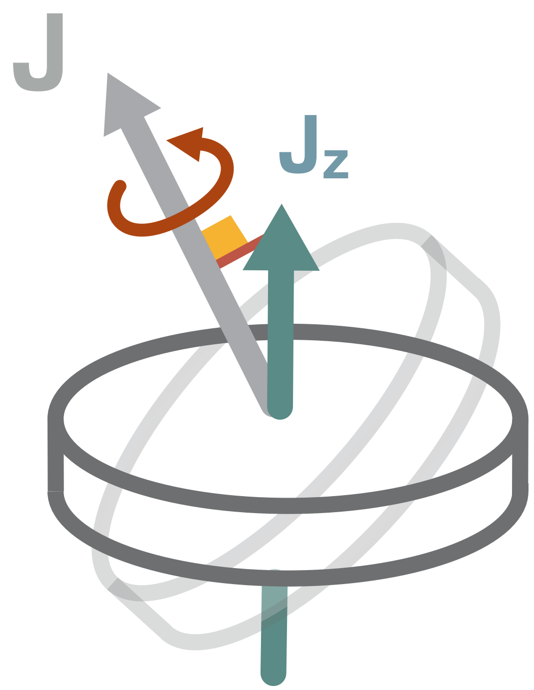
K=J

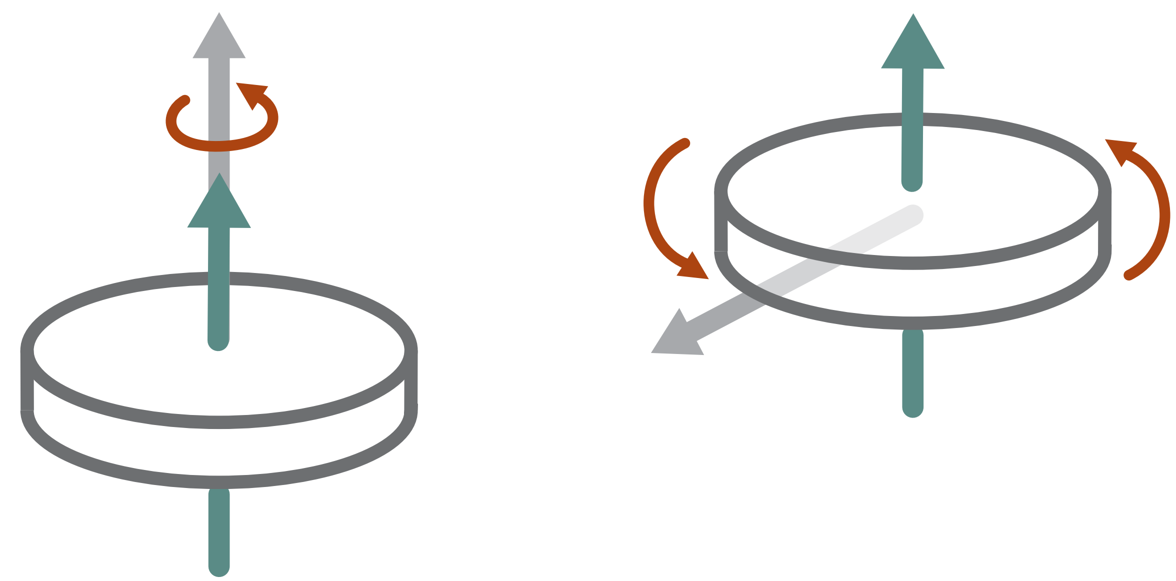
Exercise today

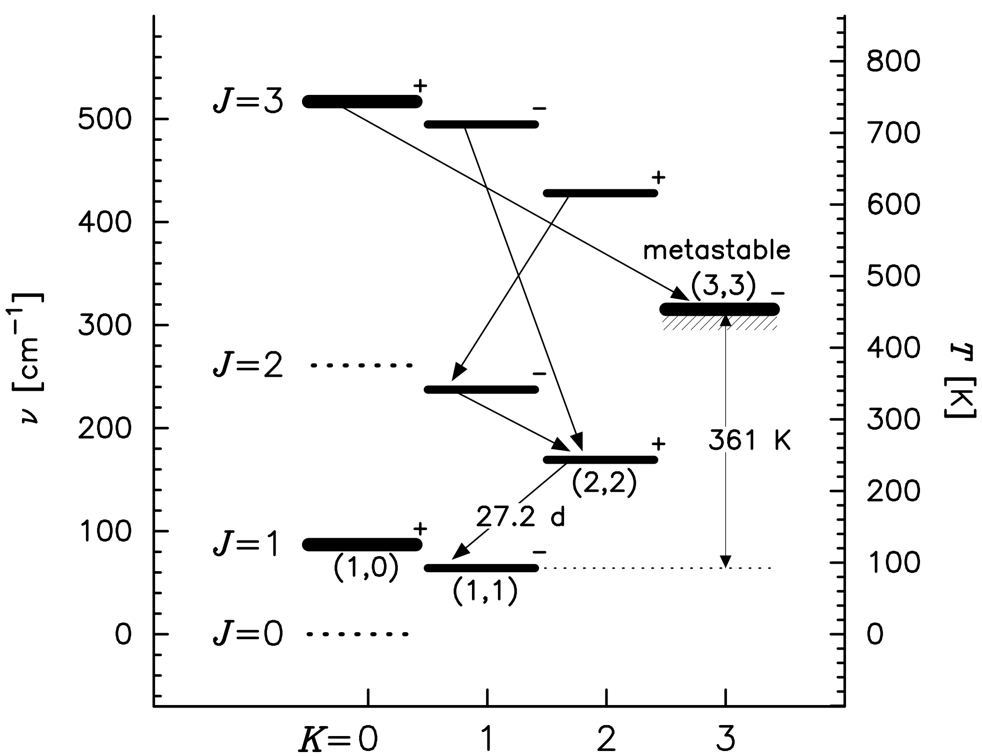
1 how it rotates when

K=0

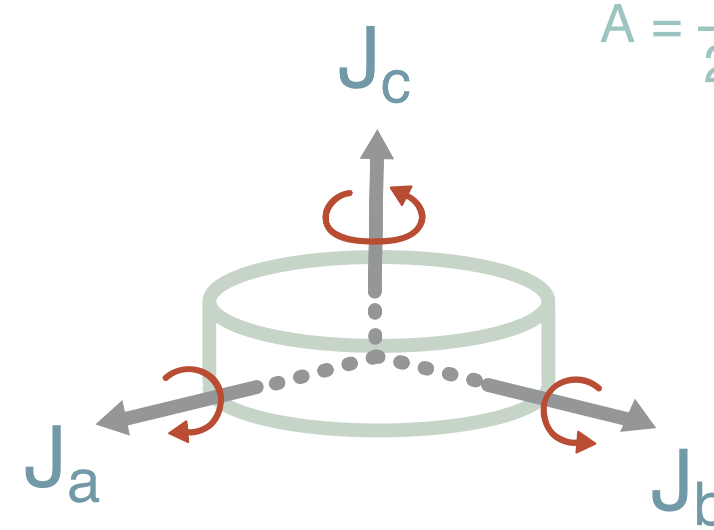
K=J







$A = \frac{1}{2I_a}$



$I_a = I_b < I_c$

$A = B > C$

oblate

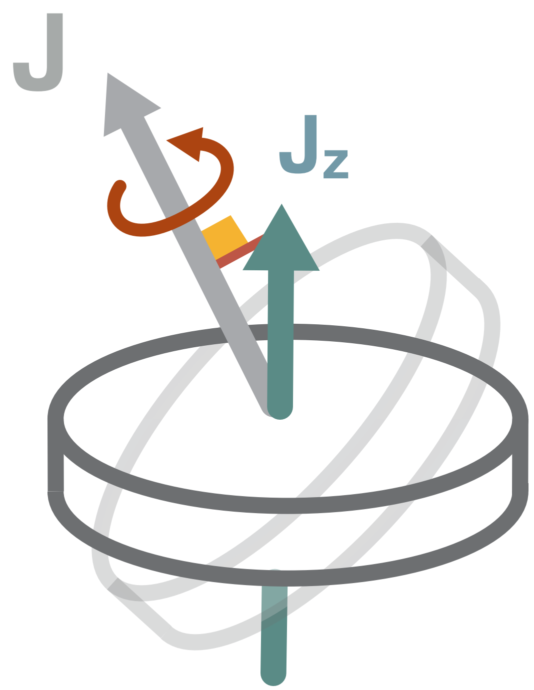
$$E = BJ(J+1) - (B-C)K^2$$

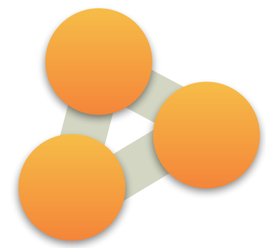
Exercise today

1 how it rotates when

$K=0$

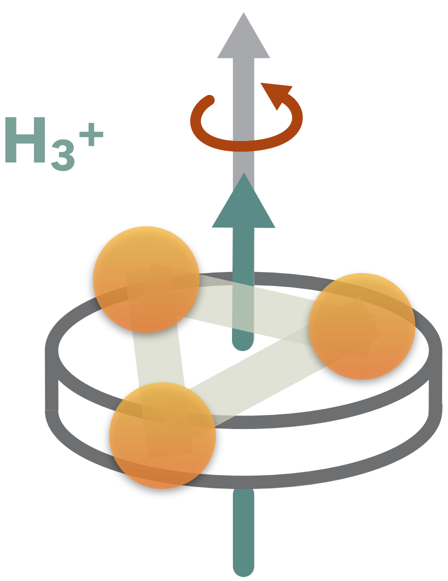
$K=J$

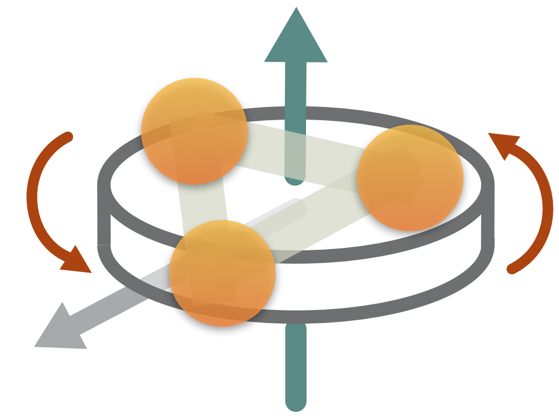




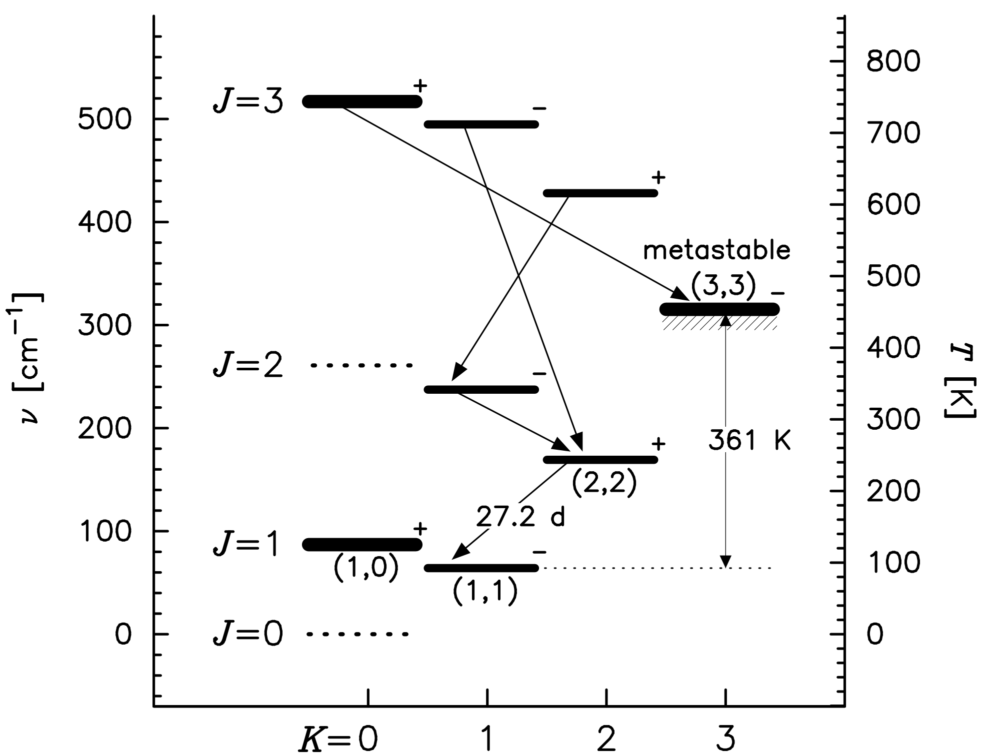
H_3^+

para H_3^+





ortho H_3^+



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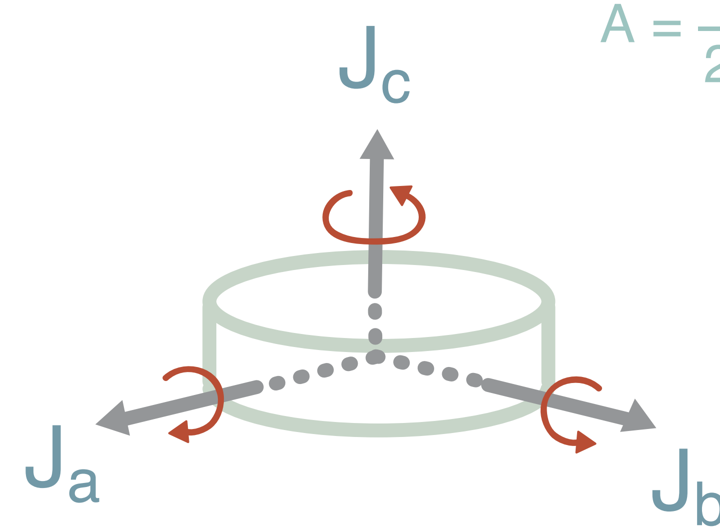

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