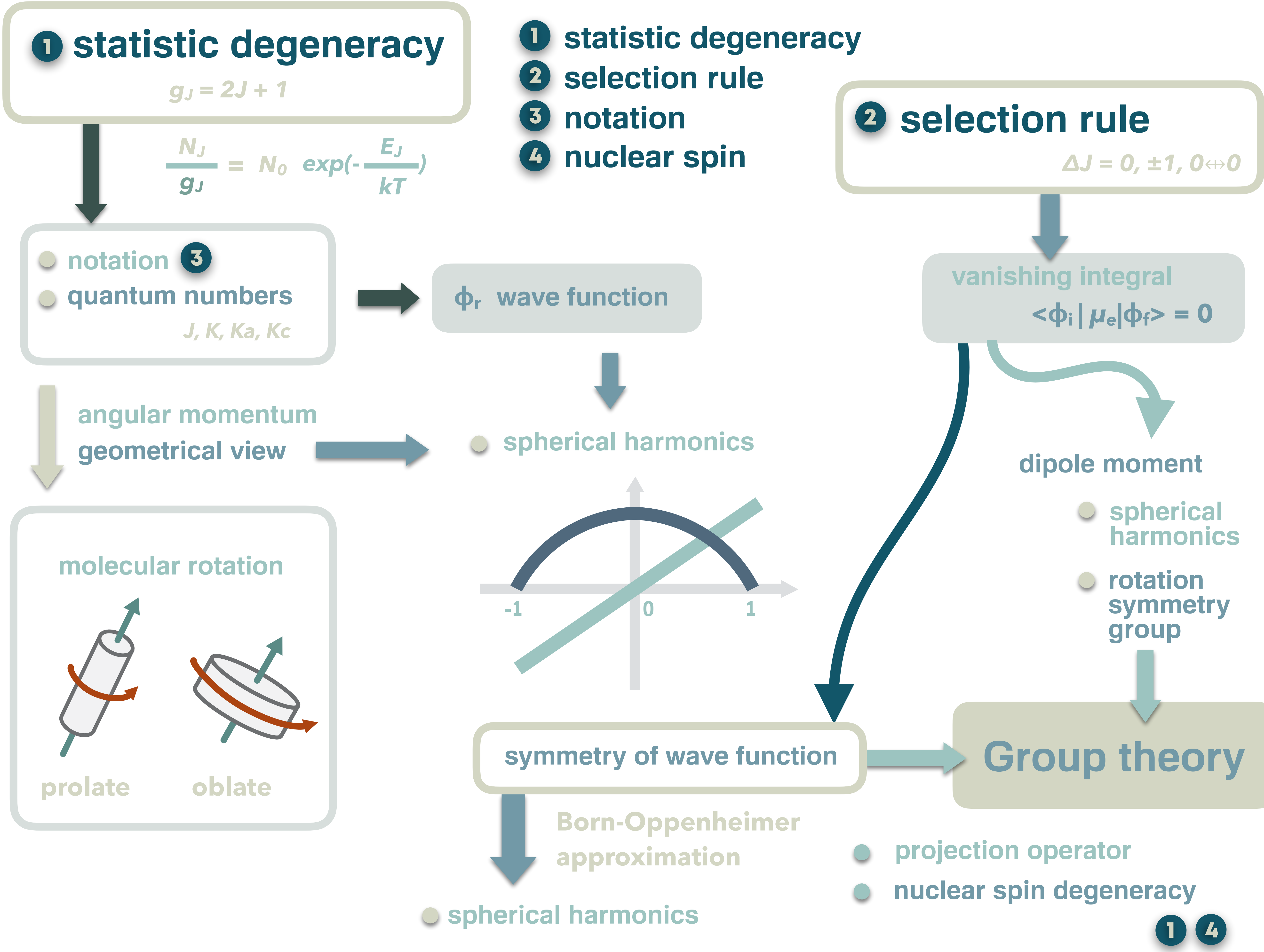
Why it is worthwhile taking time for spherical harmonics?

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 $\Delta J = 0, \pm 1, 0 \leftrightarrow 0$



1 statistic degeneracy
$g_J = 2J + 1$
$\frac{N_J}{g_J} = N_0 \exp(-\frac{E_J}{kT})$
1 statistic degeneracy
2 selection rule
3 notation
4 nuclear spin
2 selection rule
$\Delta J = 0, \pm 1, 0 \nleftrightarrow 0$
notation 3
quantum numbers
J, K, Ka, Kc
ϕ_r wave function
vanishing integral
$<\phi_i | \mu_e | \phi_f> = 0$
angular momentum
geometrical view
spherical harmonics
dipole moment
spherical harmonics
rotation symmetry group
molecular rotation
-1
0
1
prolate
oblate
symmetry of wave function
Group theory
Born-Oppenheimer approximation
projection operator
nuclear spin degeneracy
1 4
spherical harmonics

❷ selection rule

vanishing integral

$\langle \phi_i | \mu_e | \phi_f \rangle = 0$

why transition probability given in this form?

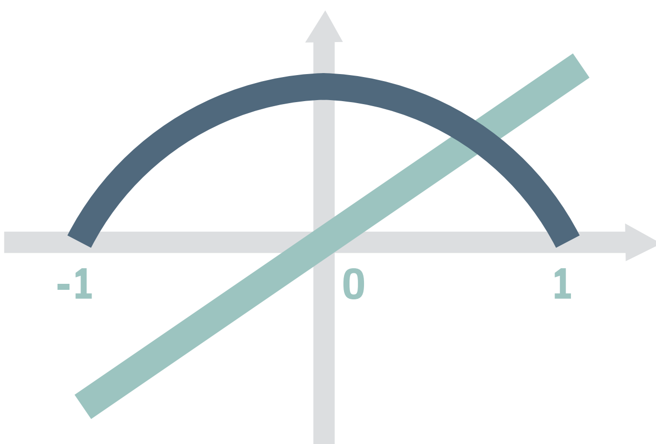
- remember Thomson scattering
- perturbation theory

symmetry of wave function

electric dipole moment

is decomposed to

- spherical harmonics orthogonal



Born-Oppenheimer approximation

H_2 : simple example of vanishing integral

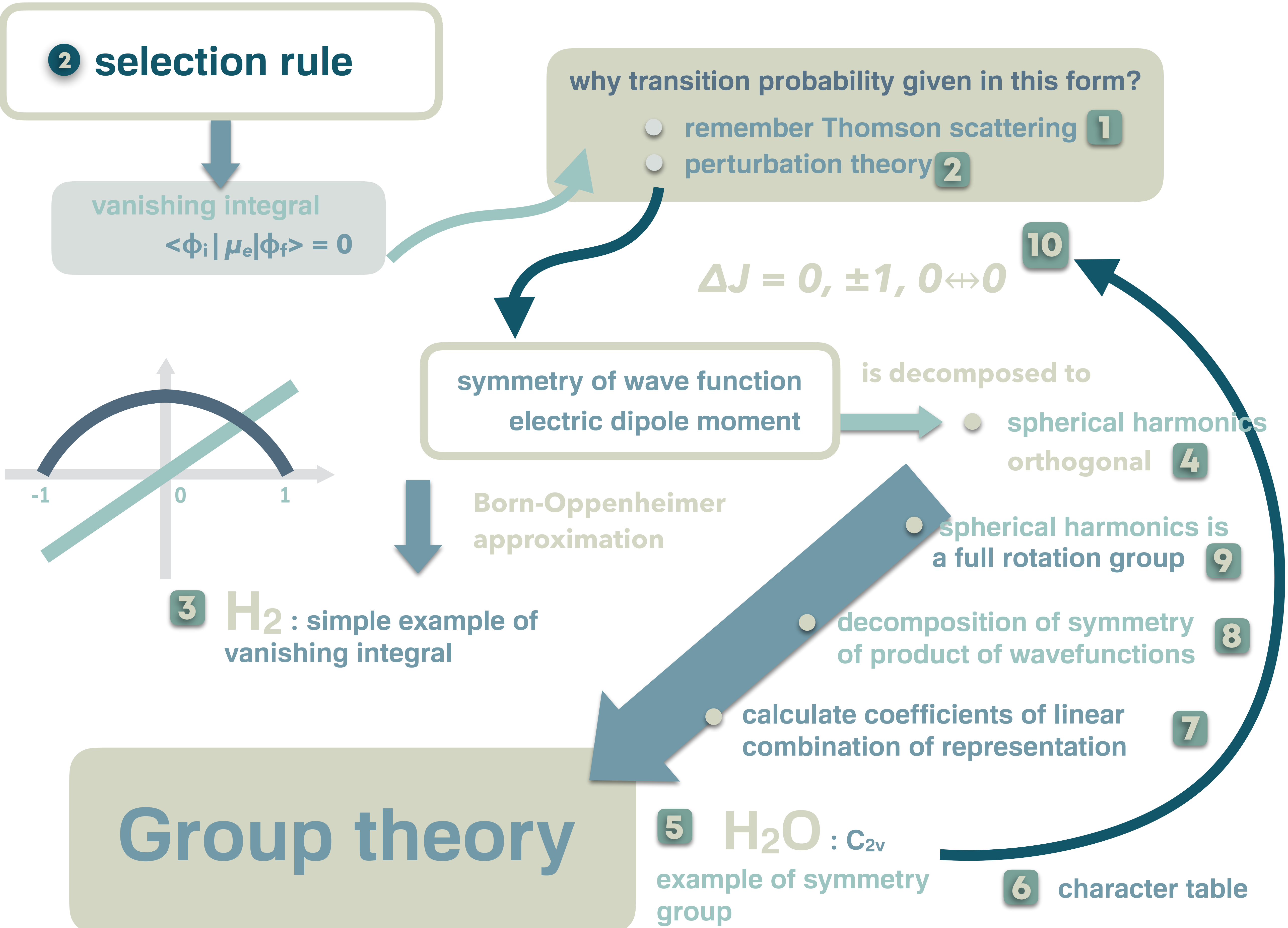
- spherical harmonics is a full rotation group
- decomposition of symmetry of product of wavefunctions
- calculate coefficients of linear combination of representation

Group theory

H_2O : C_{2v}

example of symmetry group

character table


2 selection rule
vanishing integral
$\langle \phi_i | \mu_e | \phi_f \rangle = 0$
why transition probability given in this form?
remember Thomson scattering 1
perturbation theory 2
10
$\Delta J = 0, \pm 1, 0 \leftrightarrow 0$
symmetry of wave function
electric dipole moment
is decomposed to
spherical harmonics
orthogonal 4
-1
0
1
Born-Oppenheimer approximation
spherical harmonics is a full rotation group 9
3 H_2 : simple example of vanishing integral
decomposition of symmetry of product of wavefunctions 8
calculate coefficients of linear combination of representation 7
Group theory
5 H_2O : C_{2v}
example of symmetry group
6 character table

Selection rule

1. $< \phi_1 | \mu_e | \phi_2 >$

   we have learned **transition probability** is

2. $< \phi_1 | \mu_e | \phi_2 > = 0$ when

   that **transition** would no happen

3. $\Delta J = \pm 1$ only **transition** that are allowed

4. how strong would that **transition** we would not know

Selection rule

$\Delta J = 0, \pm 1$ only **transitions** that are possible

1. μ_e is Y_{10}
2. $\langle Y_{J'm'} | Y_{Jm} \rangle = \Gamma^{J-J'} + \dots$

↓ full **rotation group**

3. $\langle \phi_1 | \mu_e | \phi_2 \rangle$ $\langle Y_{Jm} | Y_{10} | Y_{J'm'} \rangle$
4. integral non-zero only when $\Delta J = 0, \pm 1$

Rotation group

1 add A and B and take mod 4

	0	1	2	3
0	0	1	2	3
1	1	2	3	0
2	2	3	0	1
3	3	0	1	2

A (columns), B (rows)

2 multiply A and B and take last digit

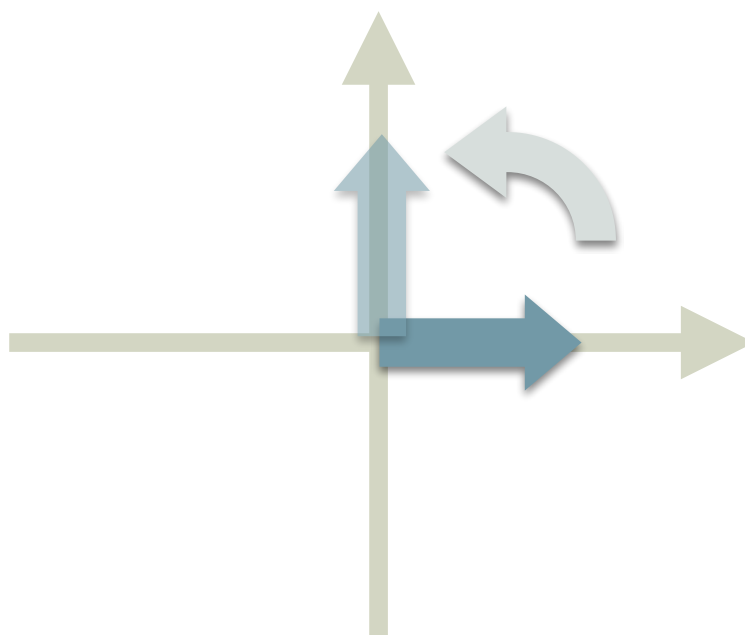
	1	3	9	7
1	1	3	9	7
3	3	9	7	1
9	9	7	1	3
7	7	1	3	9

A (columns), B (rows)

3 rotate by A and then by B

	0	$\pi/2$	π	$3\pi/2$
0	0	$\pi/2$	π	$3\pi/2$
$\pi/2$	$\pi/2$	π	$3\pi/2$	0
π	π	$3\pi/2$	0	$\pi/2$
$3\pi/2$	$3\pi/2$	0	$\pi/2$	π

A (columns), B (rows)

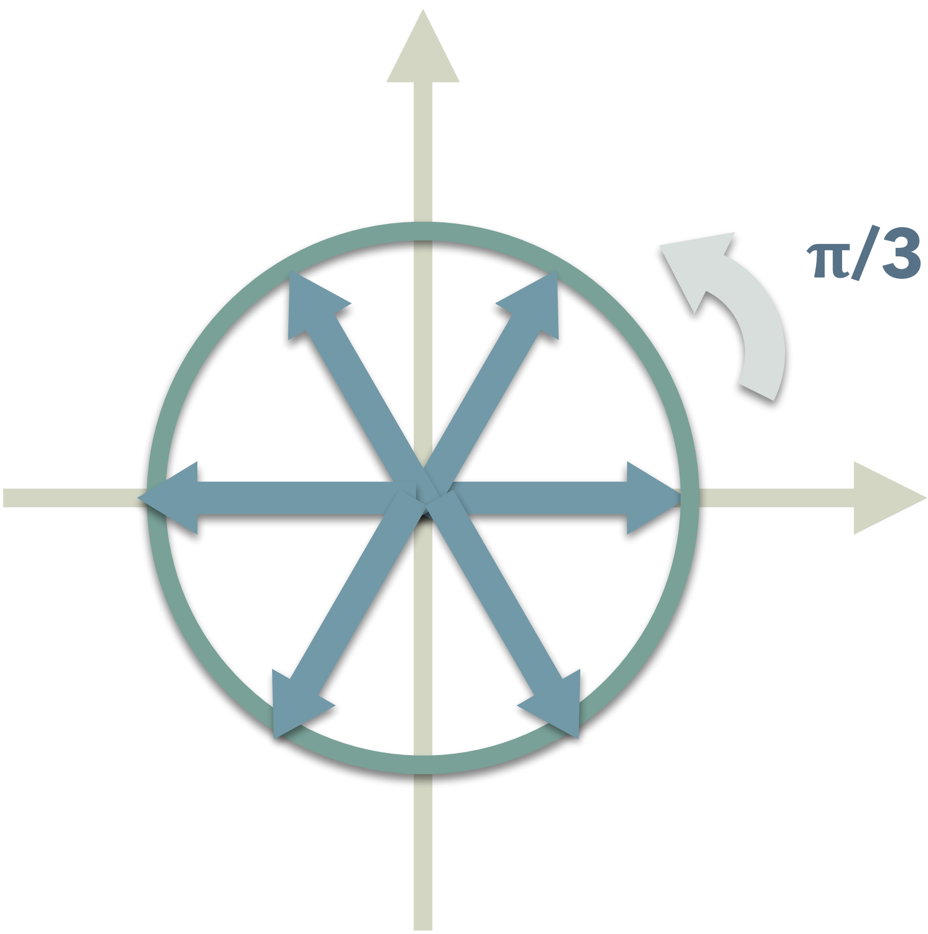


Rotation group

1 add **A** and **B** and take mod 4

	0	1	2	3
0	0	1	2	3
1	1	2	3	0
2	2	3	0	1
3	3	0	1	2

A (columns), B (rows)



3 rotate by **A** and then by **B**

	0	π/2	π	3π/2
0	0	π/2	π	3π/2
π/2	π/2	π	3π/2	0
π	π	3π/2	0	π/2
3π/2	3π/2	0	π/2	π

A (columns), B (rows)

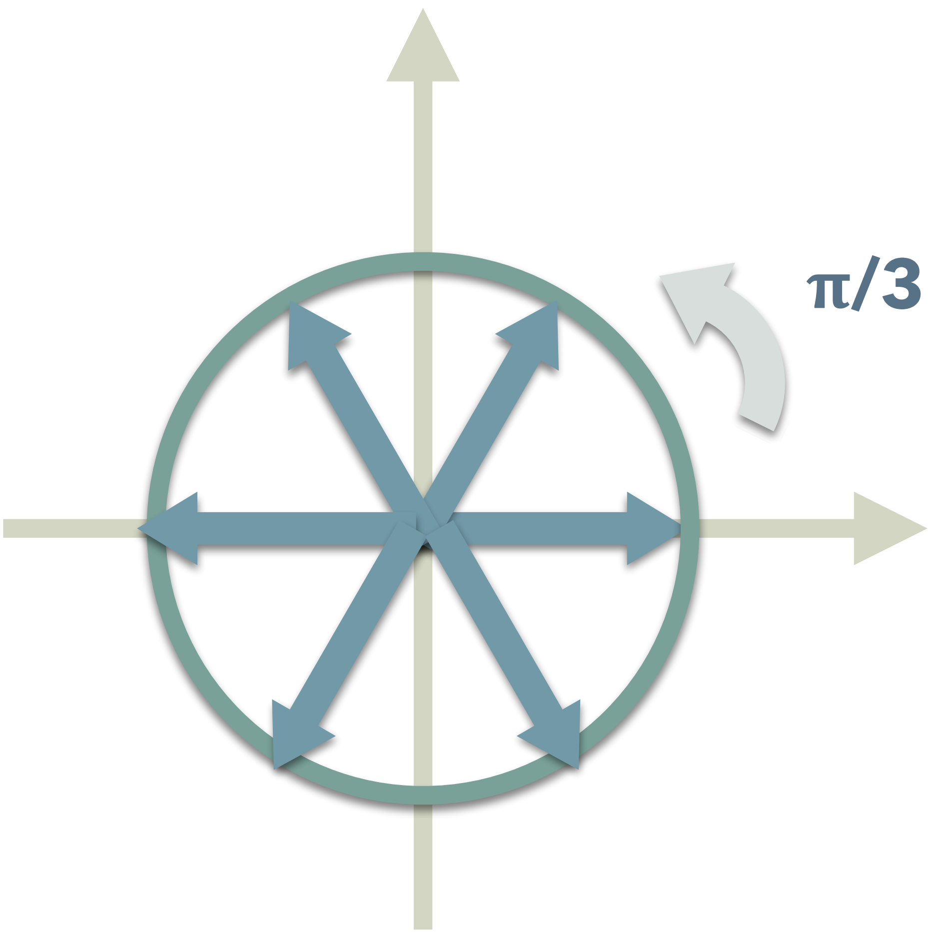
Rotation group

1 add A and B and take mod 6

	0	1	2	3	4	5
0	0	1	2	3	4	5
1	1	2	3	4	5	0
2	2	3	4	5	0	1
3	3	4	5	0	1	2
4	4	5	0	1	2	3
5	5	0	1	2	3	4

A

B



3 rotate by A and then by B

	0	π/3	2π/3	π	4π/3	5π/3
0	0	π/3	2π/3	π	4π/3	5π/3
π/3	π/3	2π/3	π	4π/3	5π/3	0
2π/3	2π/3	π	4π/3	5π/3	0	π/3
π	π	4π/3	5π/3	0	π/3	2π/3
4π/3	4π/3	5π/3	0	π/3	2π/3	π
5π/3	5π/3	0	π/3	2π/3	π	4π/3

A

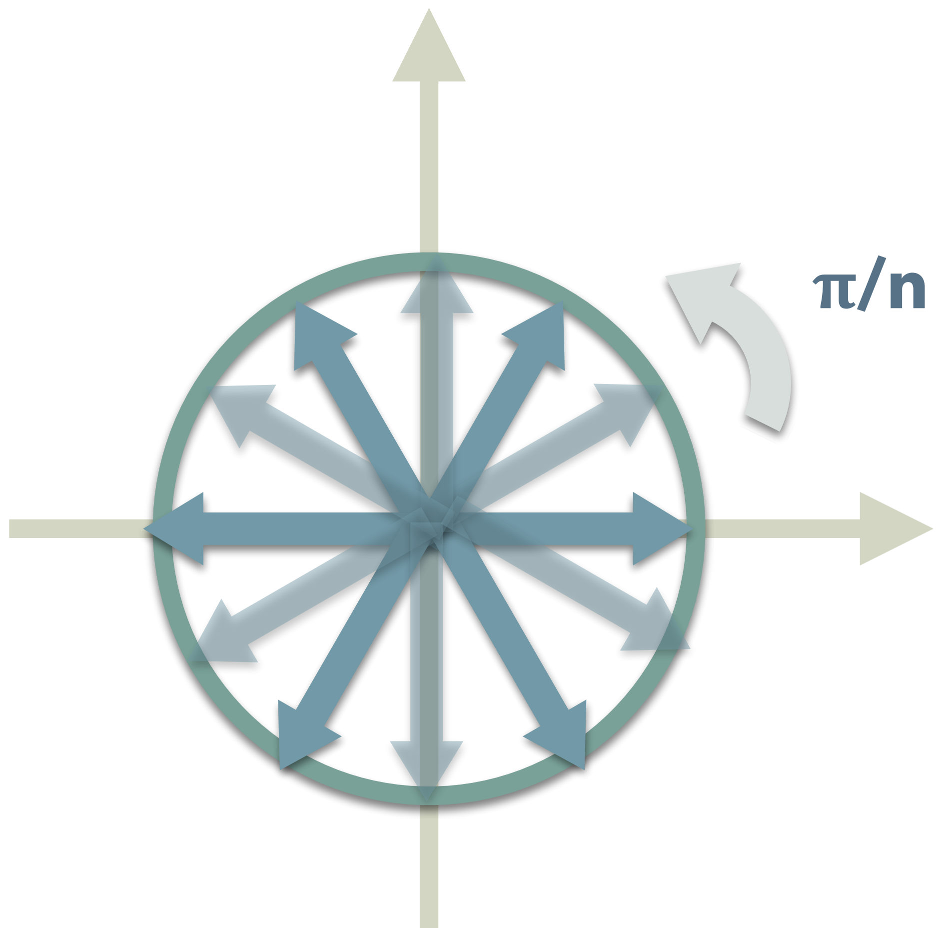
B

Rotation group

1 add A and B and take mod 6

	0	1	2	3	4	5
0	0	1	2	3	4	5
1	1	2	3	4	5	0
2	2	3	4	5	0	1
3	3	4	5	0	1	2
4	4	5	0	1	2	3
5	5	0	1	2	3	4

A (columns), B (rows)

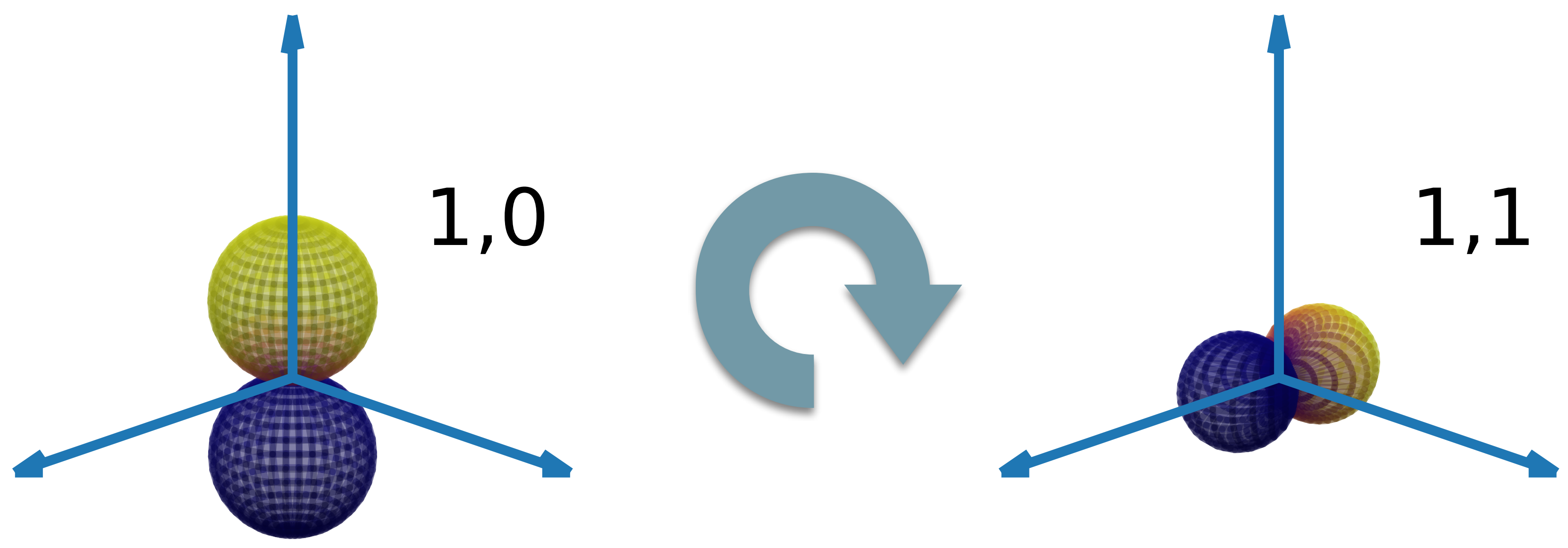


3 rotate by A and then by B

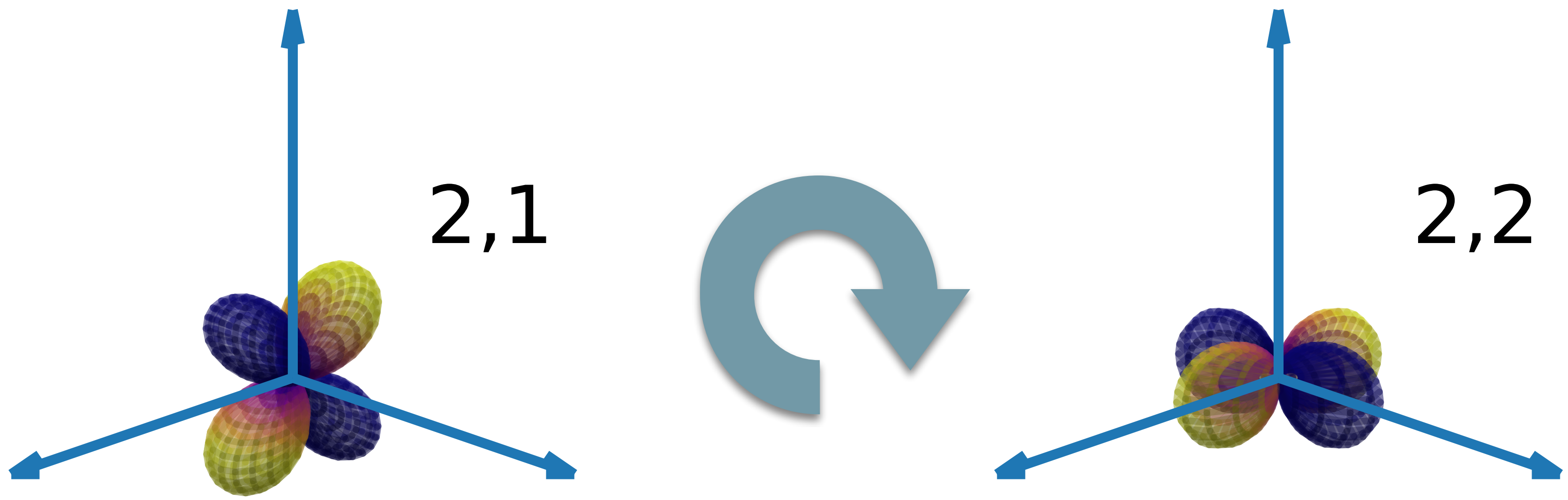
	0	π/3	2π/3	π	4π/3	5π/3
0	0	π/3	2π/3	π	4π/3	5π/3
π/3	π/3	2π/3	π	4π/3	5π/3	0
2π/3	2π/3	π	4π/3	5π/3	0	π/3
π	π	4π/3	5π/3	0	π/3	2π/3
4π/3	4π/3	5π/3	0	π/3	2π/3	π
5π/3	5π/3	0	π/3	2π/3	π	4π/3

A (columns), B (rows)

Spherical harmonics consists of a rotation group

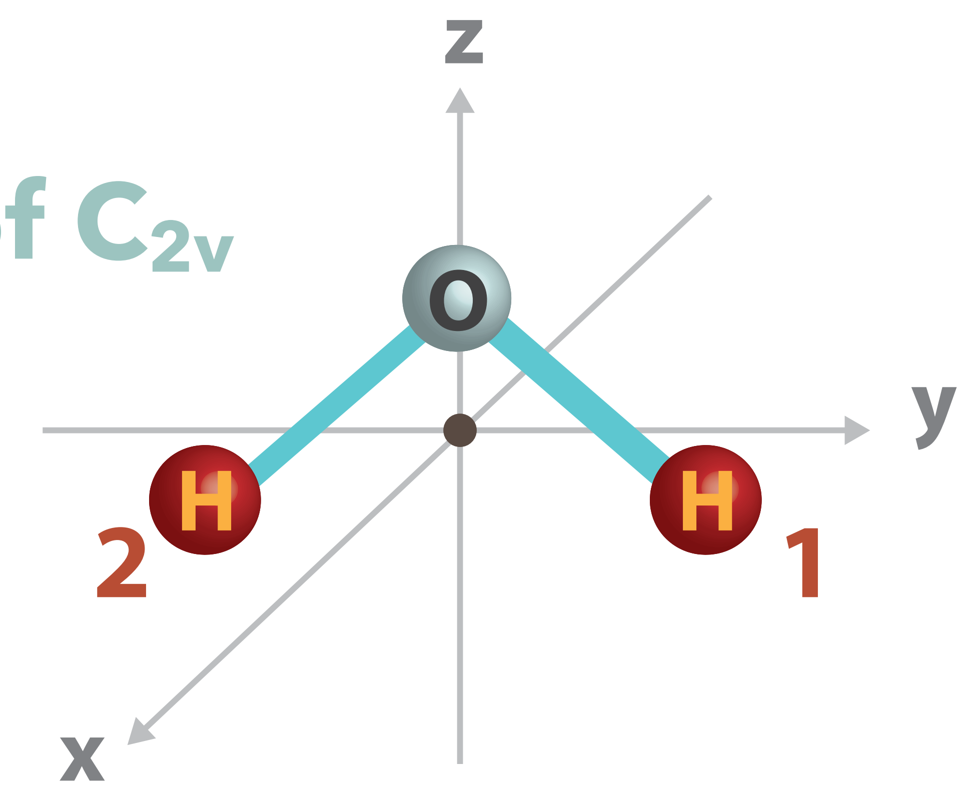


Spherical harmonics consists of a rotation group



Character table

of C_{2v}



E identity operator (do nothing)
"Einheit"

C_2 rotation of $\pi/2$ about **z** axis

$\sigma_v(xz)$ reflection about **xz** plane

Character

order of group :
number of symmetry elements

symmetry operations →

symmetry label → (representative)

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	h=4	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	-1	1	x, R_y	xz
B_2	1	-1	1	-1	y, R_x	yz

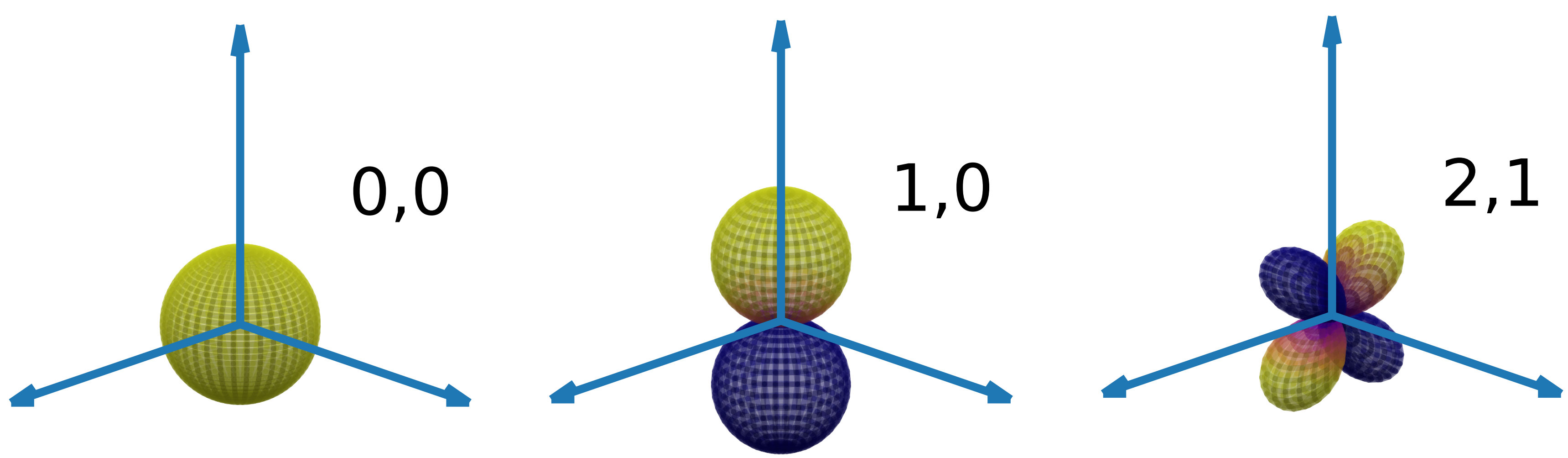
representation
(set of representatives)

base functions

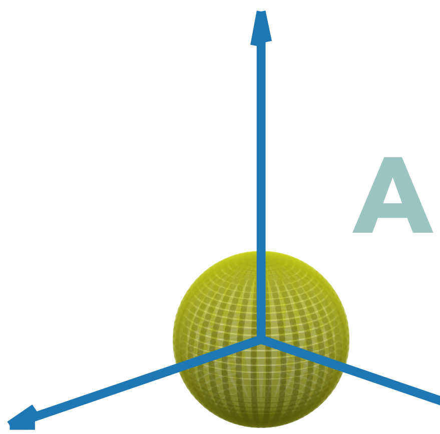
cross term
base functions

Character table Rotation group

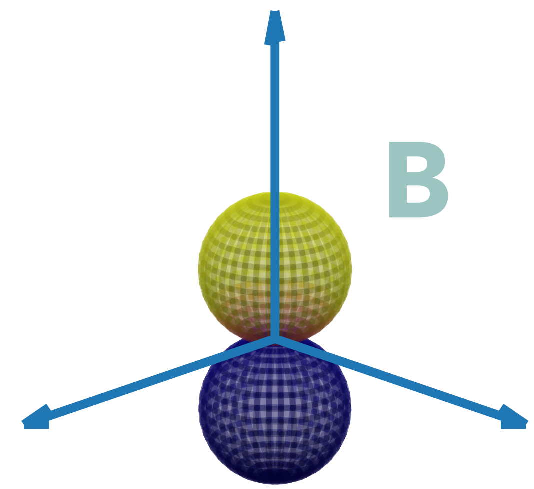
	E	π	θ	...	θ/n	h=∞
$\Gamma^{(0)}$	1	1	1	1	1	Y_{00}
$\Gamma^{(1)}$	3	-1				Y_{1m}
$\Gamma^{(2)}$	5	1				Y_{2m}
$\Gamma^{(3)}$	7	-1				Y_{3m}
...						...
$\Gamma^{(J)}$	2J+1		$\frac{\sin(J+\frac{1}{2})\theta}{\sin\frac{1}{2}\theta}$			Y_{Jm}



Coupling angular momenta



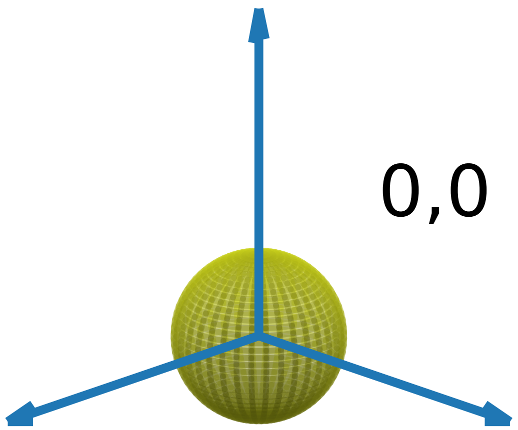
$\langle f_A | f_B \rangle$



$$\Gamma^{(A)} \otimes \Gamma^{(B)} = \Gamma^{(|A-B|)} \oplus \Gamma^{(|A-B|+1)} \oplus \,.\,.\, \oplus \Gamma^{(A+B-1)} \oplus \Gamma^{(A+B)}$$

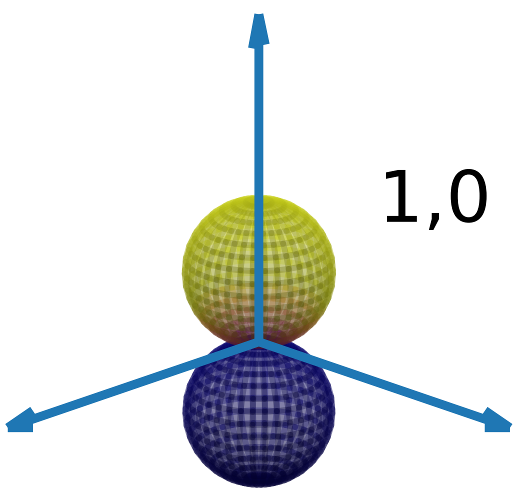
in **rotation group**

Coupling angular momenta



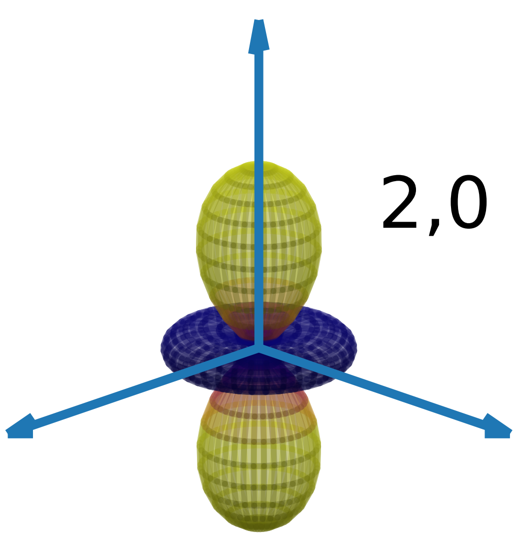
$$\Gamma^{(l_1)} \otimes \Gamma^{(l_2)} = \Gamma^{(|l_1 - l_2|)} \oplus \ldots \oplus \Gamma^{(l_1 + l_2)}$$

$$\Gamma^{(J_1)} \otimes \Gamma^{(J_2)} = \Gamma^{(|J_1 - J_2|)} \oplus \ldots \oplus \Gamma^{(J_1 + J_2)}$$



$$< Y_{00} | Y_{10} >$$

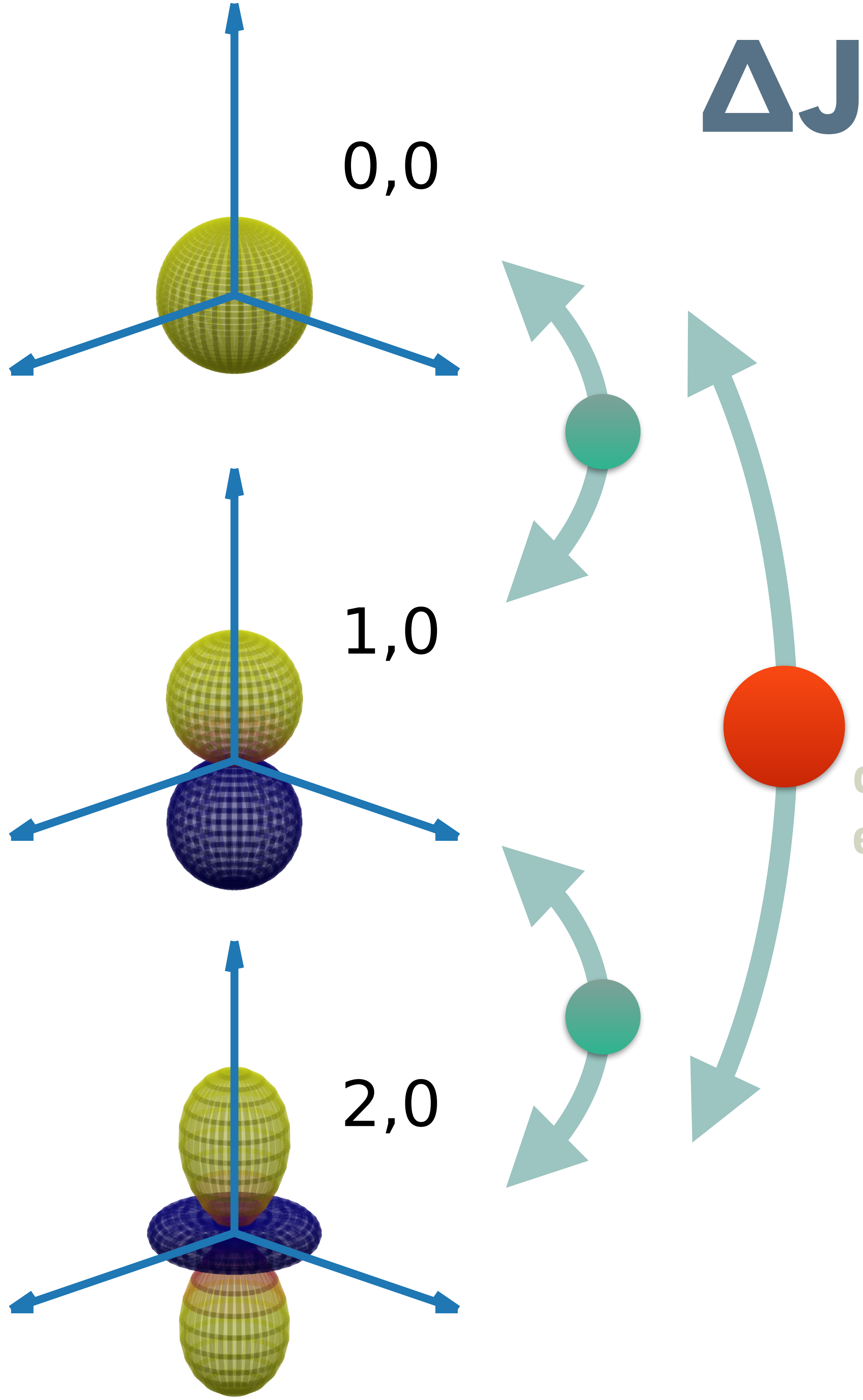
$$\Gamma^{(0)} \otimes \Gamma^{(1)} = \Gamma^{(1)}$$



$$< Y_{10} | Y_{10} >$$

$$\Gamma^{(1)} \otimes \Gamma^{(1)} = \Gamma^{(0)} \oplus \Gamma^{(1)} \oplus \Gamma^{(2)}$$

$\Delta J = 0, \pm 1$



wavefunction

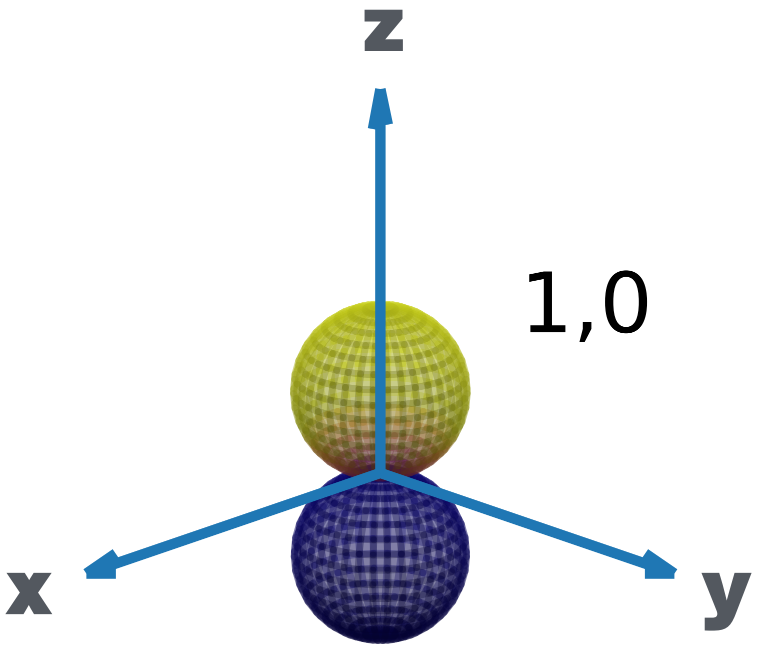
$$Y_{Jm}(z, \phi) = \Theta_{Jm}(z)\Phi_m(\phi)$$

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

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

does not happen
even if incoming energy is enough

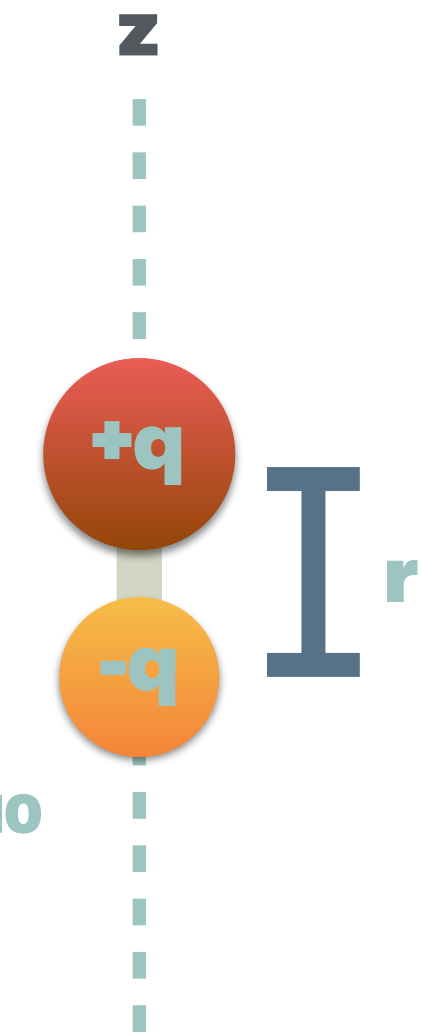
1. pure rotational transition
2. linear / asymmetric top
3. or vibrational state totally symmetric



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

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

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

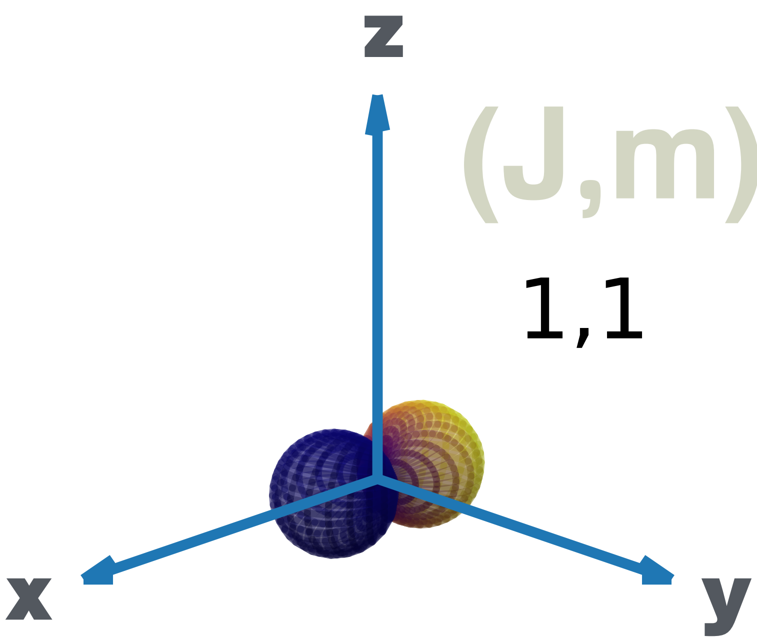


$$\mu_e = qr$$
$$= qz$$
$$= qY_{10}$$

$$Y_{10}(z,\phi) = z$$

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

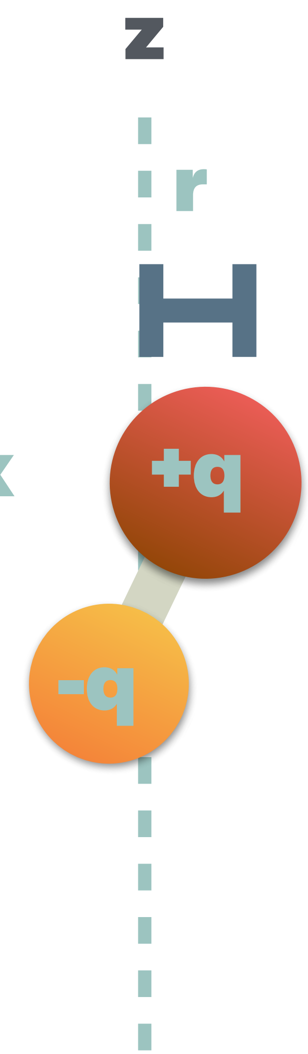
$$< \phi_1 | \mu_{ez} | \phi_2 > = < Y_{Jm} | Y_{10} | Y_{J'm'} >$$



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

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

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



$\mu_{ex} = qx$

$$Y_{11} + Y_{1-1} = \sin\theta\cos\phi$$

$$= x$$

$$Y_{11} - Y_{1-1} = \sin\theta\sin\phi$$

$$= y$$

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

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

$$= \sin\theta$$

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

$$\Phi_{-1}(\phi) = e^{-i\phi}$$

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

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

$$= -\frac{1}{2}\sin\theta$$

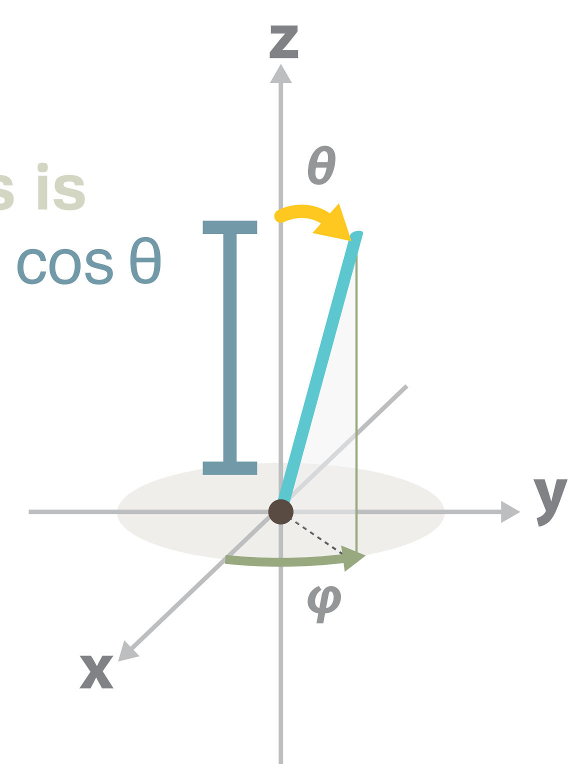
with appropriate normalization factor

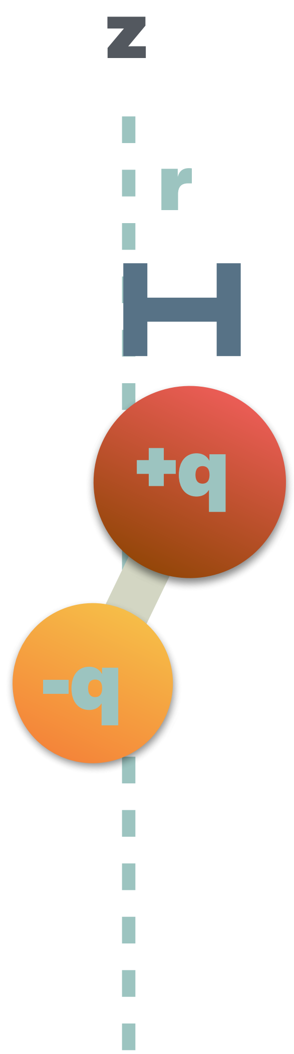
$$\sqrt{\frac{(J-m)!}{(J+m)!}}$$

$$= -\sin\theta$$

this is

$z = \cos\theta$





$\mu_{ex} = qx = Y_{11} + Y_{1-1}$

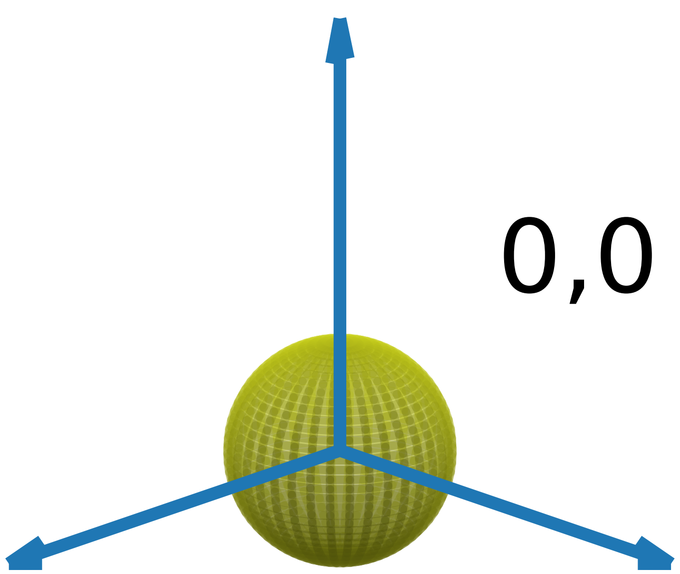
$\mu_{ey} = qy = Y_{11} - Y_{1-1}$

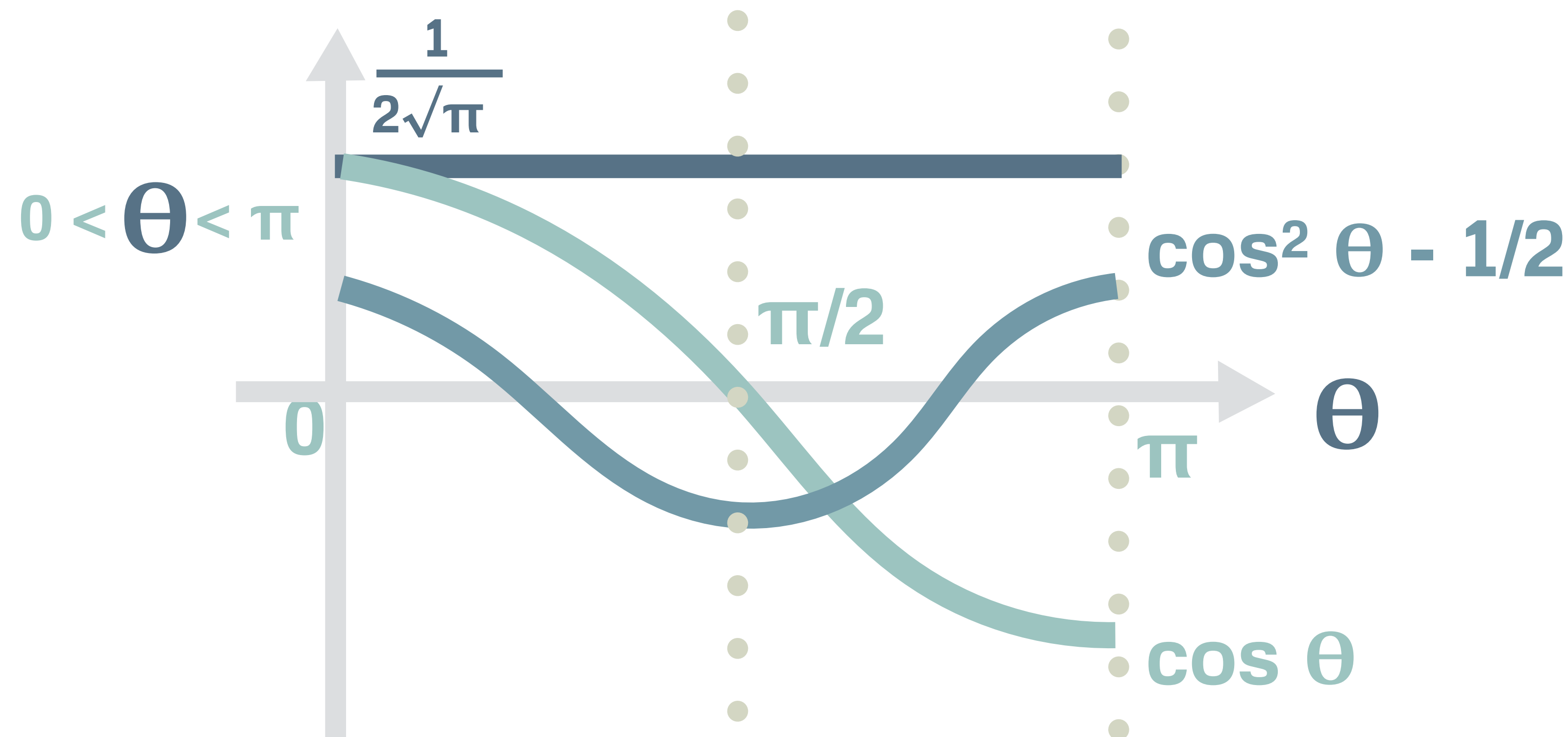
$\mu_{ez} = qz = Y_{10}$

$$< \phi_1 | \mu_e | \phi_2 > = < Y_{Jm} | Y_{1(1,0,-1)} | Y_{J'm'} >$$

in order for ≠ 0 after integration

need totally symmetric term like A_1





in order for $< Y_{Jm} | Y_{1m_1} | Y_{J'm'} > \neq 0$

$$\Gamma^{(J)} \otimes \Gamma^{(1)} \otimes \Gamma^{(J')} = \Gamma^{(0)} \oplus \ldots$$

totally symmetric term like A_1

$J_1 \geqq 1$

$$\Gamma^{(J)} \otimes \Gamma^{(1)} = \Gamma^{(|J-1|)} \oplus \Gamma^{(J)} \oplus \Gamma^{(J+1)}$$

1. $J_2-(J_1+1) = 0$

   $\Delta J=+1$

2. $J_2-J_1 = 0$

   $\Delta J=0$ (no radiation)

3. $J_2-(J_1-1) = 0$

   $\Delta J=-1$

$\Delta J=0, \pm 1$

in order for $< Y_{Jm} | Y_{10} | Y_{J'm'} > \neq 0$

$$\Gamma^{(J)} \otimes \Gamma^{(1)} \otimes \Gamma^{(J')} = \underline{\Gamma^{(0)}} \oplus \ldots .$$

totally symmetric term like A_1

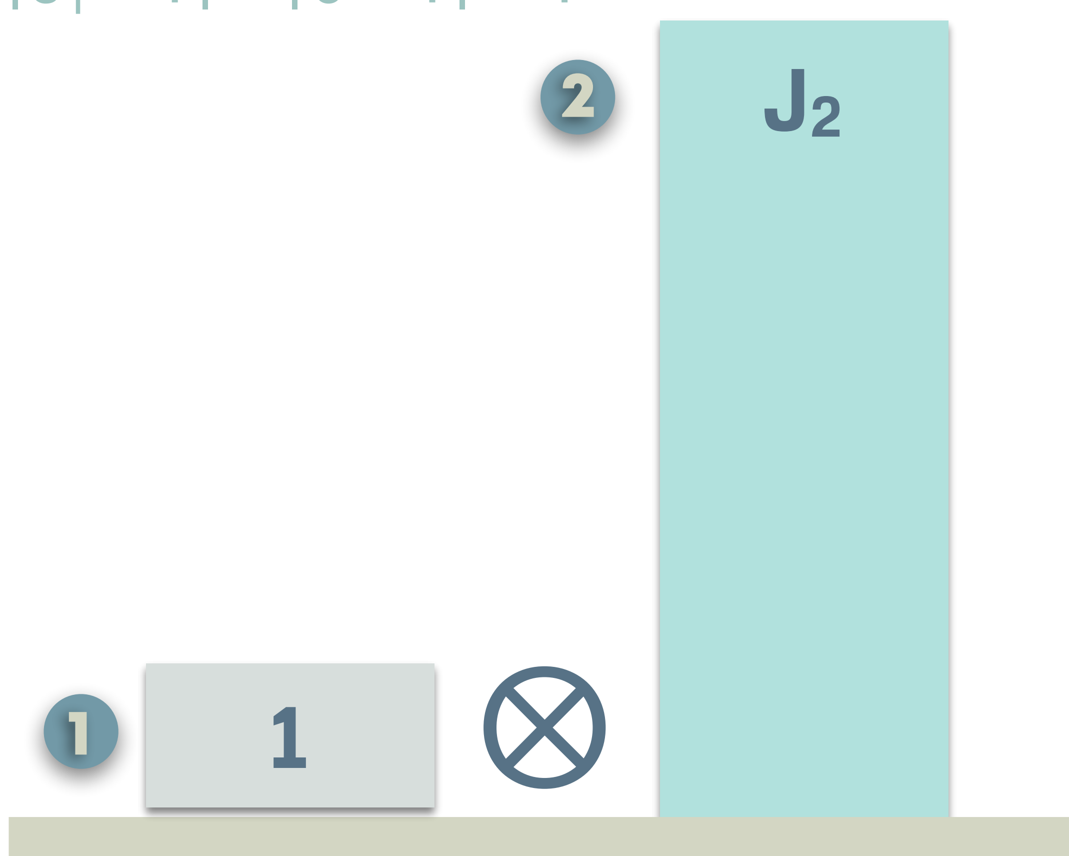
J_1=0

$$\Gamma^{(0)} \otimes \Gamma^{(1)} = \Gamma^{(1)}$$

$$\Gamma^{(J)} \otimes \Gamma^{(1)} = \Gamma^{(|J-1|)} \oplus \Gamma^{(J)} \oplus \Gamma^{(J+1)}$$

$|J_1 + 1| = |0 + 1| = 1$

$|J_1 - 1| = |0 - 1| = 1$



1. **if $J_2 \neq 0$**

   J_2-1 = 0

   ΔJ=+1

2. **if J_2=0**

   $$\Gamma^{(0)} \otimes \Gamma^{(1)} = \Gamma^{(1)}$$

   no $\Gamma^{(0)}$

ΔJ=0, ±1

but **0↮0**

Selection rule how about m?

$$< Y_{Jm} | Y_{1m_1} | Y_{J'm'} > \propto e^{-i(m+m_1-m')\phi}$$

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

$< \phi_1 | \mu | \phi_2 > = \int \phi_1^* \mu \phi_2 d\tau$

$\mu_{ex} = qx = Y_{11} + Y_{1-1}$

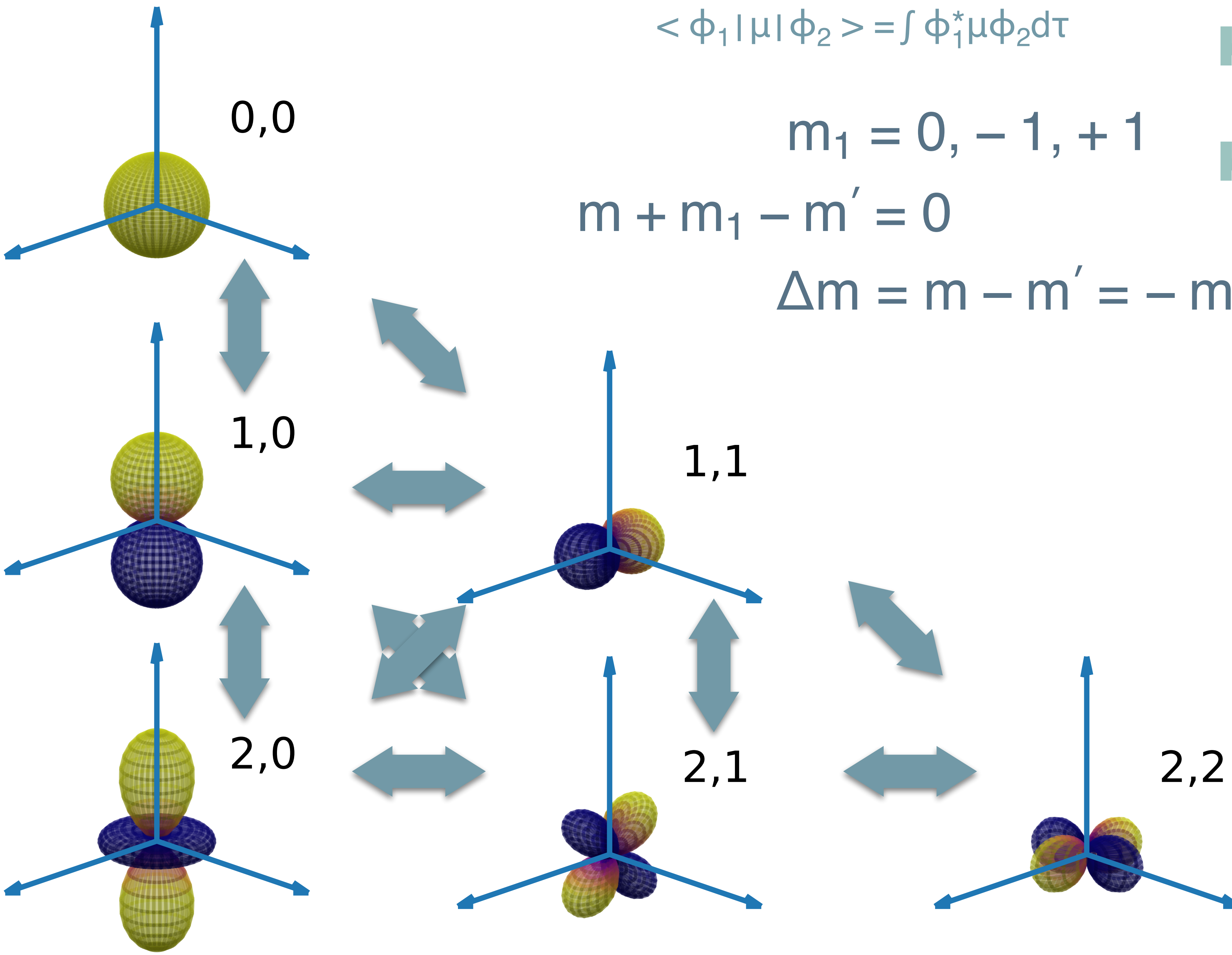
$\mu_{ey} = qy = Y_{11} - Y_{1-1}$

$\mu_{ez} = qz = Y_{10}$

$m_1 = 0, -1, +1$

$m + m_1 - m' = 0$

$\Delta m = m - m' = -m_1 = 0, -1, +1$



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 $\Delta J = 0, \pm 1, 0 \nleftrightarrow 0$