Why it is worthwhile taking time for spherical harmonics?

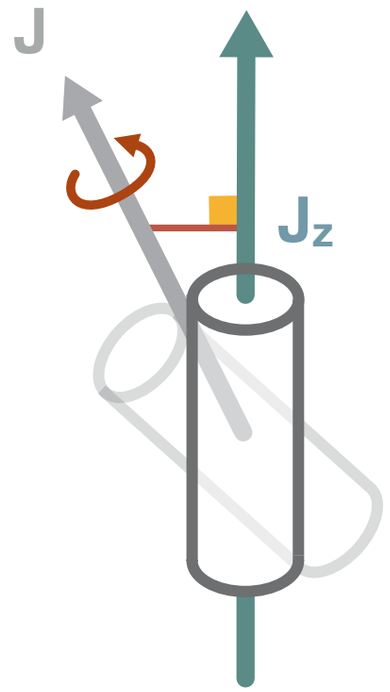
1. it is a wave function — but, of what ?
2. rotational energy — $E = Bh\,J(J+1)$
3. angular momentum — J, K
4. symmetry — $(-1)^J$
5. statistic degeneracy — $g_J = 2J + 1$
6. selection rule — expansion — $\Delta J = 0, \pm 1, 0 \leftrightarrow 0$

Plan today

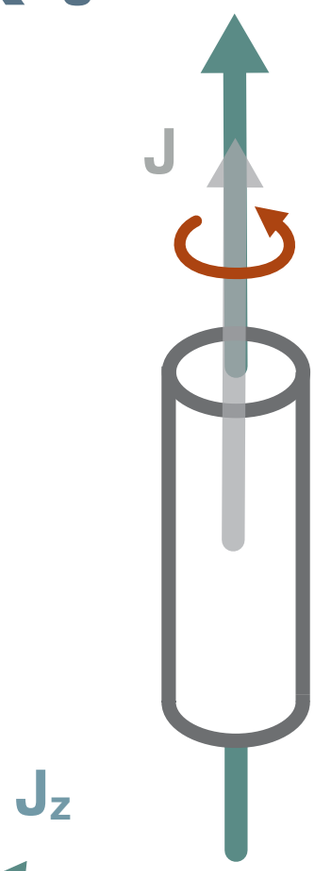
1. correction of last lecture — *m^2 != K^2*
2. perturbation theory — *what is transition?*
3. group theory — *C_{2V} only*
4. H_2 — *what is ortho and para H_2?*
5. Why ortho ↔ para?

---

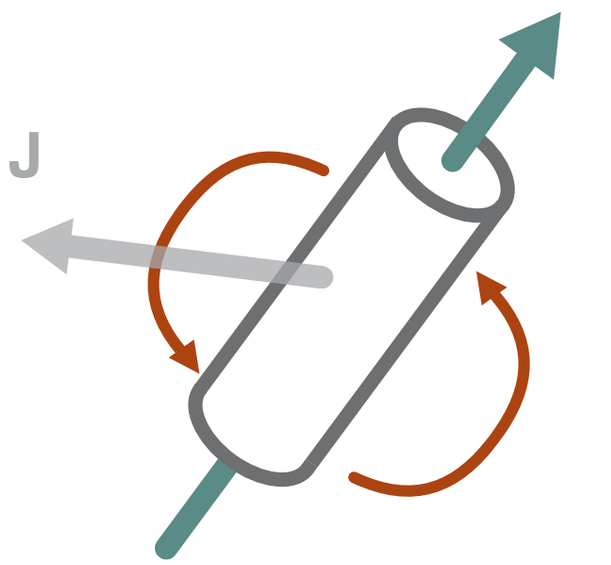
6. selection rule — *$\Delta J = 0, \pm 1, 0 \leftrightarrow 0$*



$K_{=J}$



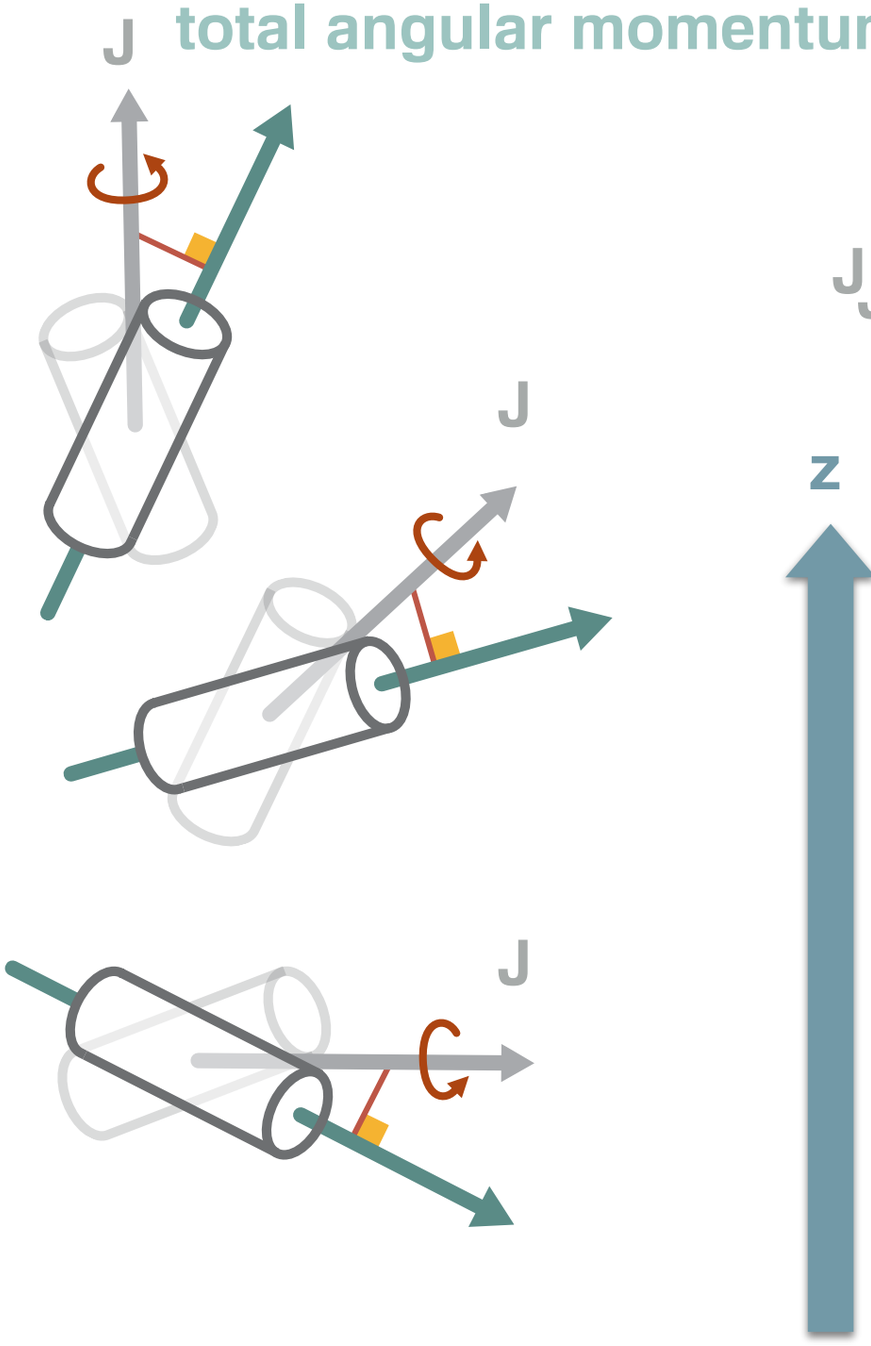
: molecular axis



$K_{=0}$

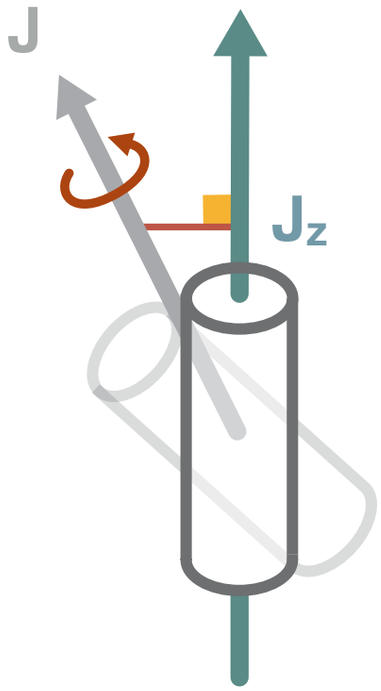
$m_{=J}$

total angular momentum



$m_{=0}$

m : laboratory axis



wavefunction

tilt in lab

$|J, K, m\rangle$

total

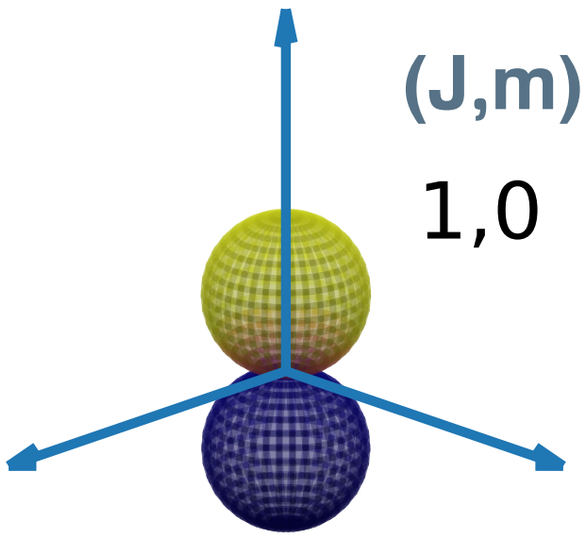
along molecular axis

along laboratory axis

determines total angular momentum

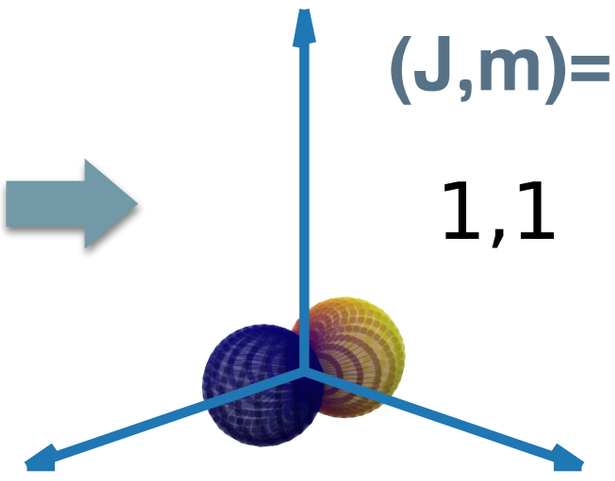
how much angular momentum is along molecular **z** axis

which direction **J** is looking in lab



(J,m)=

1,0



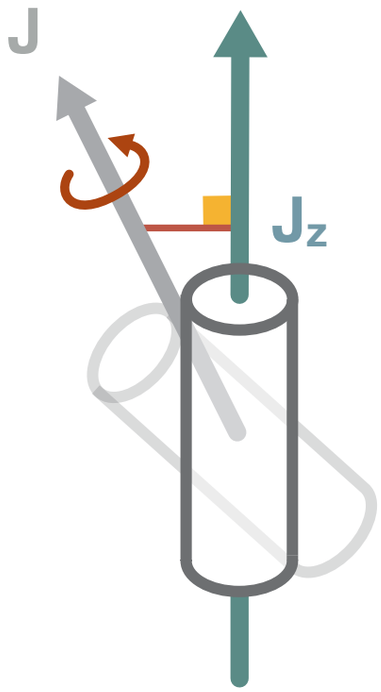
(J,m)=

1,1

which direction **J** is looking does not seem to change the shape of wavefunction

it does

this somehow makes sense, but …



wavefunction

tilt in lab

which direction **J** is looking does not seem to change the shape of wavefunction

|J, K, m>

it does

total

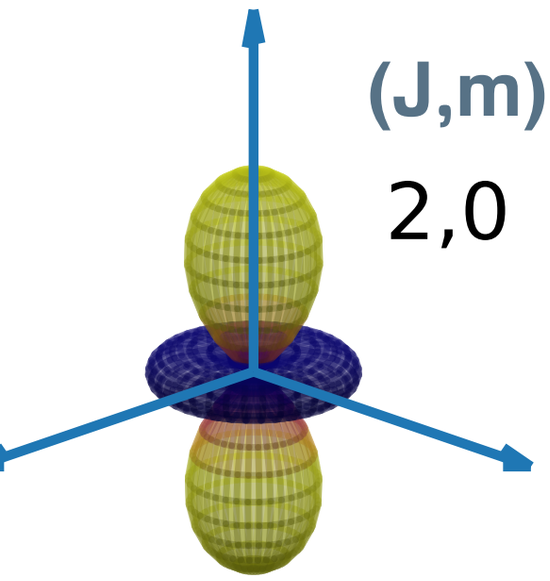
determines total angular momentum

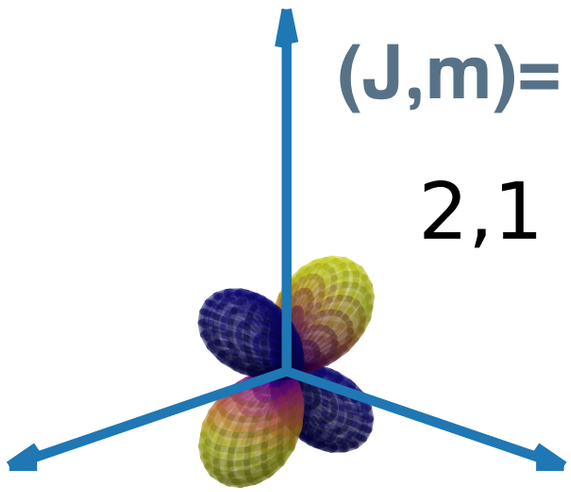
along molecular axis

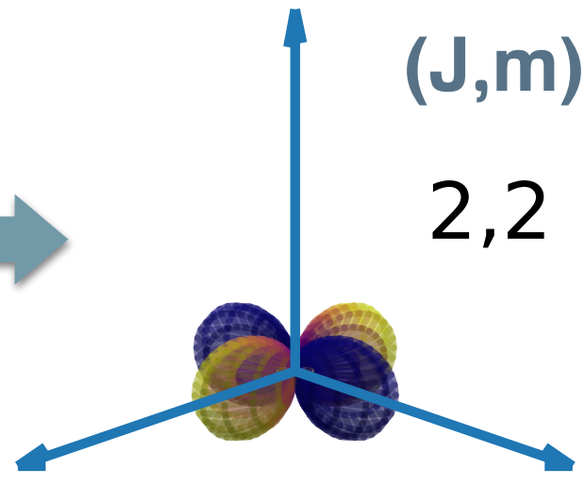
how much angular momentum is along molecular **z** axis

along laboratory axis

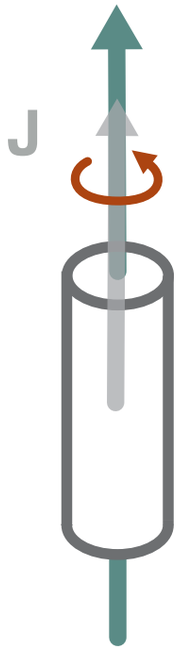
which direction **J** is looking in lab



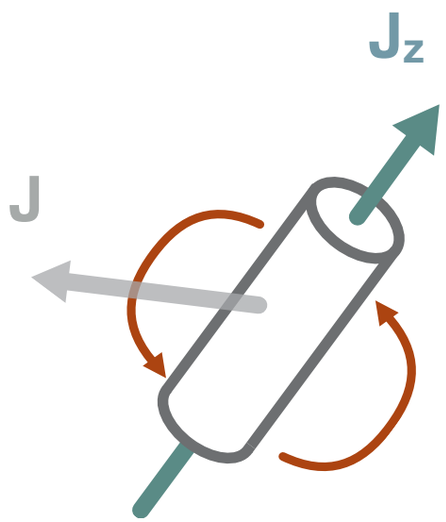




J_z : molecular axis



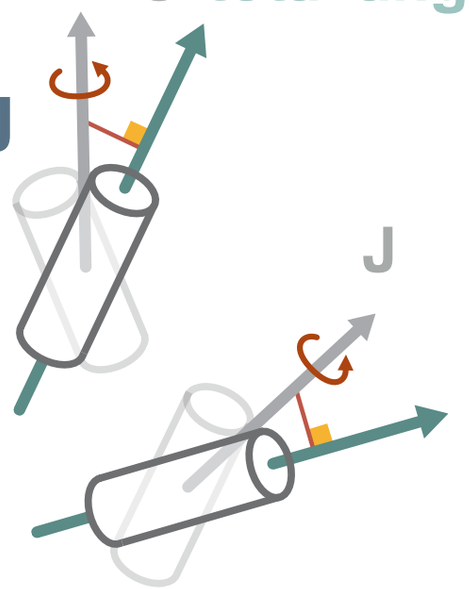
K=J

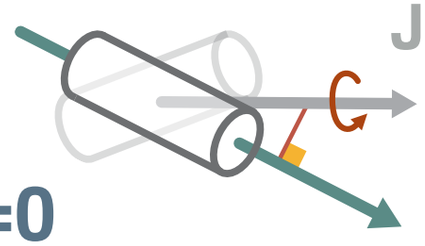


K=0

J total angular momentum

m=J





m=0

: laboratory axis

associated Legendre

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

as long as there is no field

no electric / magnetic field

m does not show up in energy

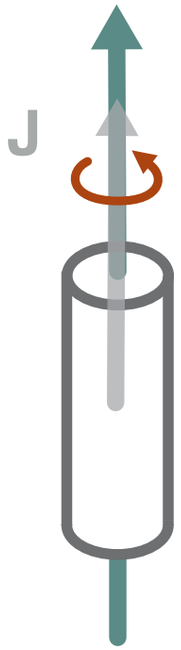
$$E = BJ(J+1)$$

m did not show up here

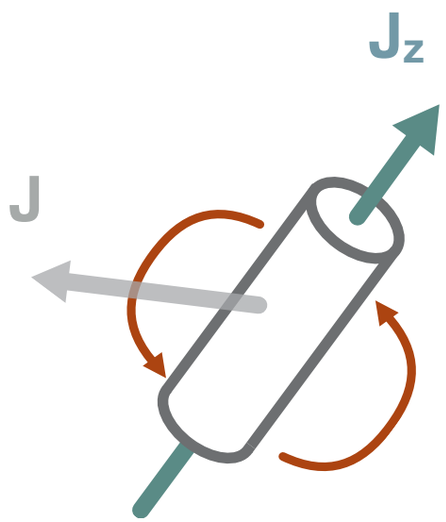
2J + 1

-J, -J+1, ..., J-1, J

J_z : molecular axis



K=J



K=0

K does

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

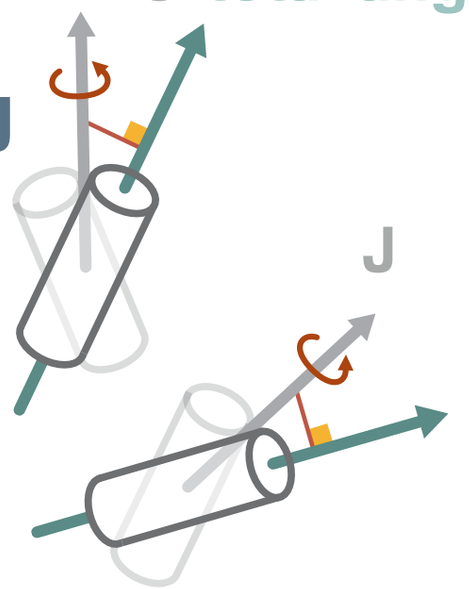
associated Legendre

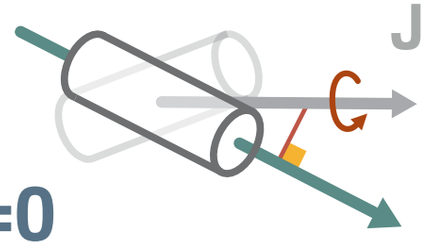
$$\frac{d}{dx}[(1 - x^2)\frac{dv}{ex} + [J(J + 1) - \frac{m^2}{1 - x^2}]v = 0$$

$$E = BJ(J + 1)$$ **m did not show up here**

J total angular momentum

m=J





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: laboratory axis

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

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

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

vanishing integral

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

dipole moment

- spherical harmonics
- rotation symmetry group

Group theory

- projection operator
- nuclear spin degeneracy

1 4

- notation 3
- quantum numbers

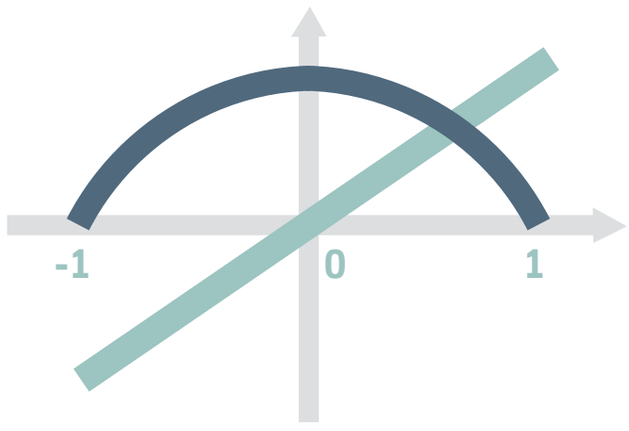
J, K, Ka, Kc

ϕ_r wave function

angular momentum

geometrical view

- spherical harmonics

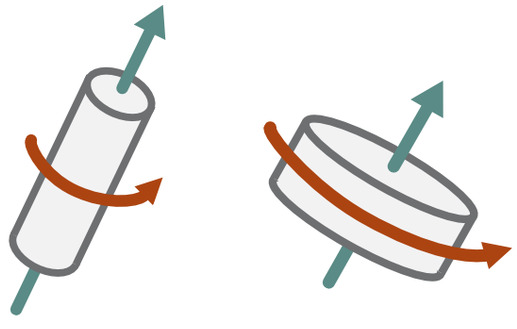


symmetry of wave function

Born-Oppenheimer approximation

- spherical harmonics

molecular rotation



prolate oblate

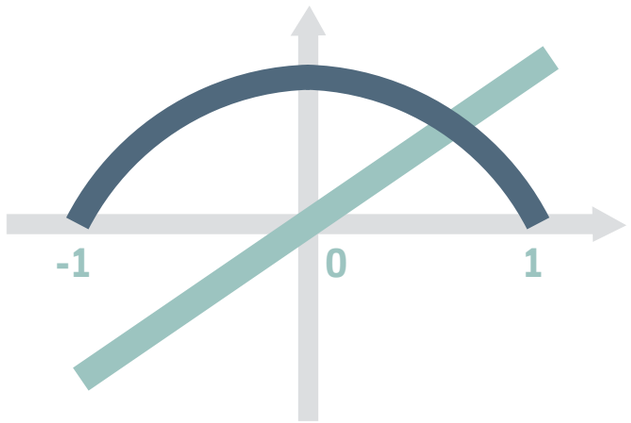
❷ selection rule

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?

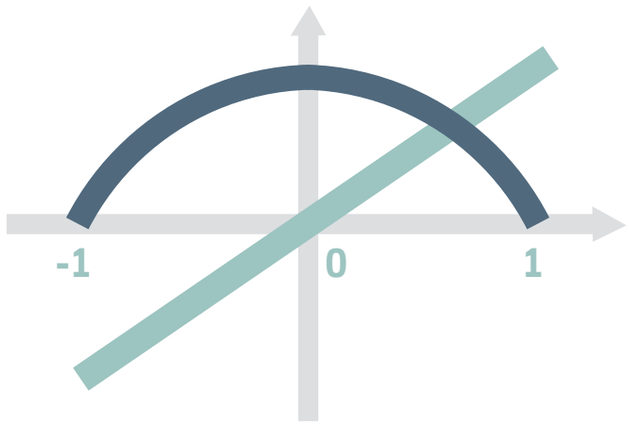
- remember Thomson scattering 1
- perturbation theory 2

$\Delta J = 0, \pm 1, 0 \leftrightarrow 0$ 10

symmetry of wave function
electric dipole moment

is decomposed to

- spherical harmonics orthogonal 4



Born-Oppenheimer approximation

- spherical harmonics is a full rotation group 9
- decomposition of symmetry of product of wavefunctions 8
- calculate coefficients of linear combination of representation 7

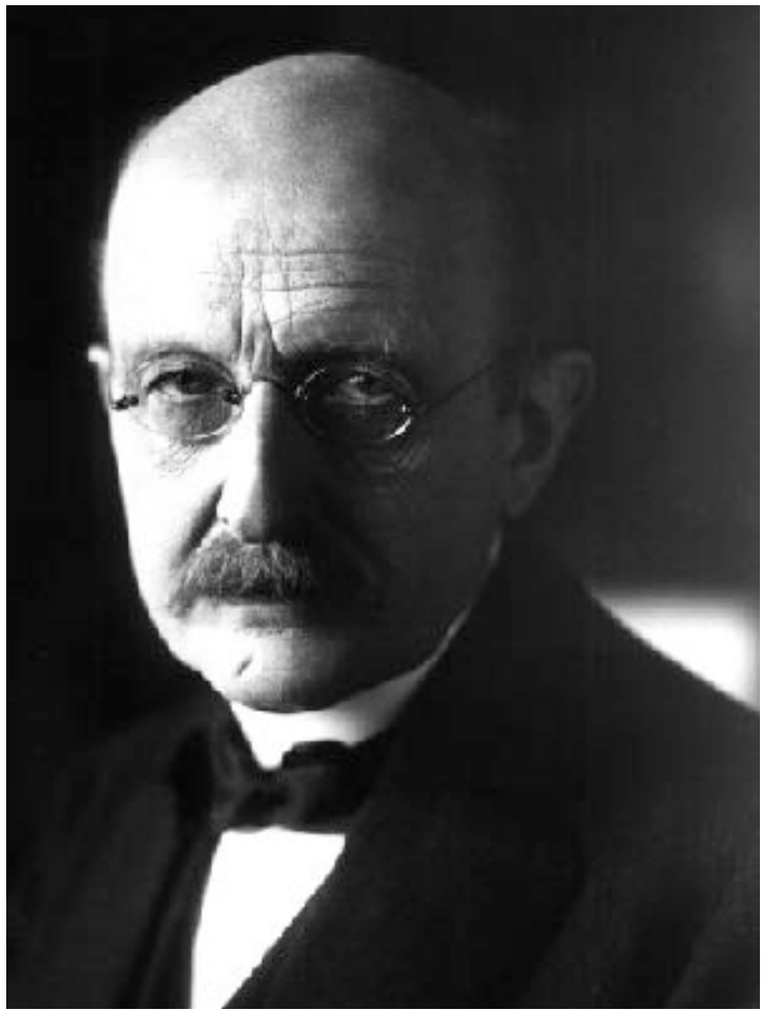
3 H_2 : simple example of vanishing integral

Group theory

5 H_2O : C_{2v} example of symmetry group

6 character table

Thomson scattering



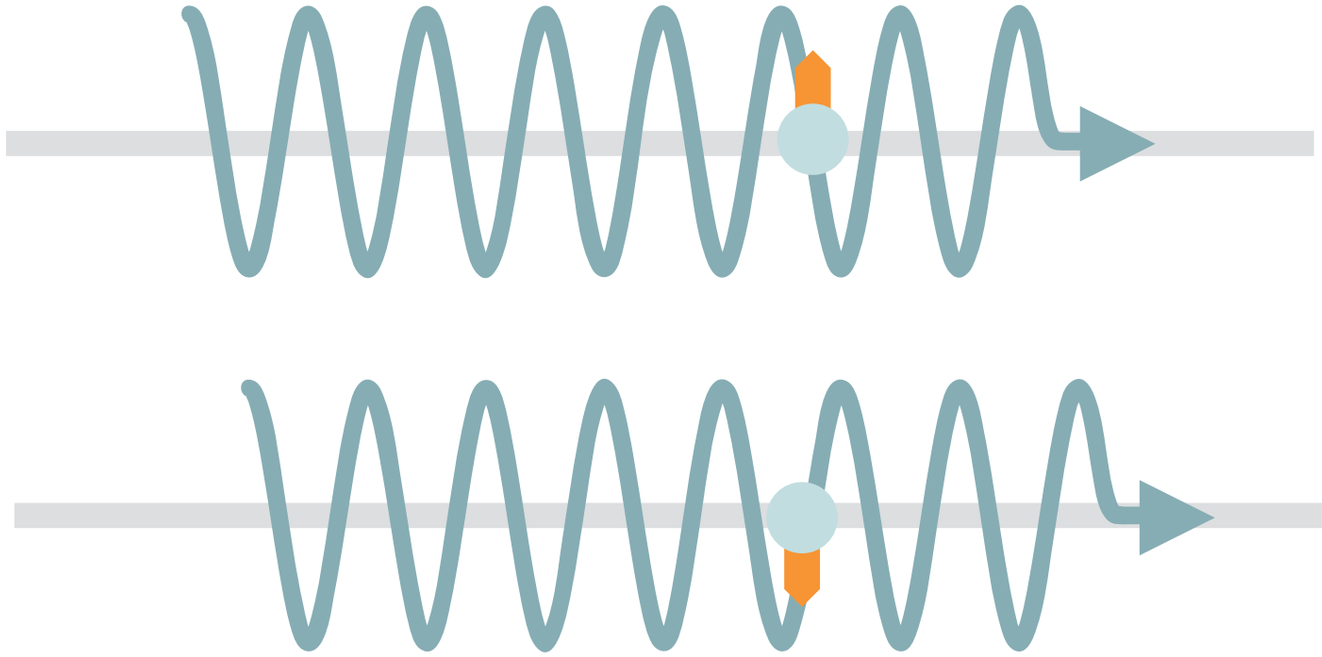
Max Planck

J. J. Thomson

David Hilbert

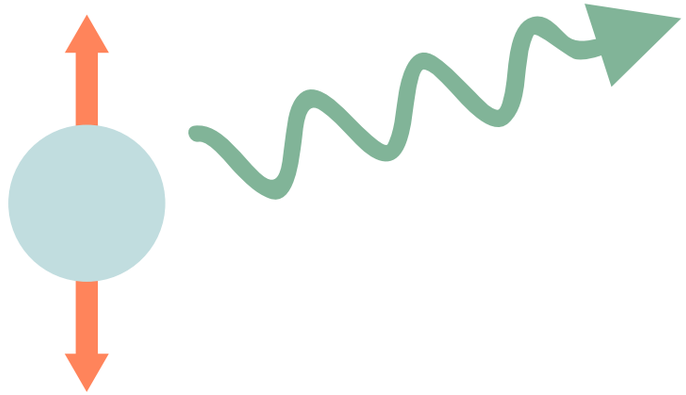
Dipole approximation

1. E is proportional to $\dot{u}$
2. E is proportional to q
3. radiates perpendicular to $\dot{u}$



Power

$$\frac{dP}{d\Omega} = \frac{\ddot{d}^2}{4\pi c^3} \sin^2\theta$$

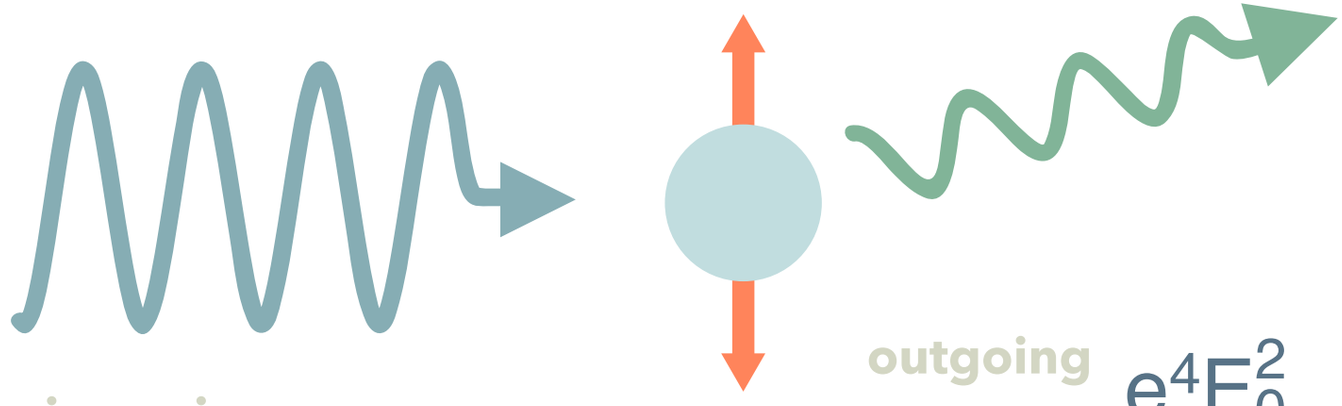


Thomson cross section

$$P = < S > \sigma_T$$

$$\sigma_T = \frac{P}{< S >}$$

$$= \frac{8\pi}{3} \frac{e^4}{m^2 c^4}$$



incoming

$$< S > = \frac{c}{8\pi} E_0^2$$

outgoing

$$P = \frac{e^4 E_0^2}{3 m^2 c^3}$$

Poynting vector

~specific intensity I_ν

Thomson scattering

1. Scattering is a re-emission
2. Frequency independent
3. Polarized as in the incident light
4. Forward scattering

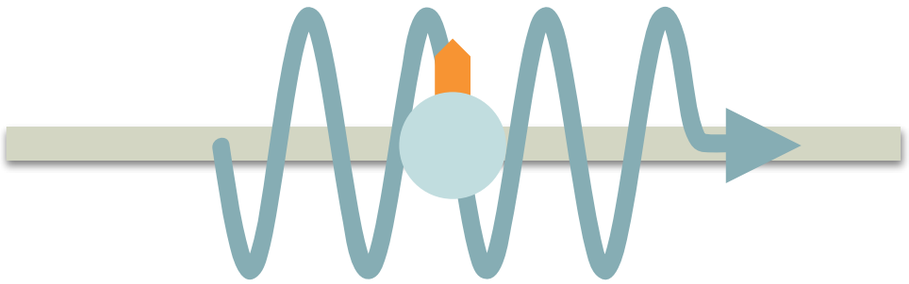
$$\frac{dP}{d\Omega} = \frac{\ddot{d}^2}{4\pi c^3} \sin^2 \theta$$

Perturbation theory

$$H\Psi_0 = E\Psi_0$$

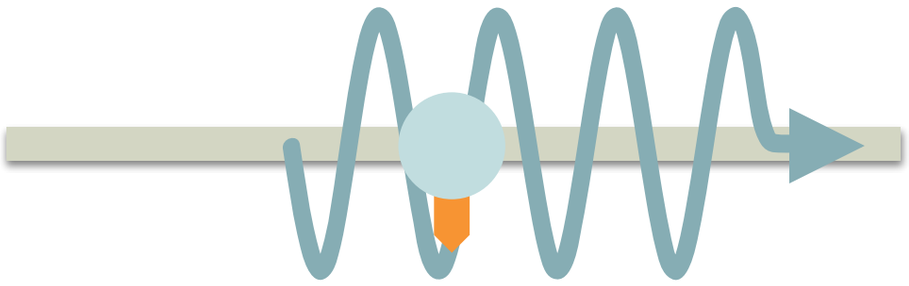
energy

steady state



here comes perturbation

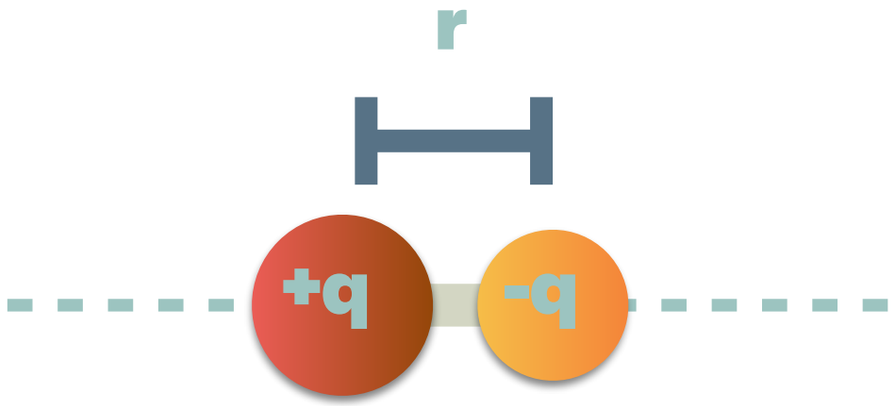
= electric field



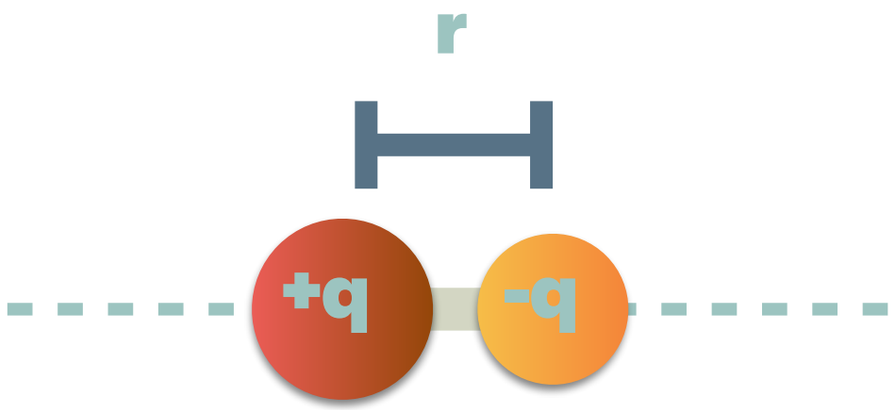
how much?

charge displaced

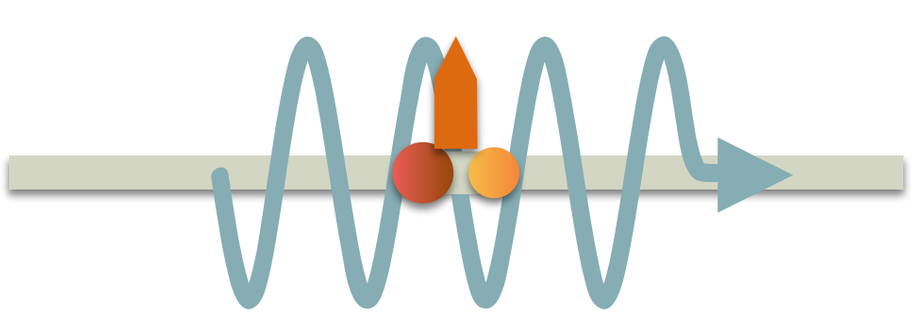
= energy shift


r
+q
-q

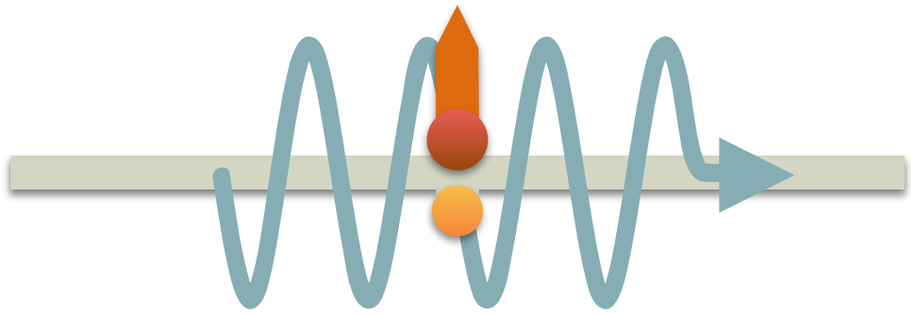
r

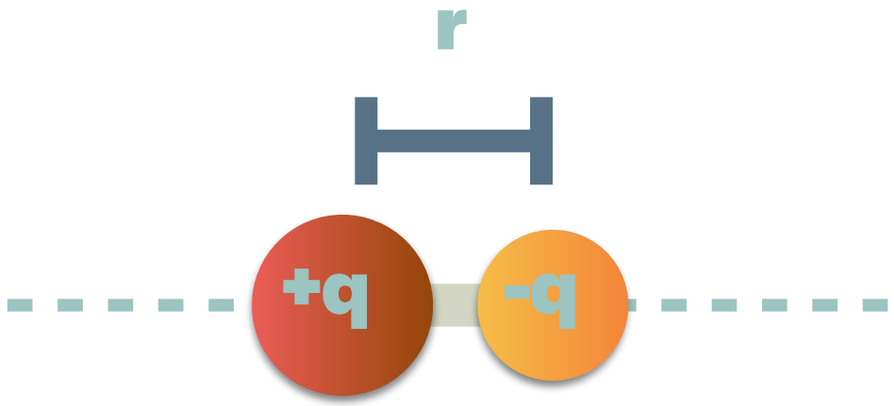


$\mu_e = qr$



E field





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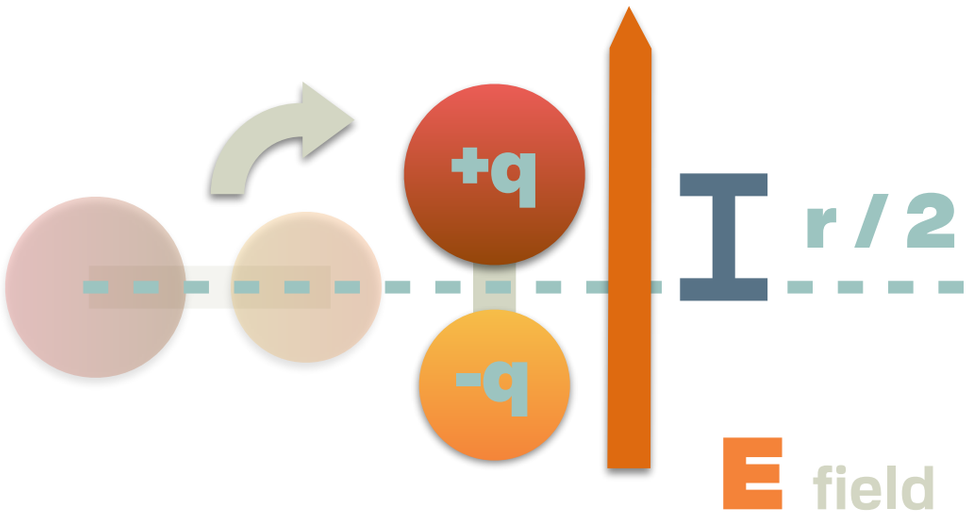
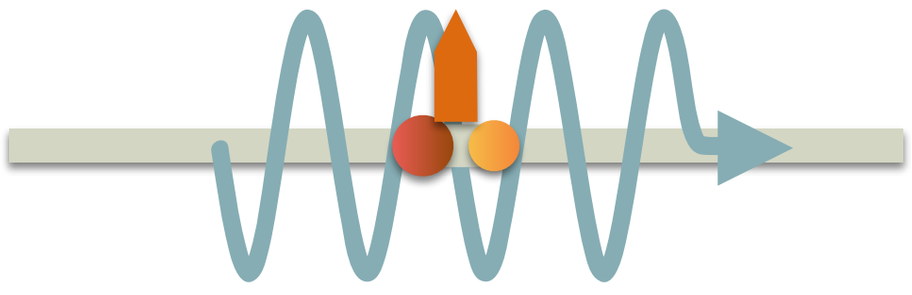
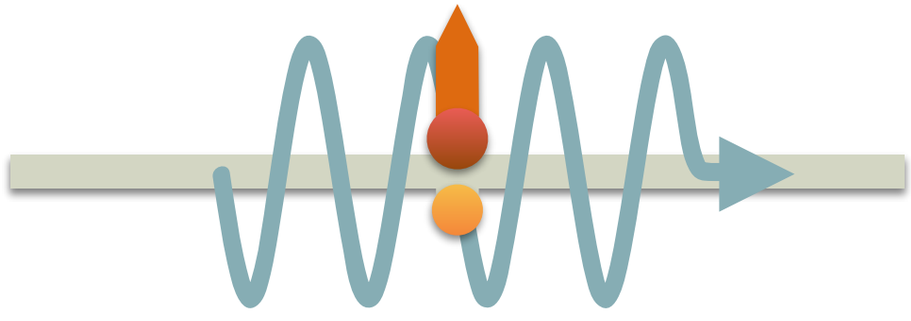


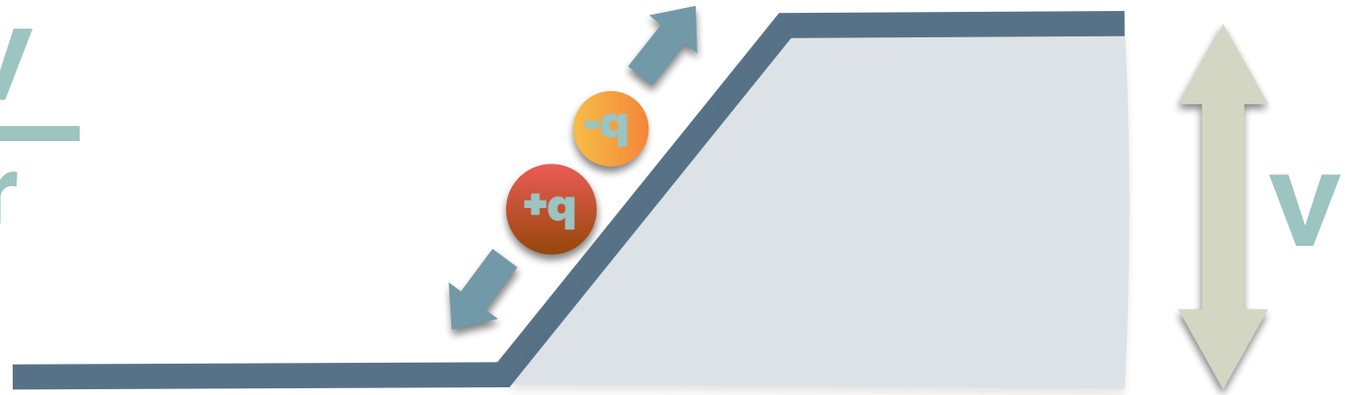


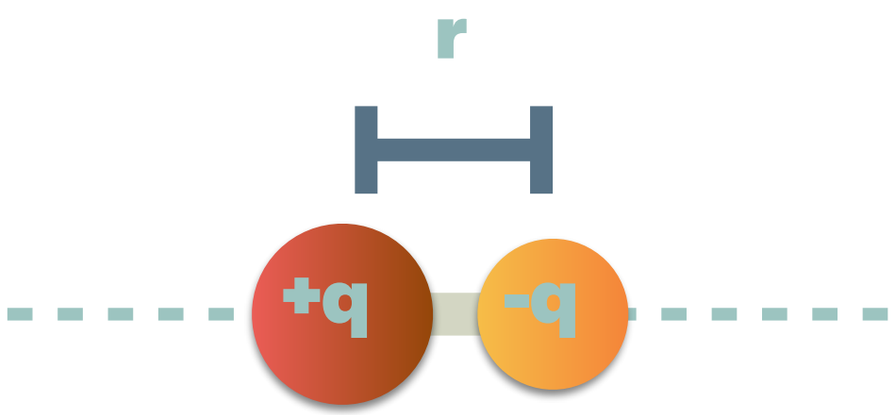
E field



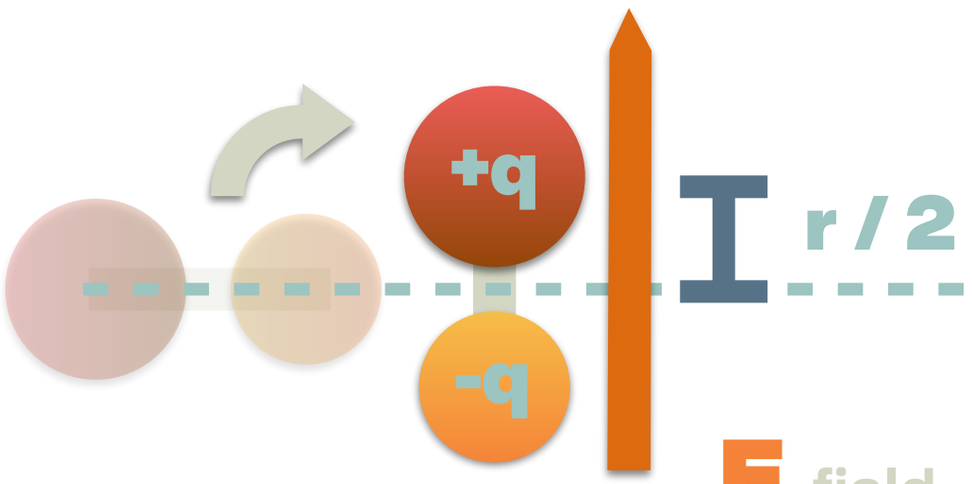
field

$$E = \frac{V}{r}$$

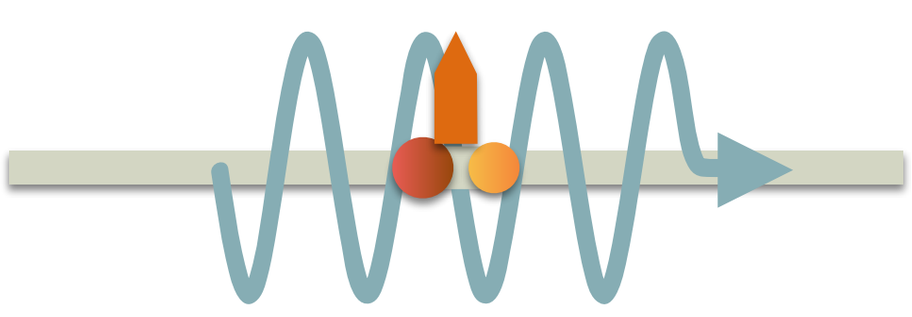




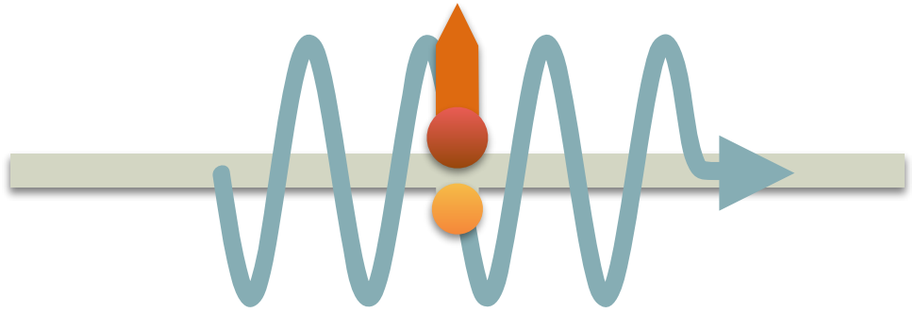
$$\mu_e = qr$$



E field

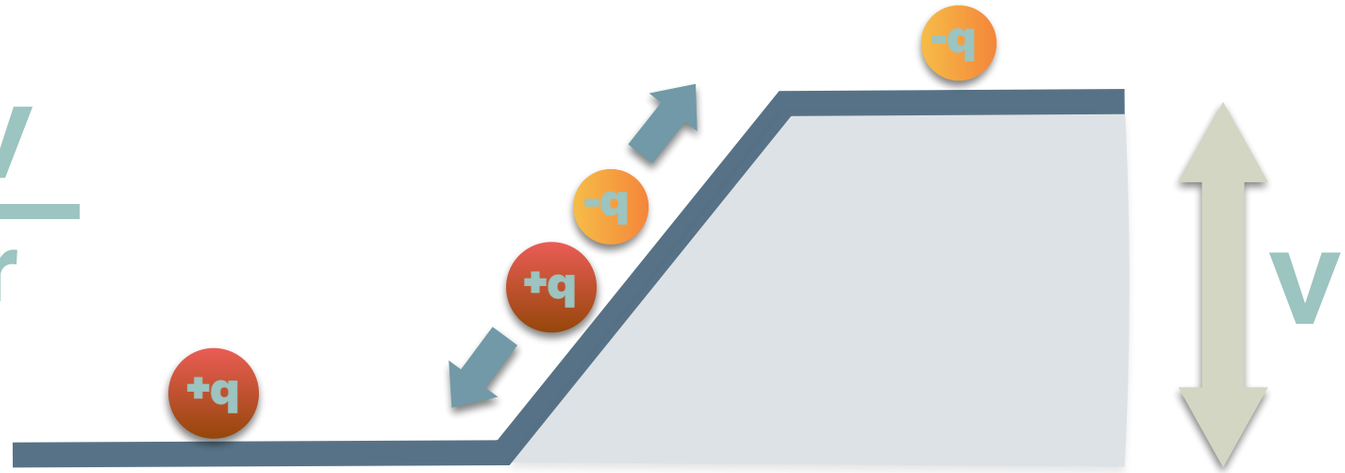


E field



field

$$E = \frac{V}{r}$$



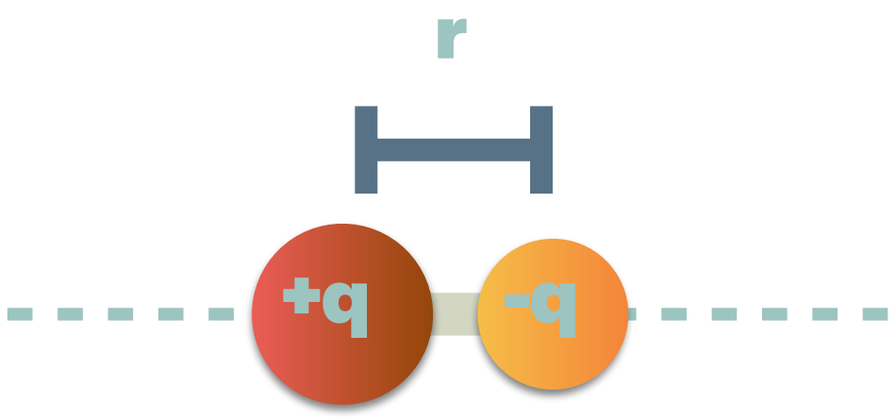
energy

$$\Delta E = q\frac{V}{2} \cdot 2$$

$$= qV \quad = qrE$$

$$= \mu_e E$$

perturbation



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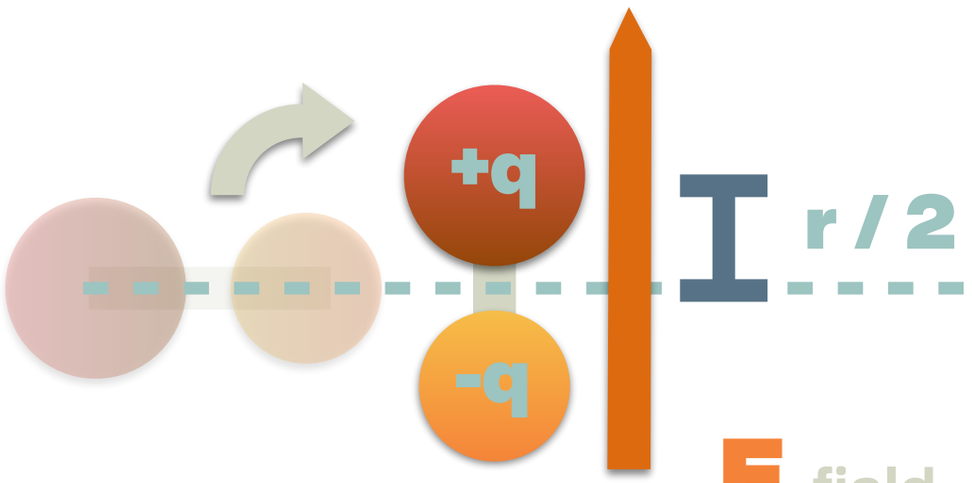
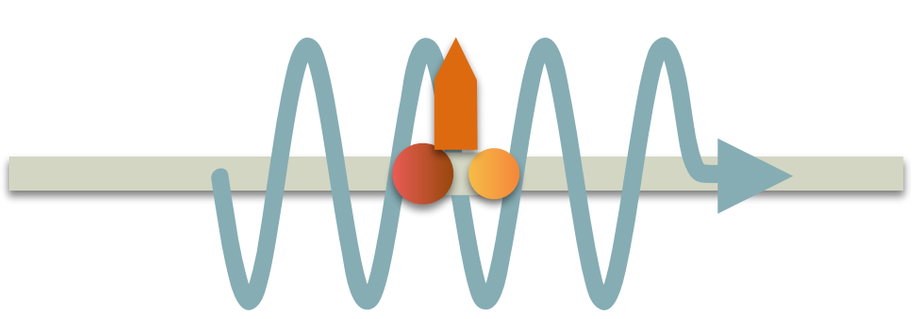
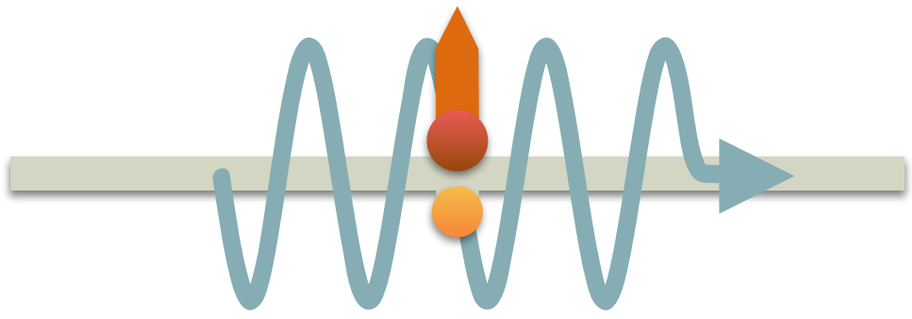


E field



E field



What is **Transition?**

time-independent

$$\Psi = \phi e^{-i\frac{E}{\hbar}t}$$

$$H\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$$

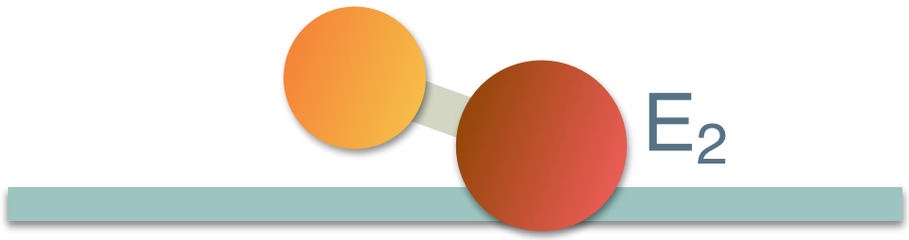
$$\frac{\partial\Psi}{\partial t} = -i\frac{E}{\hbar}\Psi$$

$$H\Psi = E\Psi$$

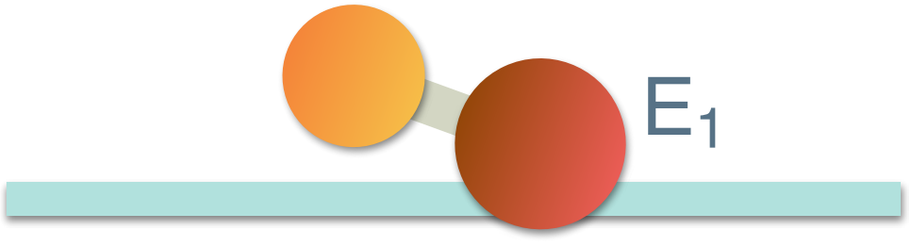
time-dependent Perturbation

V(t)

2



1



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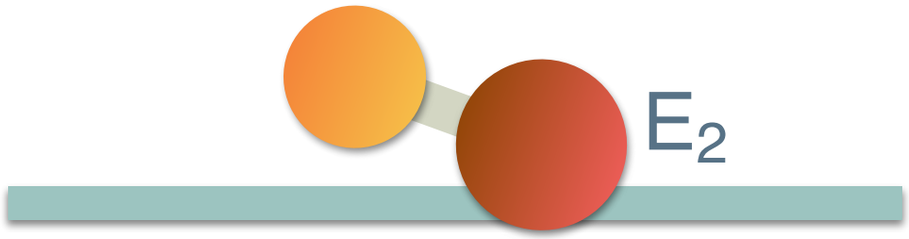
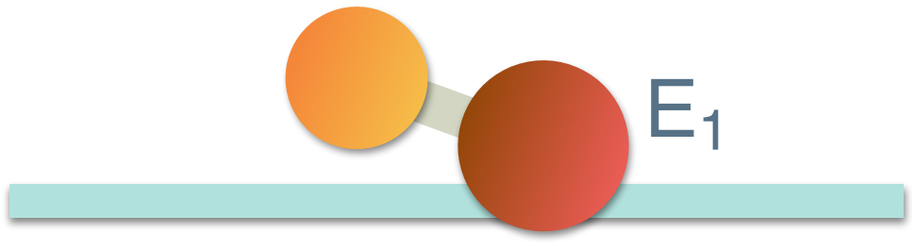


$c_2 \quad \Psi_2(t)$

$$H\Psi_2 = E_2\Psi_2$$

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

1



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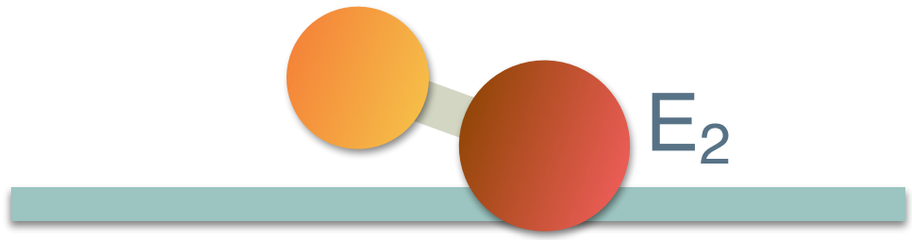
time-dependent Perturbation

V(t)

2



c_2 $\Psi_2(t)$

$$H\Psi_2 = E_2\Psi_2$$

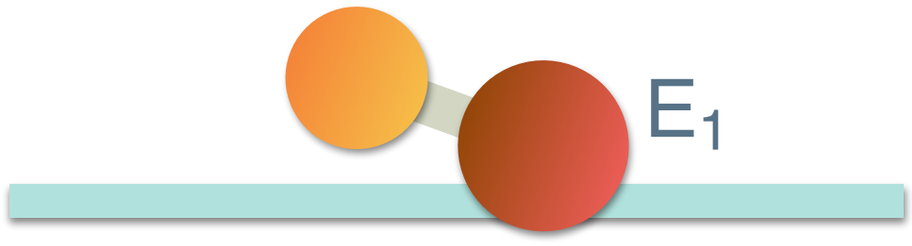
$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

$$\Psi = c_1(t)\Psi_1 + c_2(t)\Psi_2$$

$c_1(t = 0) = 1$ $\quad$ $c_2(t = 0) = 0$

$c_2(t) = ?$

1



$$(H + V)\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$$

Perturbation

c_1 $\Psi_1(t)$

$$H\Psi_1 = E_1\Psi_1$$

What is Transition?

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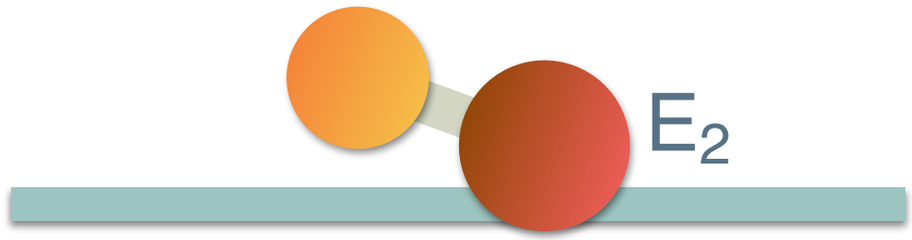
time-dependent Perturbation

V(t)

2



c_2 $\Psi_2(t)$

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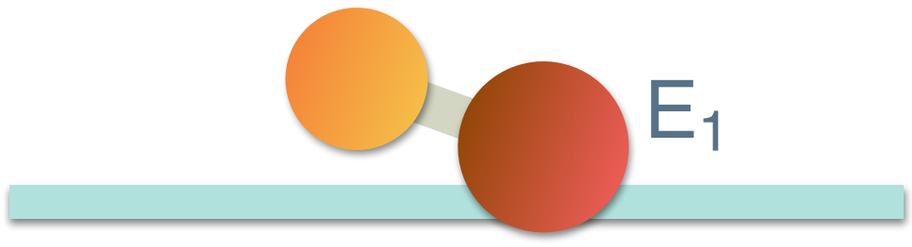
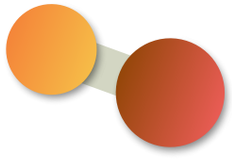


1

$$P(t) = |c_2|^2$$

how likely we will find



in **2** at **t**

$$(H + V)\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$$

Perturbation

c_1 $\Psi_1(t)$

$$H\Psi_1 = E_1\Psi_1$$

What is Transition?

time-independent

$$\Psi = \phi e^{-i\frac{E}{\hbar}t}$$

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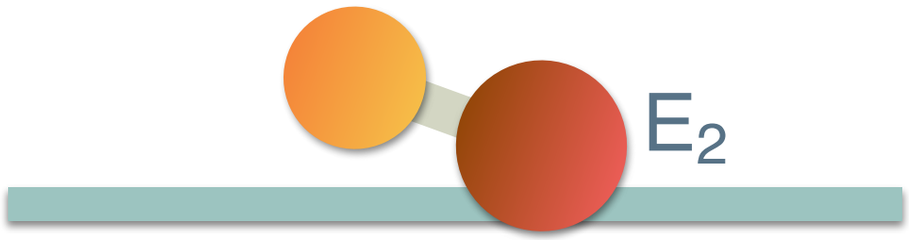
$$H\Psi = E\Psi$$

time-dependent Perturbation

2



c_2 $\Psi_2(t)$

$$H\Psi_2 = E_2\Psi_2$$

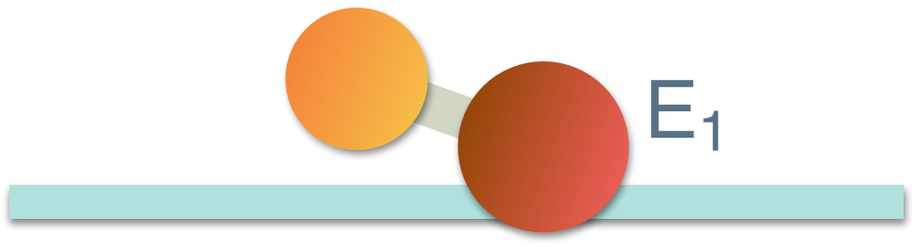
$V(t)$

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

$$\Psi = c_1(t)\Psi_1 + c_2(t)\Psi_2$$

$c_1(t = 0) = 1$ $\quad$ $c_2(t = 0) = 0$

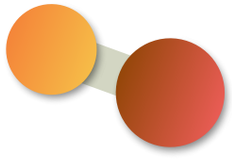
$c_2(t) = ?$



1

$$P(t) = |c_2|^2$$

how likely we will find in **2** at **t**



$$(H + V)\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$$

Perturbation

c_1 $\Psi_1(t)$

$$H\Psi_1 = E_1\Psi_1$$

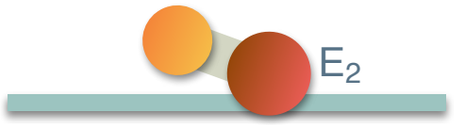
Transition probability

1 2

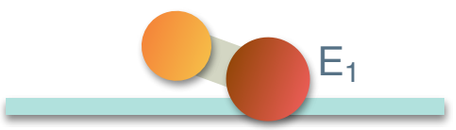
$$(H + V)\Psi = -\frac{\hbar}{i}\frac{\partial \Psi}{\partial t}$$

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

$$\Psi_1 = \phi_1 e^{-i\frac{E_1}{\hbar}t}$$

2  $c_2 \quad \Psi_2(t) = \phi_2 e^{-i\frac{E_2}{\hbar}t}$

time-independent

1  $c_1 \quad \Psi_1(t) = \phi_1 e^{-i\frac{E_1}{\hbar}t}$

time-dependent

---

1 $(H + V)\Psi = (H + V)(c_1\Psi_1 + c_2\Psi_2)$

$= c_1H\Psi_1 + c_1V\Psi_1 + c_2H\Psi_2 + c_2V\Psi_2$

$= c_1E_1\Psi_1 + c_1V\Psi_1 + c_2E_2\Psi_2 + c_2V\Psi_2$

$H\Psi_1 = E_1\Psi_1$

2 $\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t}[c_1\Psi_1 + c_2\Psi_2]$

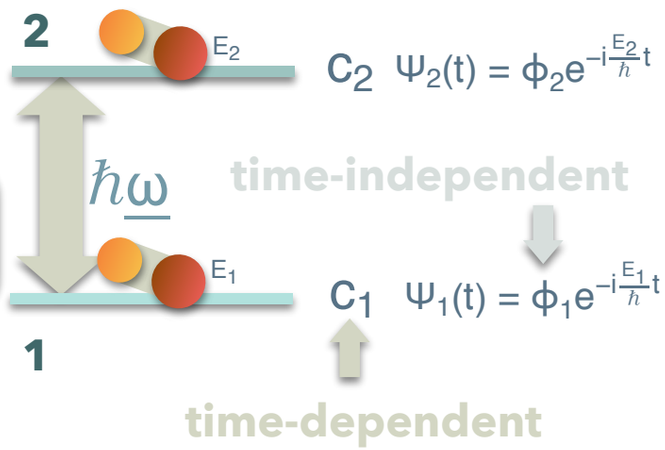
$= \frac{\partial}{\partial t}[c_1\phi_1 e^{-i\frac{E_1}{\hbar}t} + c_2\phi_2 e^{-i\frac{E_2}{\hbar}t}]$

$= \dot{c}_1\phi_1 e^{-i\frac{E_1}{\hbar}} - i\frac{E_1}{\hbar}c_1\phi_1 e^{-i\frac{E_1}{\hbar}t} + \dot{c}_2\phi_2 e^{-i\frac{E_2}{\hbar}} - i\frac{E_2}{\hbar}c_2\phi_2 e^{-i\frac{E_2}{\hbar}t}$

1 $(H+V)\Psi = c_1E_1\Psi_1 + c_1V\Psi_1 + c_2E_2\Psi_2 + c_2V\Psi_2$

2 $-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \frac{\hbar}{i}\dot{c}_1\phi_1 e^{-i\frac{E_1}{\hbar}} + E_1c_1\phi_1 e^{-i\frac{E_1}{\hbar}t} + \frac{\hbar}{i}\dot{c}_2\phi_2 e^{-i\frac{E_2}{\hbar}} + E_2c_2\phi_2 e^{-i\frac{E_2}{\hbar}t}$

$\Psi_1(t) = \phi_1 e^{-i\frac{E_1}{\hbar}t}$



1 = 2

$$c_1V\Psi_1 + c_2V\Psi_2 = \frac{\hbar}{i}\dot{c}_1\Psi_1 + \frac{\hbar}{i}\dot{c}_2\Psi_2$$

$$c_1V\phi_1 e^{-i\frac{E_1}{\hbar}t} + c_2V\phi_2 e^{-i\frac{E_2}{\hbar}t} = \frac{\hbar}{i}\dot{c}_1\phi_1 e^{-i\frac{E_1}{\hbar}t} + \frac{\hbar}{i}\dot{c}_2\phi_2 e^{-i\frac{E_2}{\hbar}t}$$

from left multiply ϕ_1^* note $<\phi_1^*|\phi_1> = 1$ $<\phi_1^*|\phi_2> = 0$

$$c_1<\phi_1|V|\phi_1> e^{-i\frac{E_1}{\hbar}t} + c_2<\phi_1|V|\phi_2> e^{-i\frac{E_2}{\hbar}t} = \frac{\hbar}{i}\dot{c}_1 e^{-i\frac{E_1}{\hbar}t}$$

$$c_1V_{11}e^{-i\frac{E_1}{\hbar}t} + c_2V_{12}e^{-i\frac{E_2}{\hbar}t} = \frac{\hbar}{i}\dot{c}_1 e^{-i\frac{E_1}{\hbar}t}$$

x $e^{i\frac{E_1}{\hbar}t}$

$$c_1V_{11} + c_2V_{12}e^{-i\frac{E_2-E_1}{\hbar}t} = \frac{\hbar}{i}\dot{c}_1$$

$$\frac{\hbar}{i}\dot{c}_1 = c_1V_{11} + c_2V_{12}e^{-i\underline{\omega}t}$$

$V_{11} = <\phi_1|V|\phi_1>$

$V_{12} = <\phi_1|V|\phi_2>$

$\hbar\underline{\omega} = E_2 - E_1$

$V_{11} = 0$

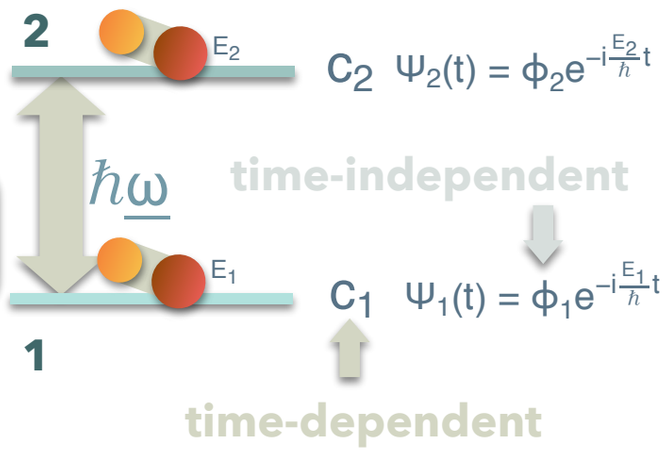
$V_{22} = 0$

need symmetry discussion

1 $(H+V)\Psi = c_1E_1\Psi_1 + c_1V\Psi_1 + c_2E_2\Psi_2 + c_2V\Psi_2$

2 $-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \frac{\hbar}{i}\dot{c}_1\phi_1 e^{-i\frac{E_1}{\hbar}} + E_1c_1\phi_1 e^{-i\frac{E_1}{\hbar}t} + \frac{\hbar}{i}\dot{c}_2\phi_2 e^{-i\frac{E_2}{\hbar}} + E_2c_2\phi_2 e^{-i\frac{E_2}{\hbar}t}$

$\Psi_1(t) = \phi_1 e^{-i\frac{E_1}{\hbar}t}$



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$$c_1V\phi_1 e^{-i\frac{E_1}{\hbar}t} + c_2V\phi_2 e^{-i\frac{E_2}{\hbar}t} = \frac{\hbar}{i}\dot{c}_1\phi_1 e^{-i\frac{E_1}{\hbar}t} + \frac{\hbar}{i}\dot{c}_2\phi_2 e^{-i\frac{E_2}{\hbar}t}$$

from left multiply ϕ_2^* note $<\phi_1^*|\phi_1> = 1$ $<\phi_1^*|\phi_2> = 0$

$$c_1 <\phi_2|V|\phi_1> e^{-i\frac{E_1}{\hbar}t} + c_2 <\phi_2|V|\phi_2> e^{-i\frac{E_2}{\hbar}t} = \frac{\hbar}{i}\dot{c}_2 e^{-i\frac{E_2}{\hbar}t}$$

$$c_1V_{21}e^{-i\frac{E_1}{\hbar}t} + c_2V_{22}e^{-i\frac{E_2}{\hbar}t} = \frac{\hbar}{i}\dot{c}_2 e^{-i\frac{E_2}{\hbar}t}$$

x $e^{i\frac{E_2}{\hbar}t}$

$$c_1V_{21}e^{i\frac{E_2-E_1}{\hbar}t} + c_2V_{22} = \frac{\hbar}{i}\dot{c}_2$$

$$\frac{\hbar}{i}\dot{c}_2 = c_1V_{21}e^{i\underline{\omega}t}$$

$V_{11} = <\phi_1|V|\phi_1>$

$V_{12} = <\phi_1|V|\phi_2>$

$\hbar\underline{\omega} = E_2 - E_1$

$V_{11} = 0$

$V_{22} = 0$

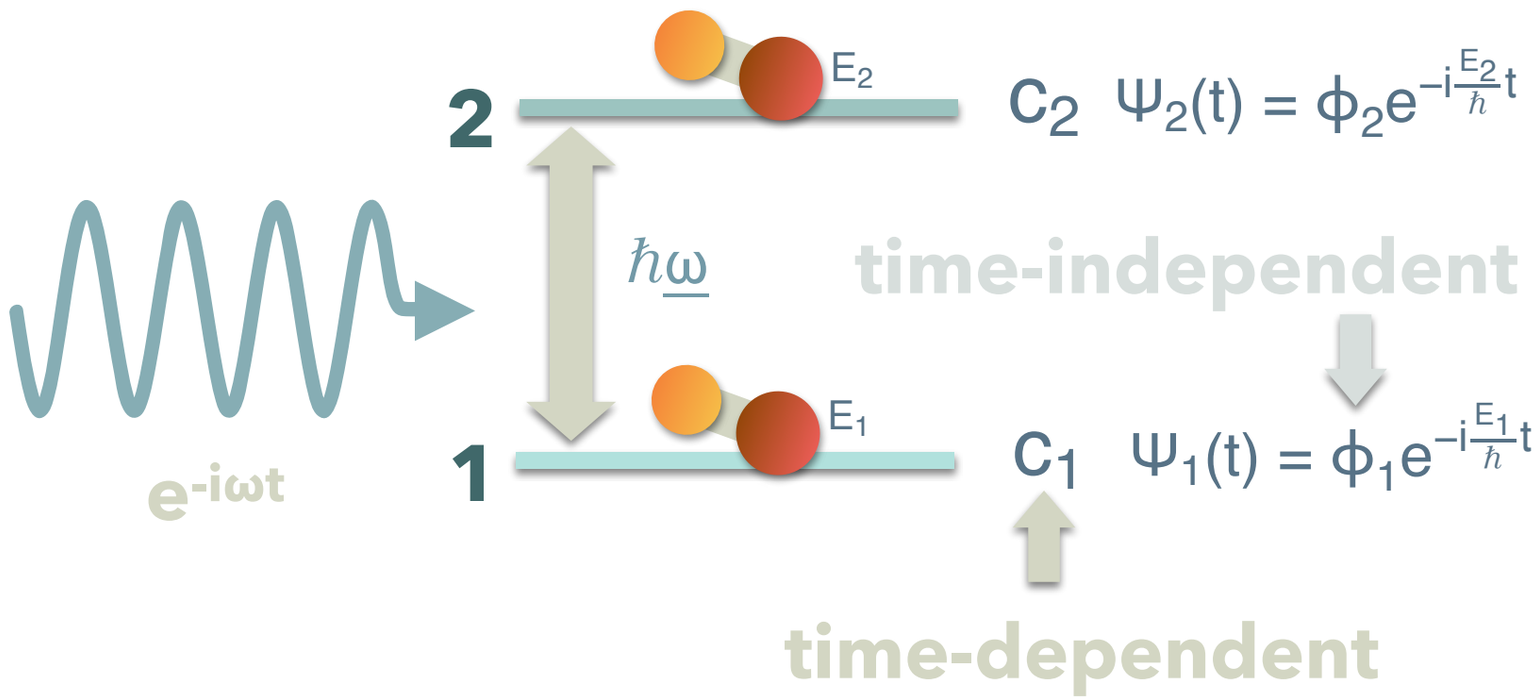
need symmetry discussion

$$\frac{\hbar}{i}\dot{c}_2 = c_1 V_{21} e^{i\underline{\omega}t}$$

$$V_{21} = \langle \phi_2 | V | \phi_1 \rangle$$

$$V = \Delta E = \boldsymbol{\mu_e E}$$

$$V_{21} \propto \mu_e E = \mu_e E e^{-i\omega t}$$



$$\frac{\hbar}{i}\dot{c}_2 = c_1 V_{21} e^{i\underline{\omega}t}$$

$$c_1(0) = 1 \qquad c_2(0) = 0$$

approximation

$$c_1(t) \sim 1 \qquad c_2(t) \sim 0$$

$$c_2(t) = \int \mu_e E e^{-i\omega t} e^{i\underline{\omega}t} dt$$

$$= \mu_e E \int e^{-i(\omega - \underline{\omega})t} dt$$

$$= \mu_e E \left[\frac{e^{-i(\omega-\underline{\omega})t}}{i(\omega - \underline{\omega}}\right]_0^t$$

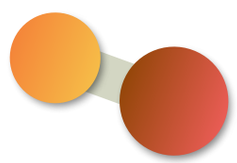
resonance $\omega \rightarrow \underline{\omega}$

$$= \mu_e E \frac{e^{-i(\omega-\underline{\omega})t} - 1}{i(\omega - \underline{\omega})} = -\mu_e E \frac{\sin \frac{i(\omega - \underline{\omega})t}{2}}{\frac{i(\omega - \underline{\omega})}{2}} = -\mu_e E t$$

Transition probability

$$P(t) = |c_2|^2$$

how likely we will find



in **2** at **t**

$$|c_2(t)| = \mu_e E t$$

for unit time **t=1**

$$|c_2(t=1)| = |\mu_e E|$$

$$P(t=1) = |c_2|^2 = |\mu_e E|^2$$

Einstein A coefficient

Group theory for astrochemist

group element = { **A** **B** **C** **D** **E** }

1. you apply **multiply** **A** on **B**
2. get **C**
3. whatever you multiply, result is one of **group elements**

a group is

1. **closed**
2. **has 1** — identity
3. **inverse** — inverse element A^{-1}
4. **associative** — $A(BC) = (AB)C$

4. once it is recognized as a **group**

we can use its mathematical property for free

example

element can be number, operation, function

group element = { **A** **B** **C** **E** }

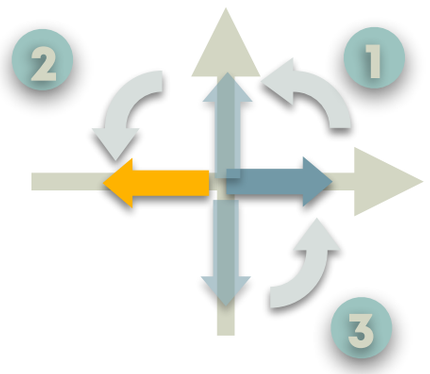
rotate π

do nothing

rotate π/2

rotate 3π/2

1. you apply **multiply** **A** on **B**
2. get **C**
3. whatever you multiply, result is one of **elements**



1. **closed**
2. **has E**
3. **inverse**
4. **associative**

identity

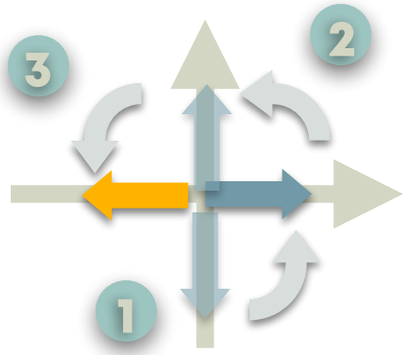
C for **A**

B for **B**

A(BC) = (AB)C

4. once it is recognized as a **group**

we can use its mathematical property for free



Group theory

does not care what exactly elements are

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

B

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

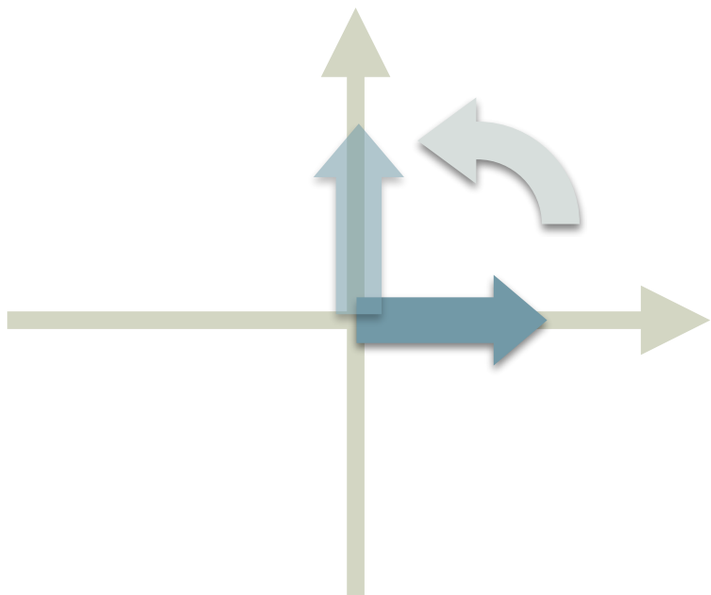
B

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

B



Group theory

for astrochemist

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

B

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

B

B

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

B

Multiplication table

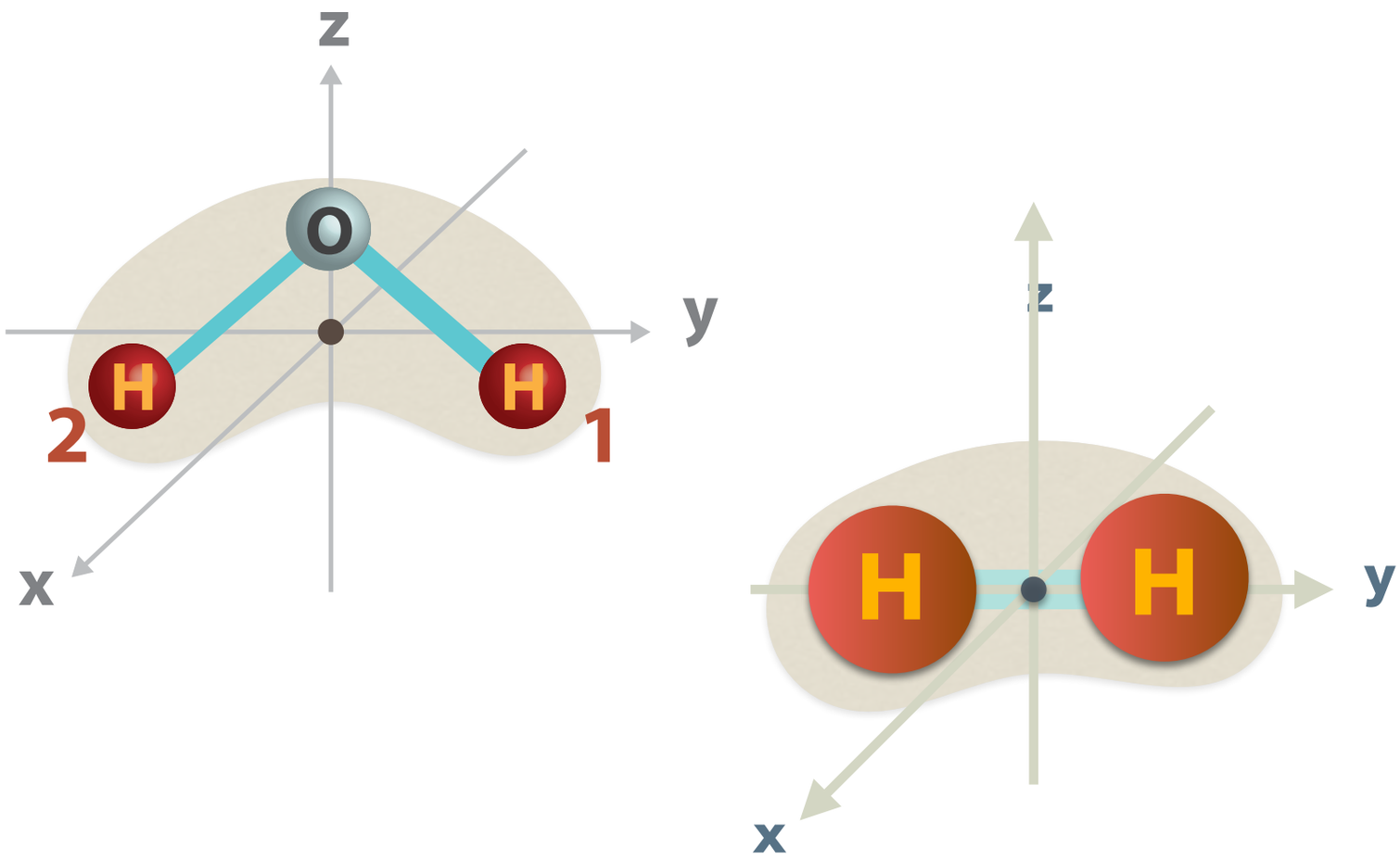
do something after something

multiplication of operation

when multiplication tables are same

they are same Group

Why group theory?



Why molecular symmetry?

Why group theory?

we want to know shape of wavefunction

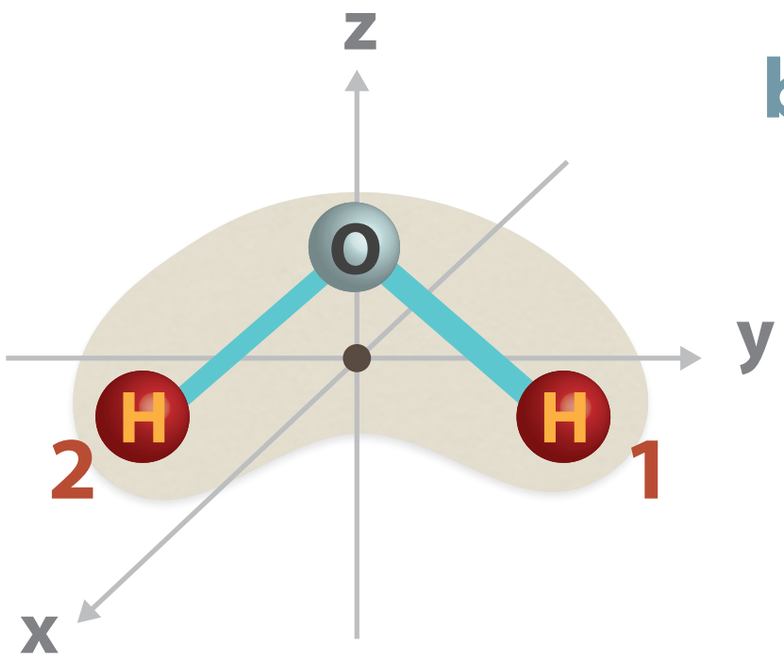
but without actually calculating it

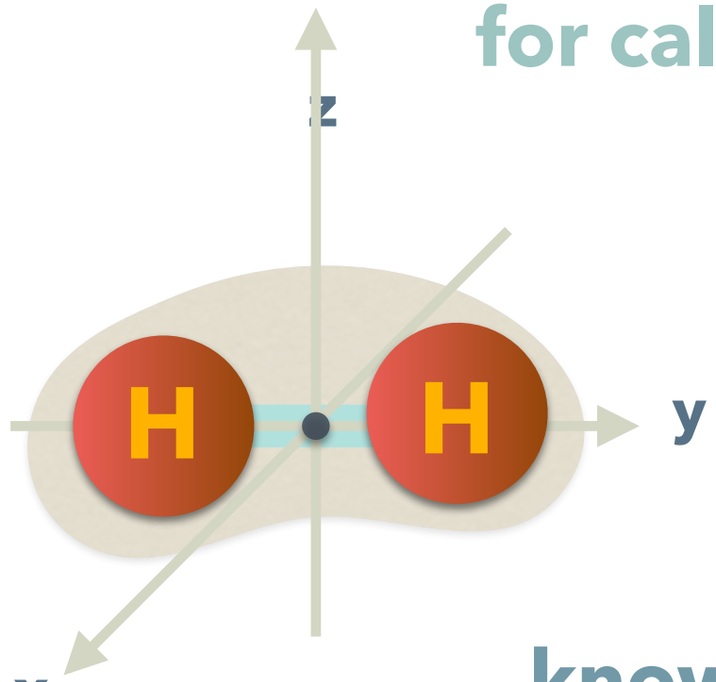
for calculation of

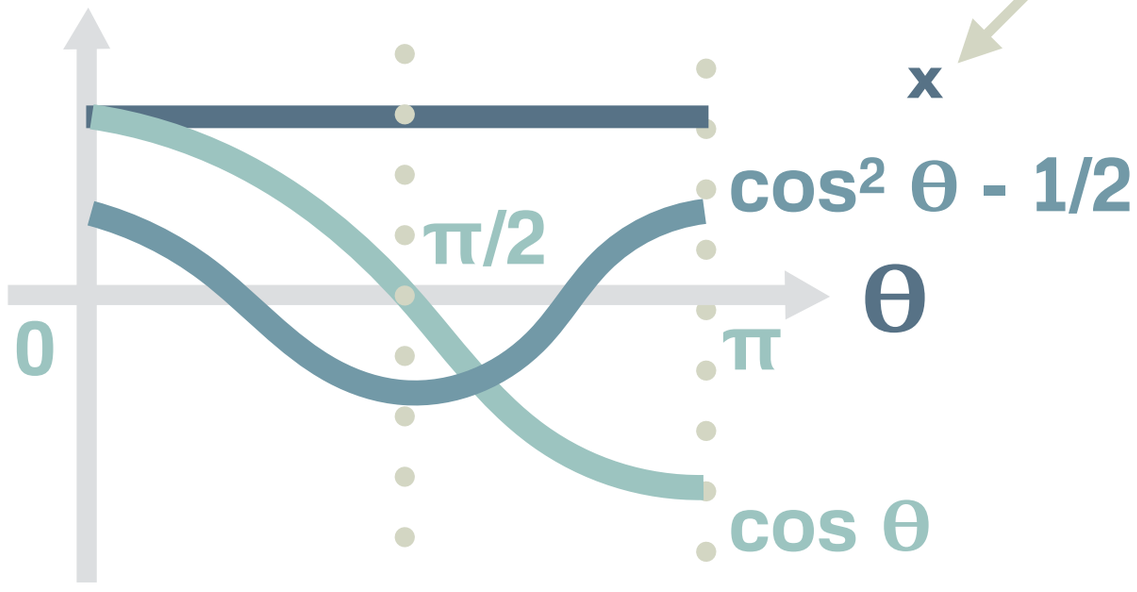
$\langle \psi_1 | O | \psi_2 \rangle$

operator

and for knowing
if it is 0 or not







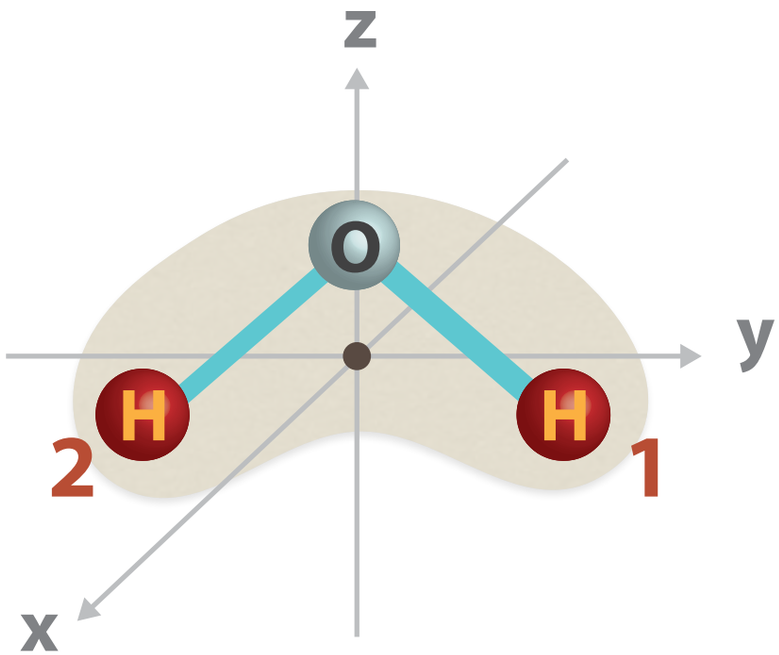
knowing symmetry of
wavefunction is enough

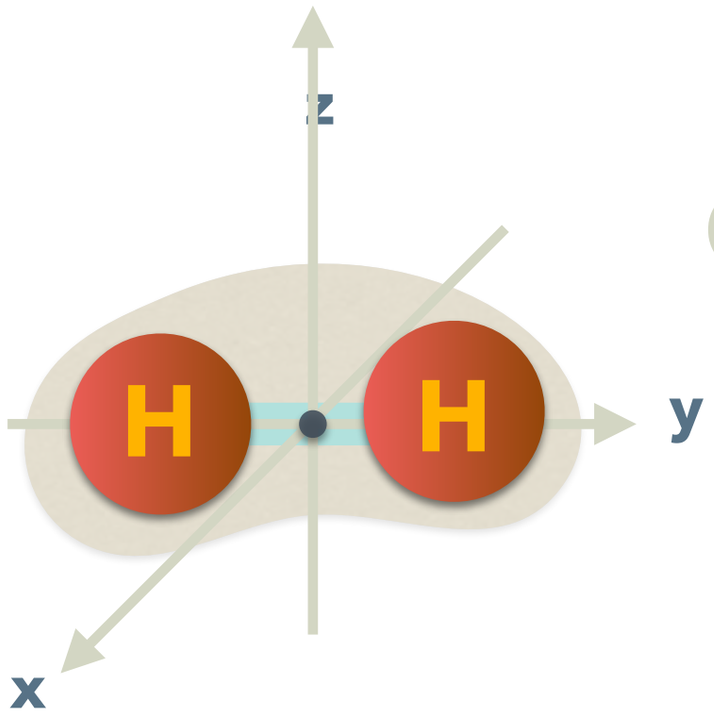
Why molecular symmetry?

Why group theory?

tells shape of wavefunction.

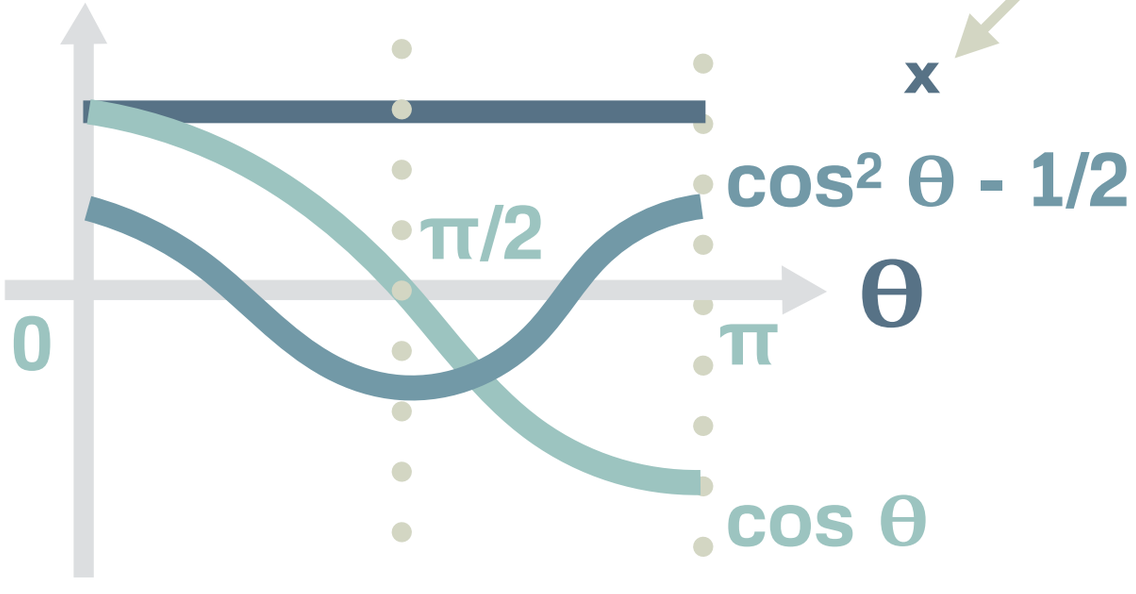
from relations between





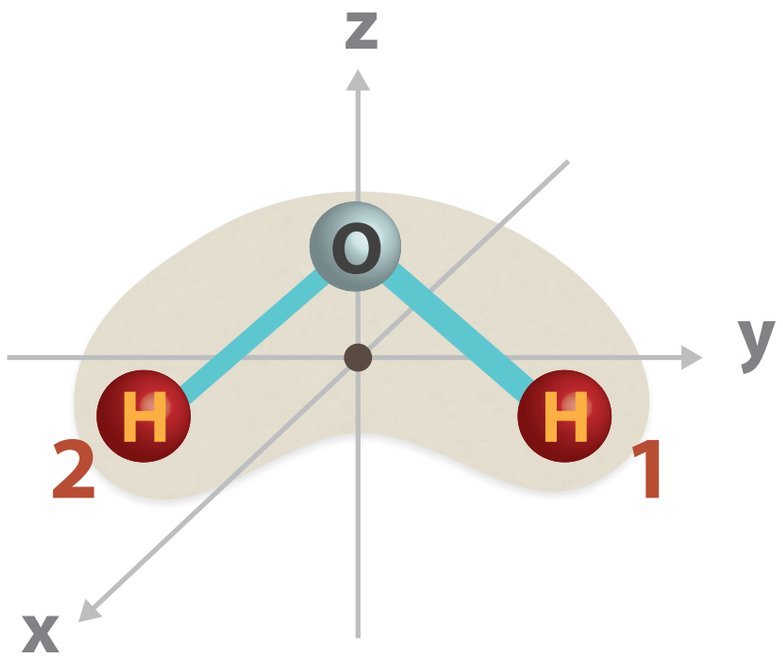
operation

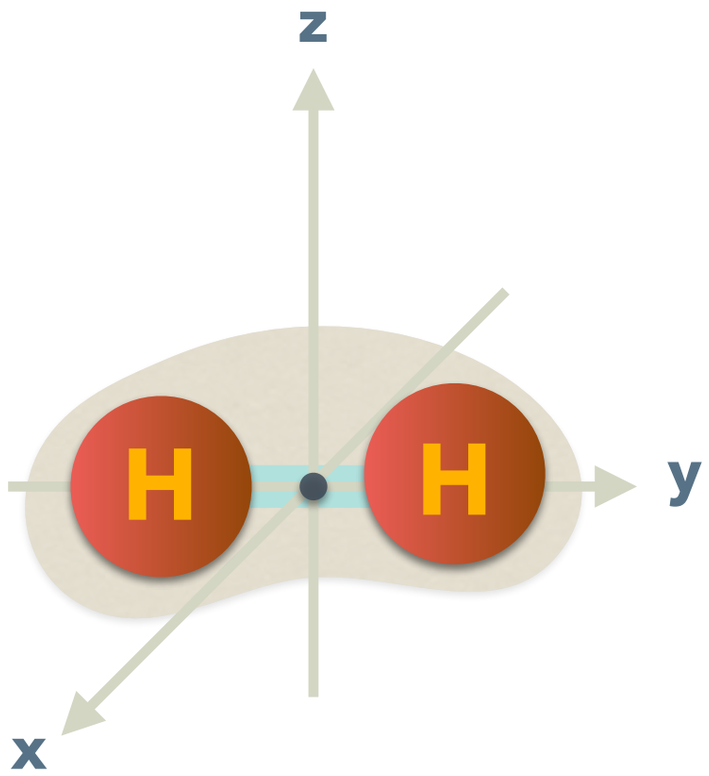
parity



Why molecular symmetry?

what kind of operations are relevant here?





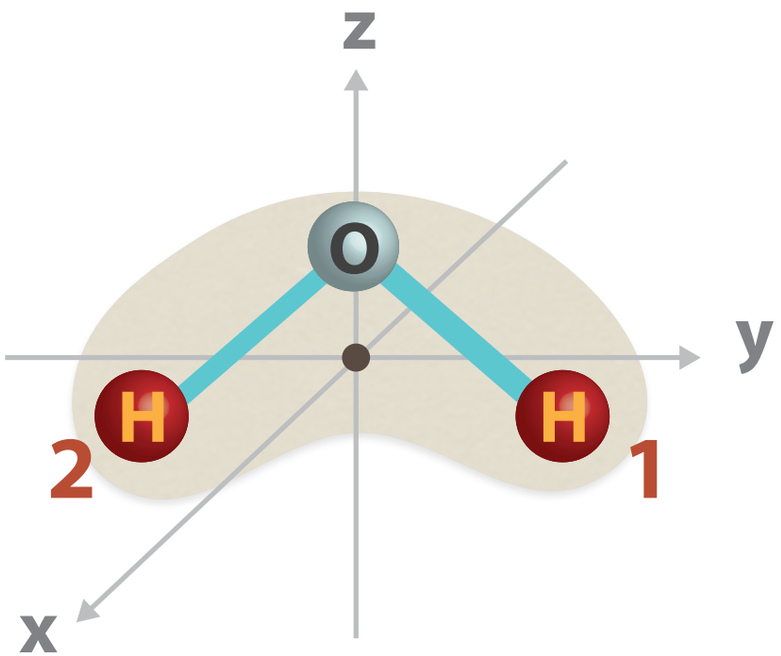
if wavefunction changes randomly

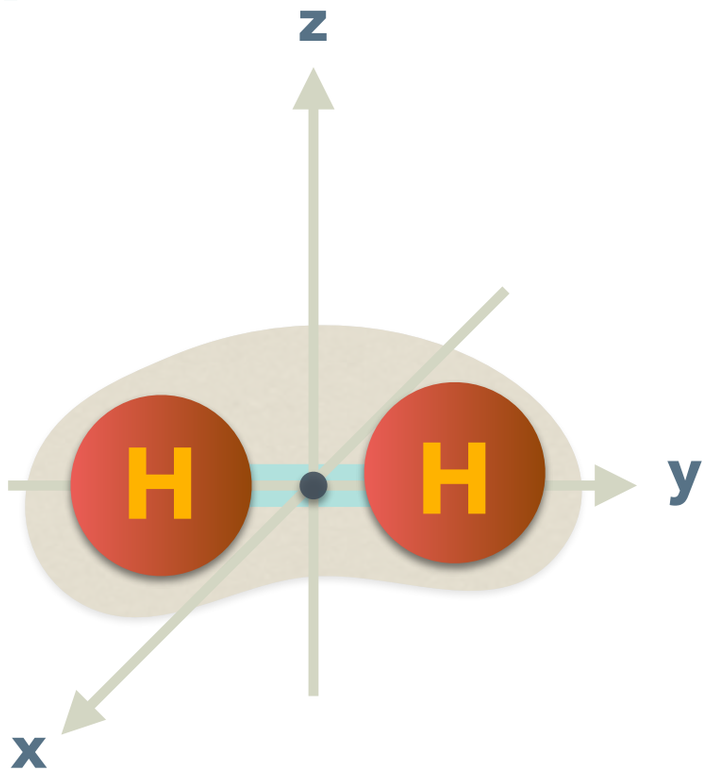
useless to tell shape of wavefunction

something that does not change shapes....

what kind of operation is relevant here?

something that does not change shapes....



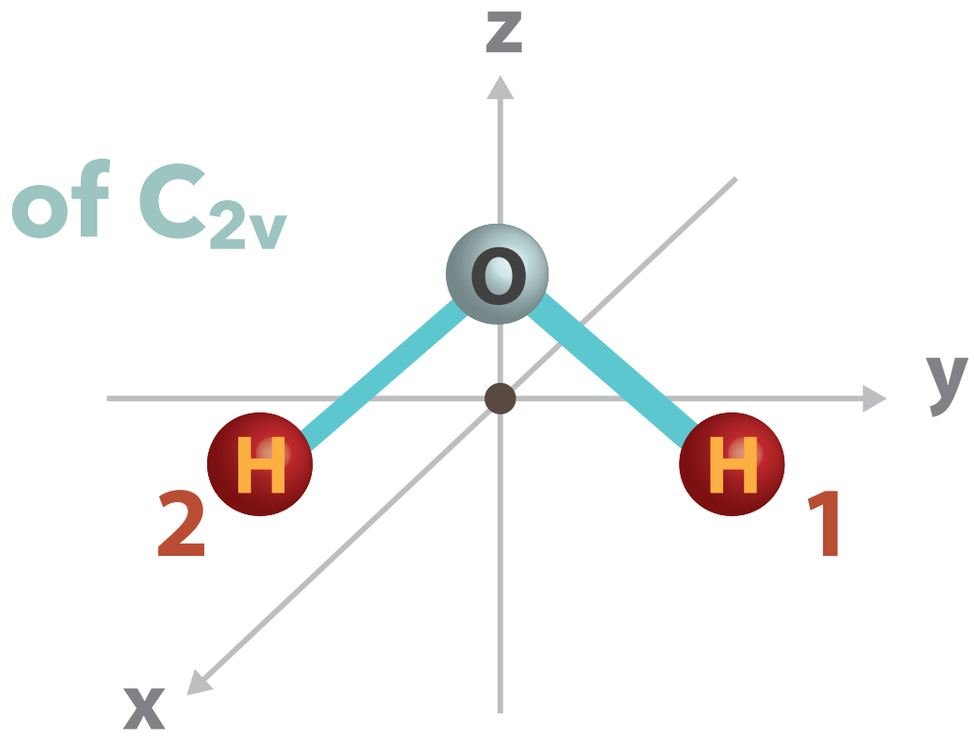


like

1. rotation by π
2. reflection about xz plane
3. reflection about yz plane
4. identity (as it is)

Character table

now we jump to



of C_{2v}

Character

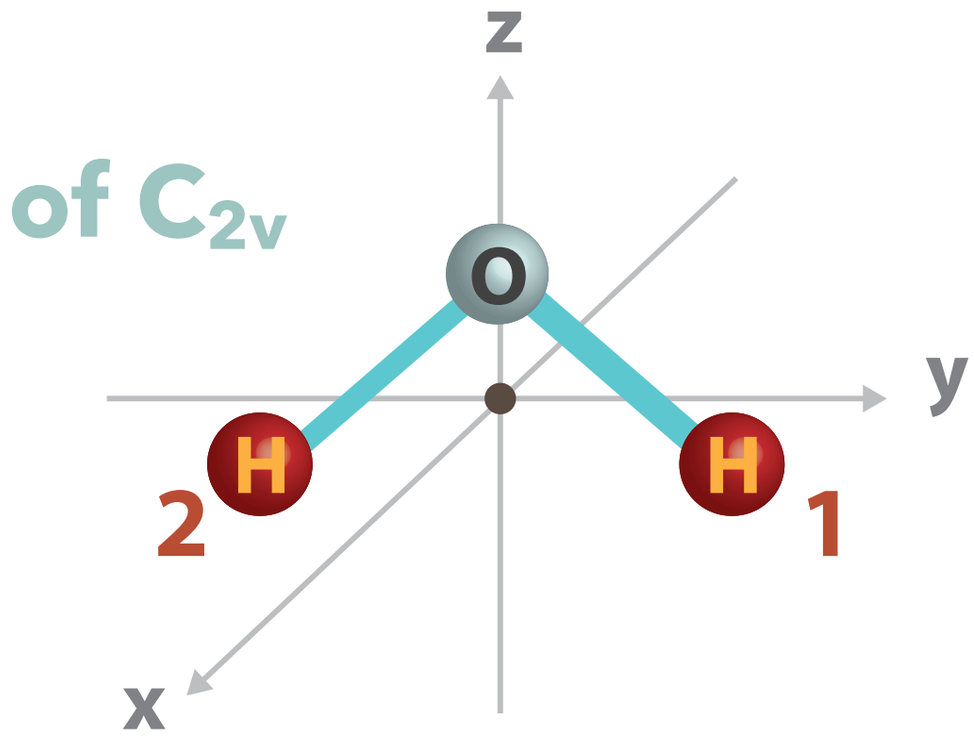
	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	h=4	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	-1	1	x, R_y	xz
B_2	1	-1	1	-1	y, R_x	yz

Character table

E identity operator (do nothing)
"Einheit"

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

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



Character

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

Character table

E identity operator (do nothing)
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C_2 rotation of $\pi/2$ about **z** axis

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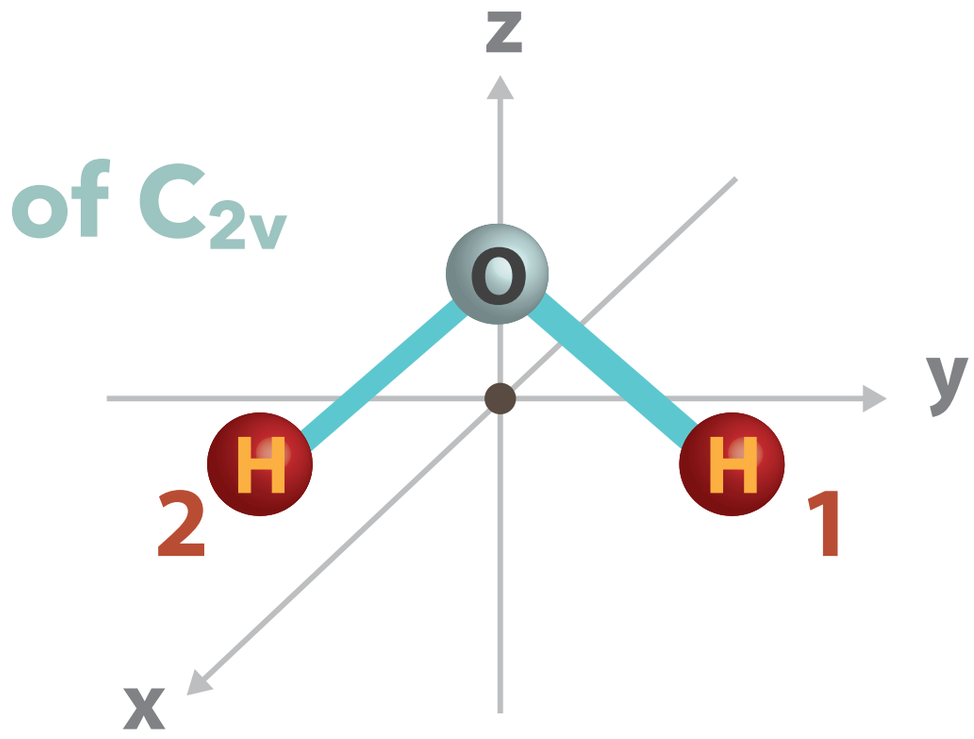


order of group :
number of symmetry elements

Character

symmetry operations

	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

symmetry label (representative)

representation
(set of representatives)

base functions

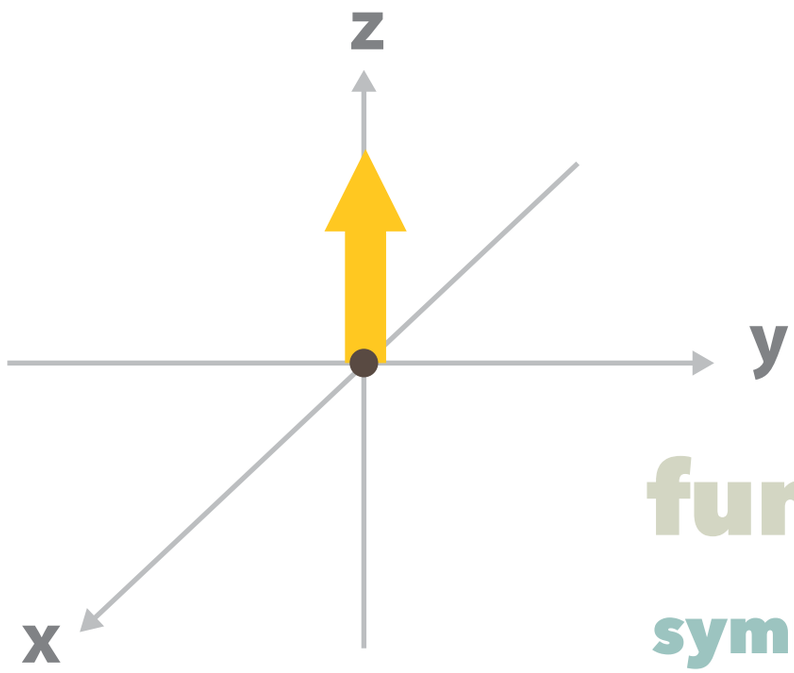
cross term
base functions

	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

symmetry label →

z is the function

$f(x,y,z) = z$



it does not change itself

by the operations

E C_2 $\sigma_v(xz)$ $\sigma'_v(yz)$

function z has A_1 symmetry

symmetry label tells the shape of functions

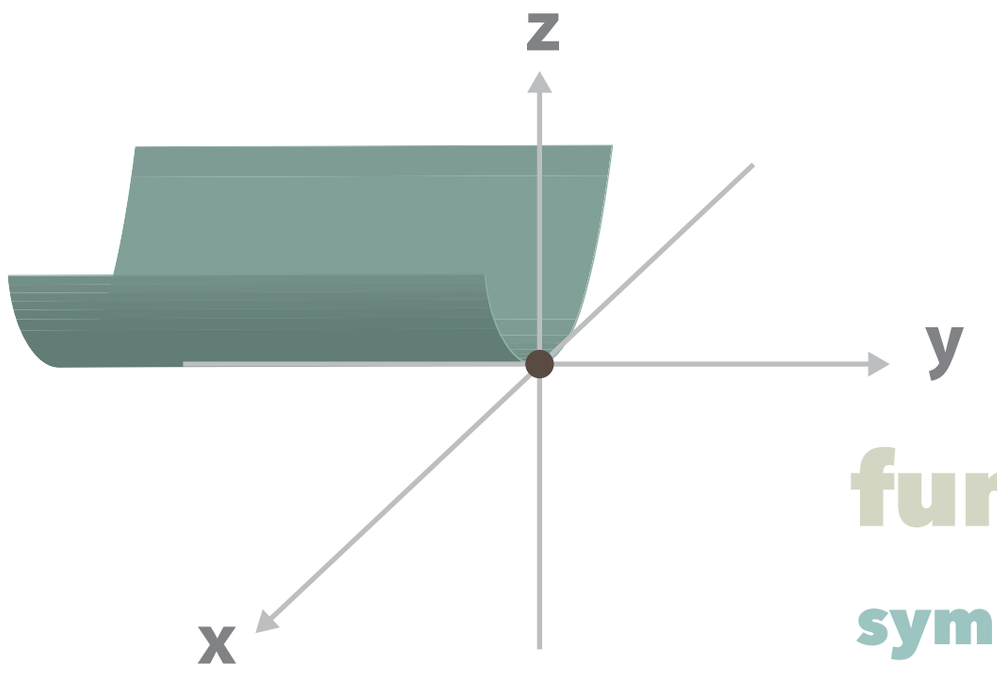
wave functions

	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

symmetry → label

x^2 is the function

$f(x,y,z) = x^2$



it does not change itself

by the operations

E C_2 $\sigma_v(xz)$ $\sigma'_v(yz)$

function x^2 has A_1 symmetry

symmetry label tells the shape of functions

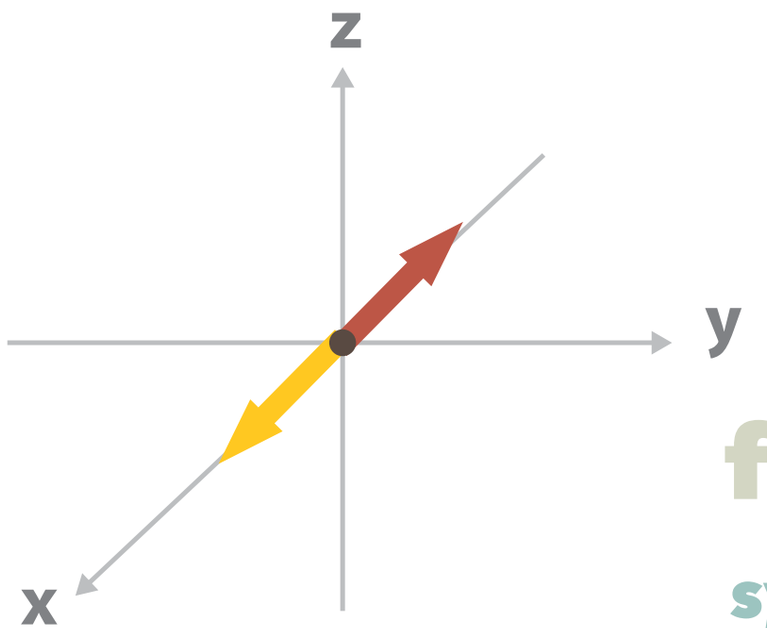
wave functions

	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

symmetry label →

x is the function

$f(x,y,z) = x$



remains same by E $\sigma'_v(yz)$

changes the sign by C_2 $\sigma_v(xz)$

E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
1	-1	-1	1

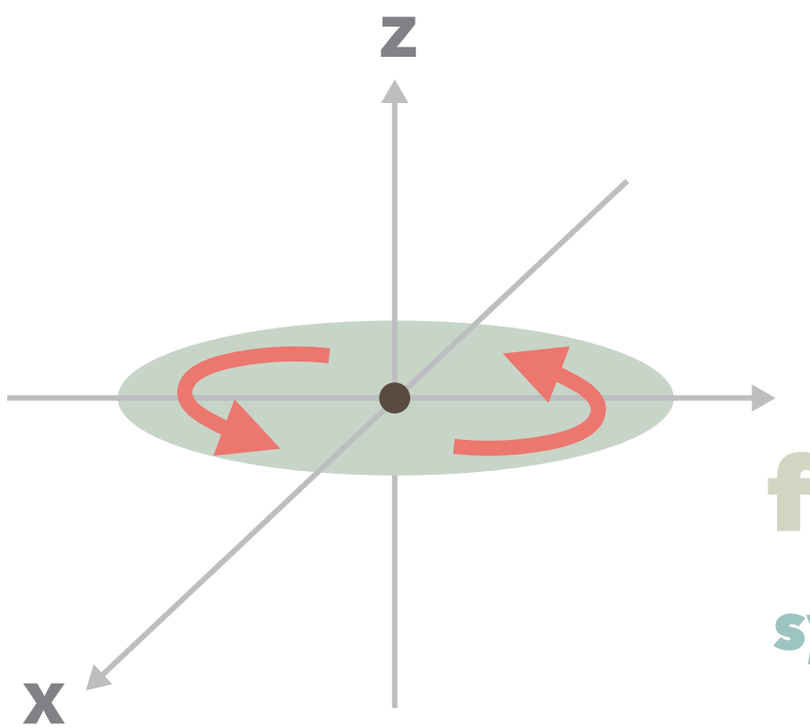
function x has B_1 symmetry

symmetry label tells the shape of functions

wave functions

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	h=4	
symmetry → label						
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

R_z is the function that rotates around z



angular momentum

remains same by E C_2

changes the sign by $\sigma_v(xz)$ $\sigma'_v(yz)$

= direction of rotation

E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
1	1	-1	-1

function R_z has A_2 symmetry

symmetry label tells the shape of functions

wave functions

What **group theory** gives us for free

symmetry → label

	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

1 as long as functions are basis of symmetry representation

$f^{A1} \times f^{A2}$ $\quad 1\times1,\ 1\times1,\ 1\times-1,\ 1\times-1$

$\quad 1 \quad 1 \quad -1 \quad -1 \quad = f^{A2}$

$f^{A2} \times f^{B1}$ $\quad 1\times1,\ 1\times-1,\ -1\times-1,\ -1\times1$

$\quad 1 \quad -1 \quad 1 \quad -1 \quad = f^{B2}$

What **group theory** gives us for free

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	h=4	
symmetry →						
label						
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

1 as long as functions are basis of symmetry representation

$f^{A1} \times f^{A2}$ $\quad 1\times1,\ 1\times1,\ 1\times-1,\ 1\times-1$

$1 \quad 1 \quad -1 \quad -1 \quad = f^{A2}$

$f^{A2} \times f^{B1}$ $\quad 1\times1,\ 1\times-1,\ -1\times-1,\ -1\times1$

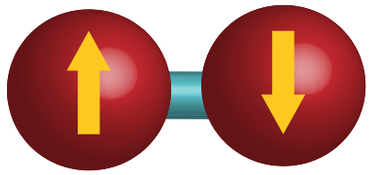
$1 \quad -1 \quad 1 \quad -1 \quad = f^{B2}$

this is why we spent so much time for group theory

2 when we integrate whole space, only f^{A1} has non-zero value

H_2

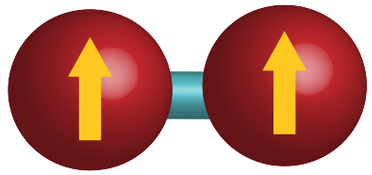
para H_2



$mI = 0$
$gI = 1$

$I = 1/2 - 1/2 = 0$

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

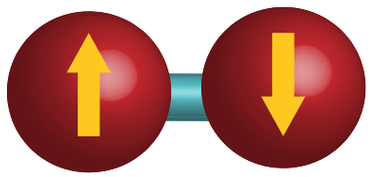
$I = 1/2 + 1/2 = 1$

is the simplest molecule

but the strangest as well

H_2

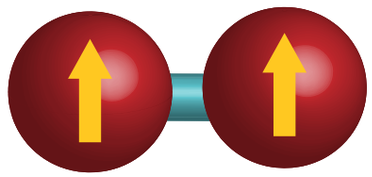
para H_2



$mI = 0$
$gI = 1$

$I = 1/2 - 1/2 = 0$

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

$I = 1/2 + 1/2 = 1$

1 nuclear spin modification

para H_2 J=0,2,4,… couples with

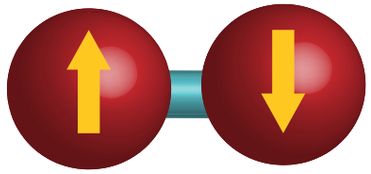
ortho H_2 J=1,3,5,… rotational levels

2 para H_2 ⟷ ortho H_2

3 quadrupole transitions only

H_2

para H_2



$mI = 0$
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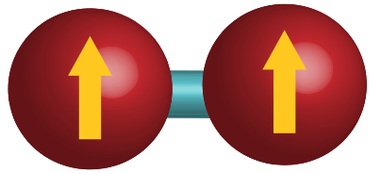
$I = 1/2 - 1/2 = 0$

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

$I = 1/2 + 1/2 = 1$

group theory does not care what the elements are

E identity operator (do nothing) **"Einheit"**

C_{2v}

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

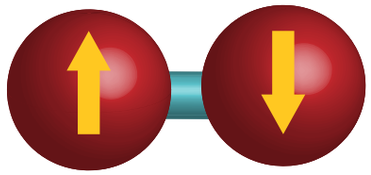
$\sigma_v(xz)$ reflection about **xz** plane

point group

geometrical

H_2

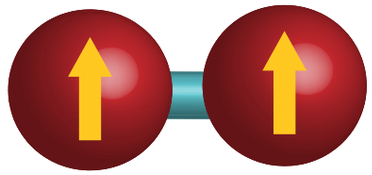
para H_2



$mI = 0$
$gI = 1$

$I = 1/2 - 1/2 = 0$

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

$I = 1/2 + 1/2 = 1$

group theory does not care what the elements are

C_{2v}

E identity operator (do nothing) "Einheit"

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

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

point group

geometrical

$C_{2v}(M)$

E identity operator (do nothing)

(12) permutation of **1** and **2**

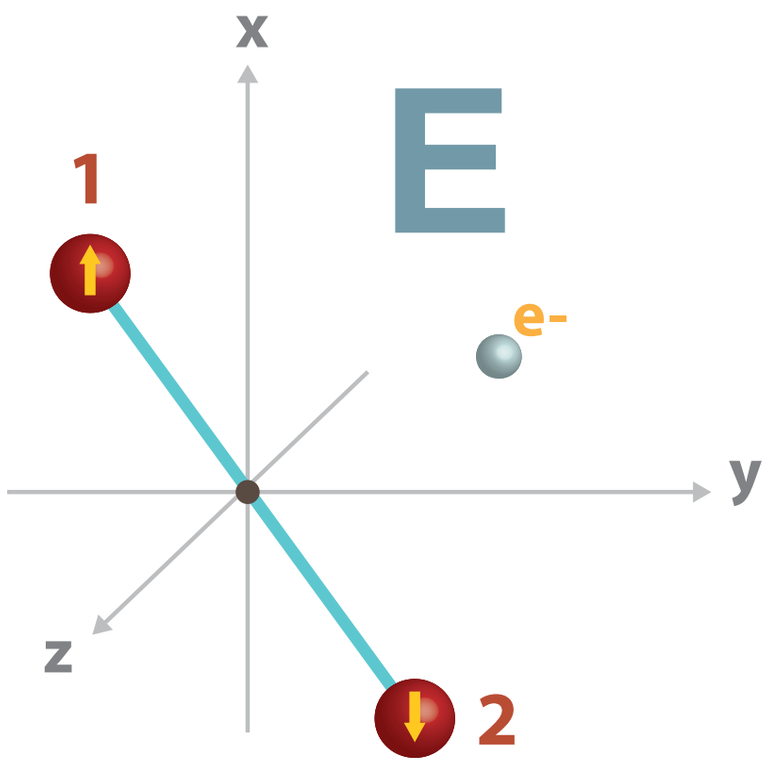
E* inversion

CNPI group

complete nuclear permutation inversion

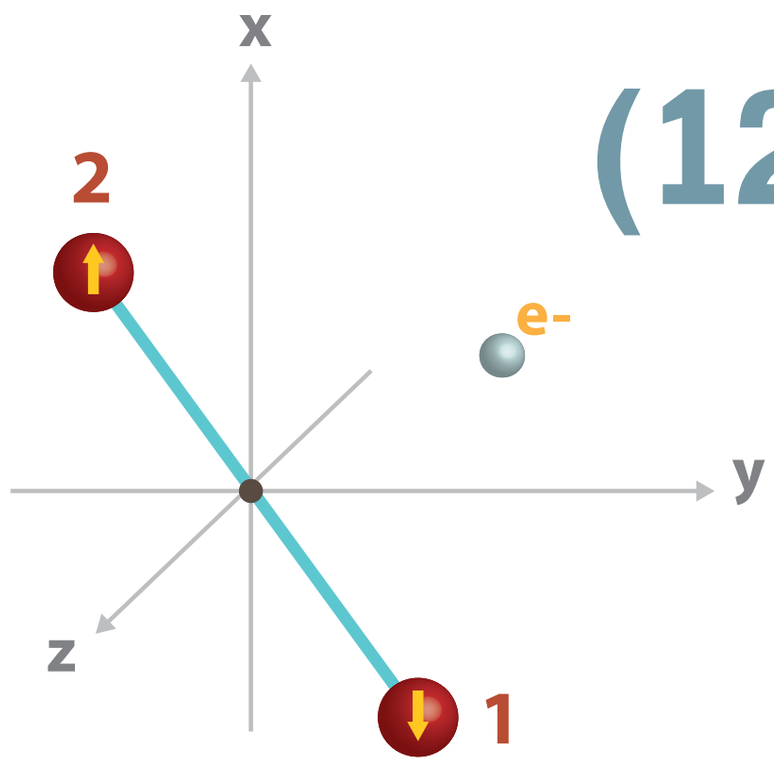
conceptual

permutation inversion group



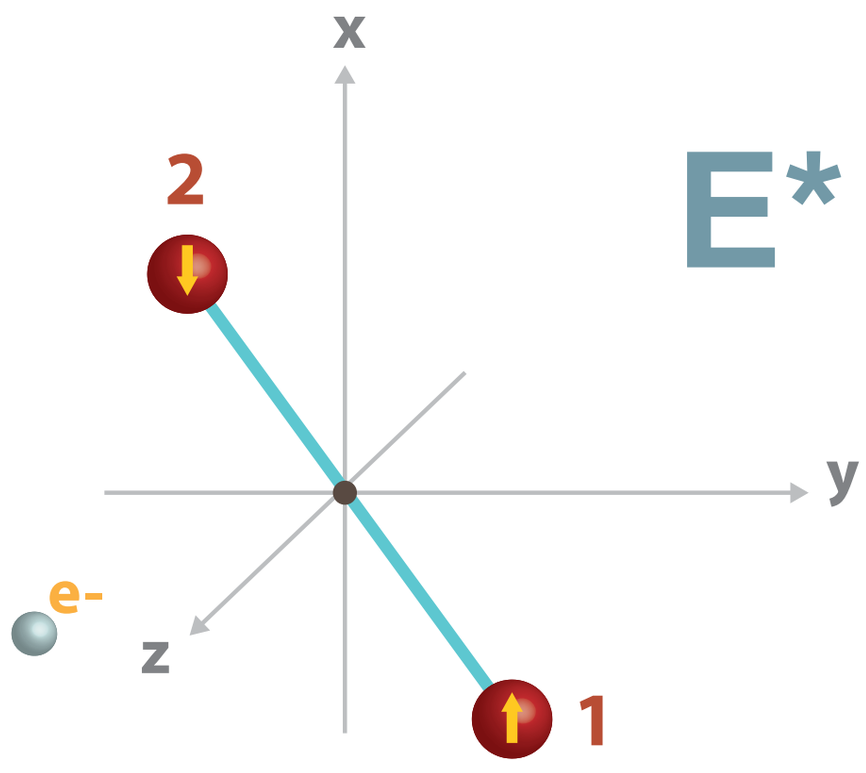
E

permutation

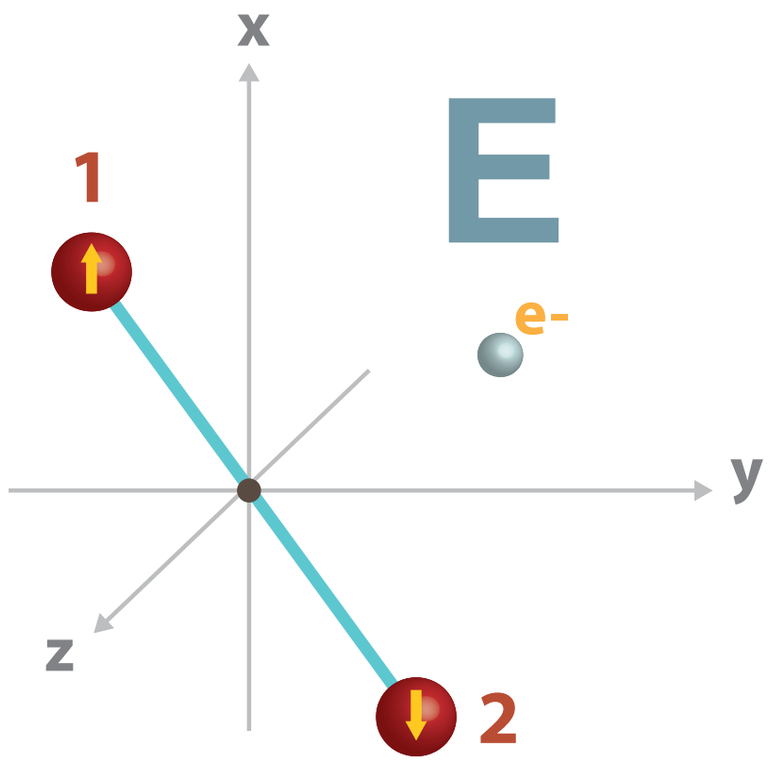


(12)

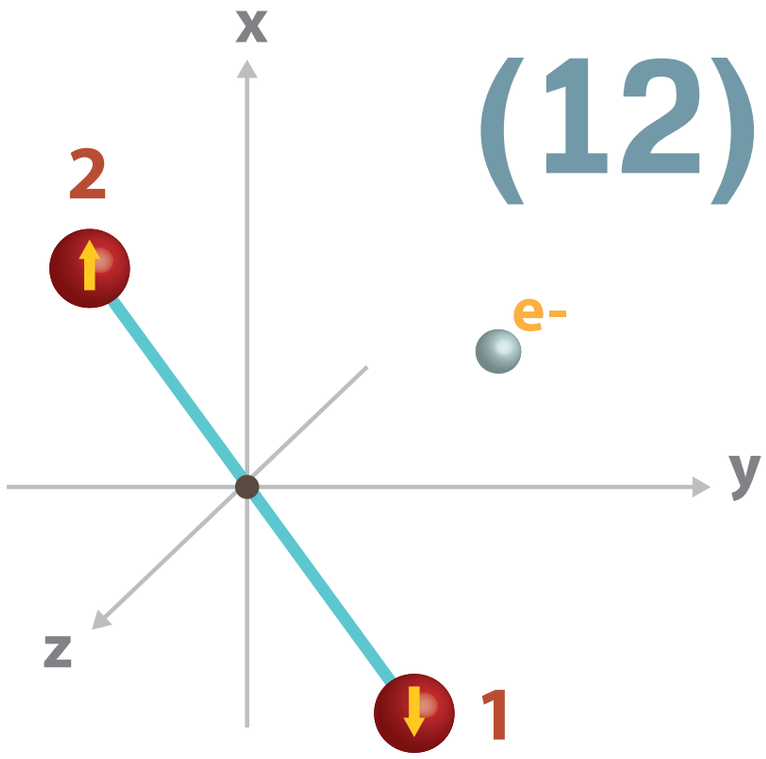
inversion



E*



permutation

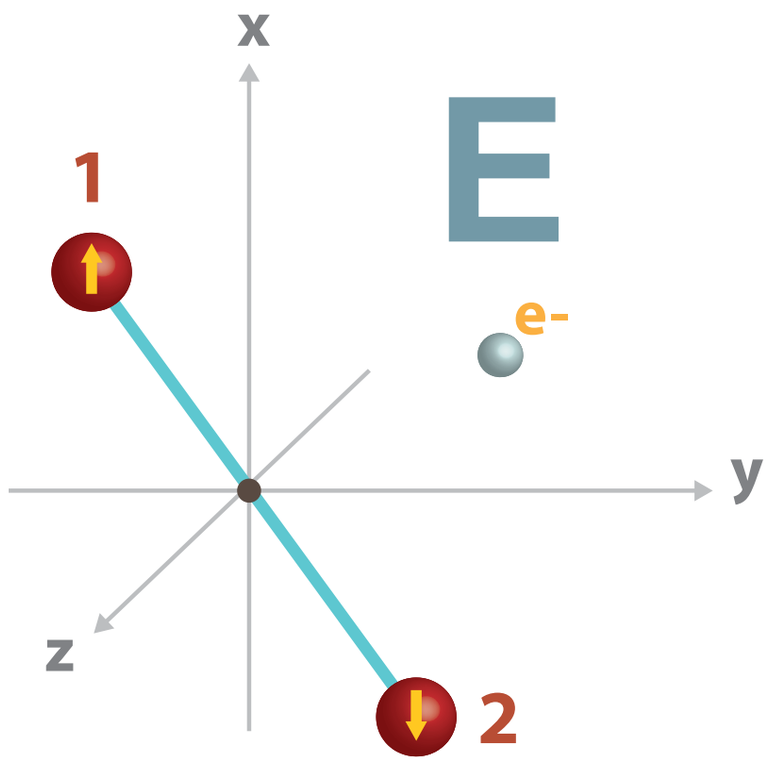


protons exchange **all** attributions

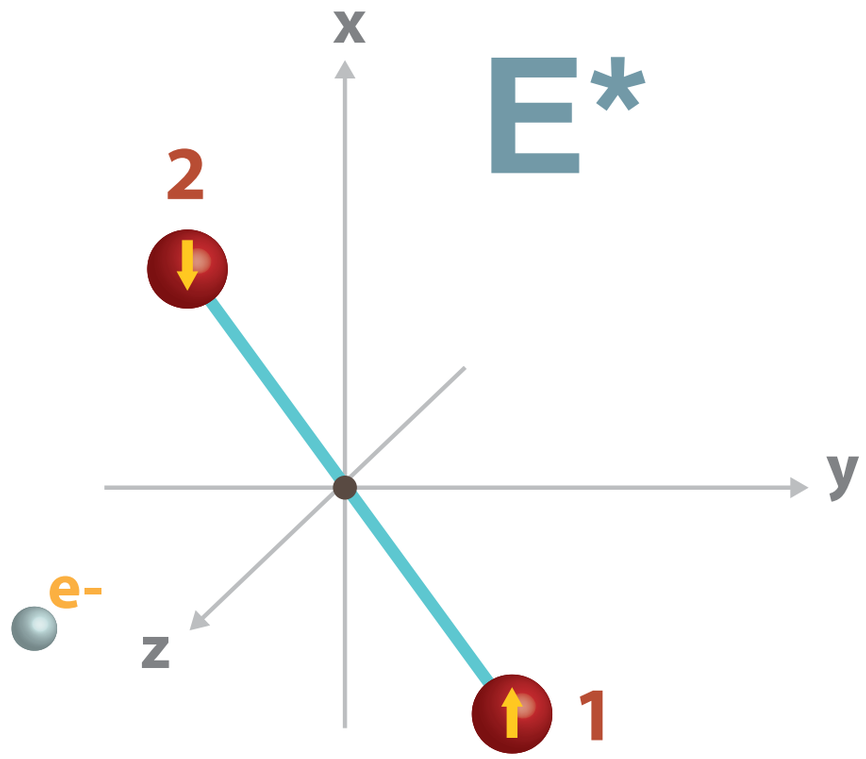
coordinate + spin

→ equivalent to changing **labels**

nuclear permutation does **not** move **electrons**



inversion

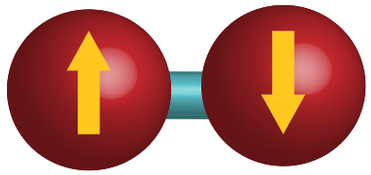


- protons take **all** attributions with them
  - → **spins** as well

- electrons invert positions as well

H_2

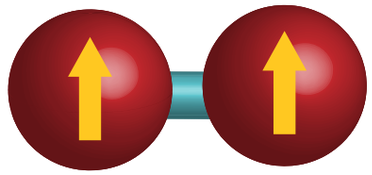
para H_2



$mI = 0$
$gI = 1$

$I = 1/2 - 1/2 = 0$

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

$I = 1/2 + 1/2 = 1$

CNPI group does not deal with shape of wavefunction

but formula of it

(12) re-labeling $x_1, y_1, z_1 \Rightarrow x_2, y_2, z_2$

E* invert sign $r \Rightarrow -r$

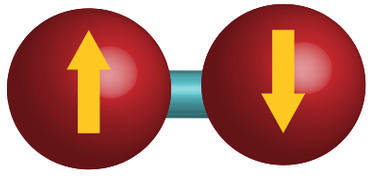
formula of H
Hamiltonian

if Hamiltonian does not change

wavefunction cannot change

H_2

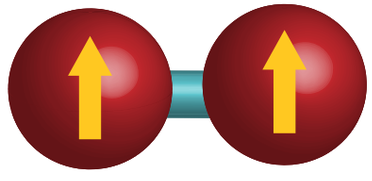
para H_2



$mI = 0$
$gI = 1$

$I = 1/2 - 1/2 = 0$

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

$I = 1/2 + 1/2 = 1$

CNPI group does not deal with **formula of H** Hamiltonian

(12) re-labeling $x_1, y_1, z_1 \Rightarrow x_2, y_2, z_2$

E* invert sign $r \Rightarrow -r$

e.g.

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

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad \frac{\partial^2}{\partial x^2}$$ does not change by **E***

What kind of **shape** is your **wavefunction**?

character table

		E	(12)	E*	(12)*
		permutation		inversion	permutation × inversion
Σ_g^+	A_1	1	1	1	1
Σ_u^-	A_2	1	1	-1	-1
Σ_g^-	B_1	1	-1	-1	1
Σ_u^+	B_2	1	-1	1	-1

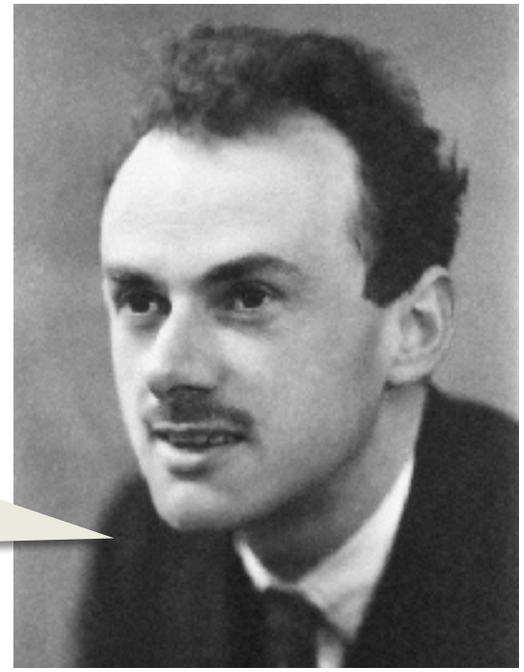
1 : operation leaves sign same $E^*\phi = \phi$

-1 : operation flips sign $(12)\ \phi = -\phi$

exchange of **fermions**

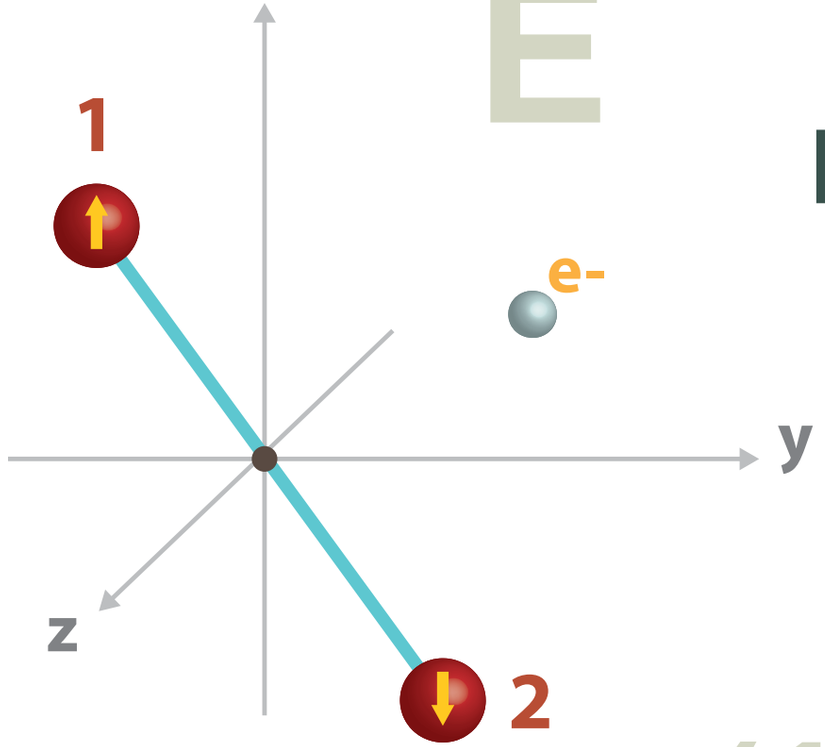
must change

the sign of total wavefunction



Pauli's exclusion principle

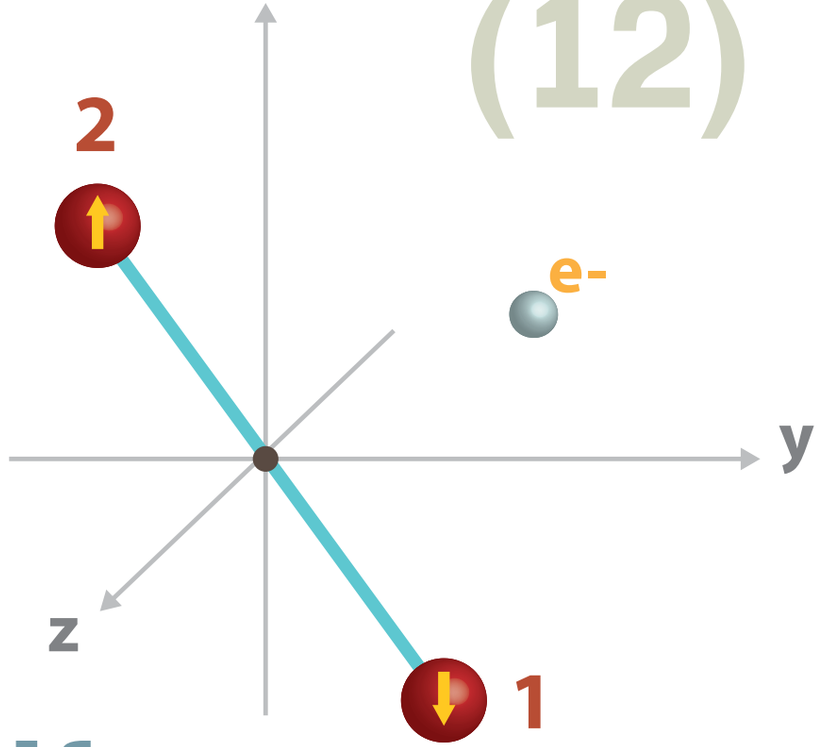
x



E

permutation

x (12)



$(12)\,\Psi = -\Psi$

effectively,
changing labels

(at the permutation of two electrons the wavefunction can behave either symmetrical or anti-symmetrical)

The solution with symmetrical eigenfunctions, on the other hand, allows any number of electrons to be in the same orbit, so that this solution cannot be the correct one for the problem of electrons in an atom.†

Dirac (1926) Proc. R. Soc. Lond. A 112, 661

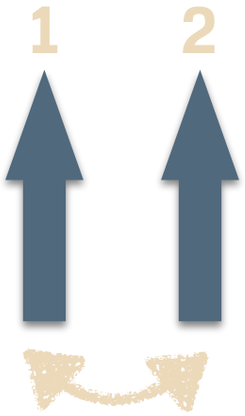
† Prof. Born has informed me that Heisenberg has independently obtained results equivalent to these. (Added in proof)—see Heisenberg, 'Zeit. fur Phys.,' vol. 38, p. 411

Diese Funktion φ hat die besondere Eigenschaft, daß sie bei Vertauschung der Quantenzahlen zweier Teilsysteme das Vorzeichen wechselt.

LMU alumnus
1958-1970 MPA/LMU

Heisenberg (1926), Zeitschrift für Physik, 38, 411

Why this is Pauli exclusion principle?



if there are two electrons
in equivalent orbits,
wavefunction would not change sign

Es kann niemals zwei oder mehrere äquivalente Elektronen im Atom geben, für welche in starken Feldern die Werte aller Quantenzahlen n, k_1, k_2, m_1 (oder, was dasselbe ist, n, k_1, m_1, m_2) übereinstimmen.

Pauli (1924), Zeitschrift für Physik, 31, 765

LMU alumnus

total

electronic vibrational rotational nuclear spin

$$\psi = \phi_e \phi_v \phi_r \phi_{ns}$$

Born-Oppenheimer approximation

electronic

no node:
totally symmetric

Σ_g^+ (12) $\phi_e = \phi_e$

vibrational

function of $|r_1 - r_2|$

no change by permutation or inversion

totally symmetric

(12) $\phi_v = \phi_v$

total

electronic vibrational rotational nuclear spin

$$\psi = \phi_e \, \phi_v \, \phi_r \, \phi_{ns}$$

totally symmetric — totally symmetric

rotational at permutation

(12) $\phi_r(\theta, \phi) = \phi_r(\pi-\theta, \phi+\pi)$

spherical harmonics $Y_{Jm}(\theta, \phi)$

$\phi_r(\pi-\theta, \phi+\pi) = (-1)^J \, \phi_r(\theta, \phi)$

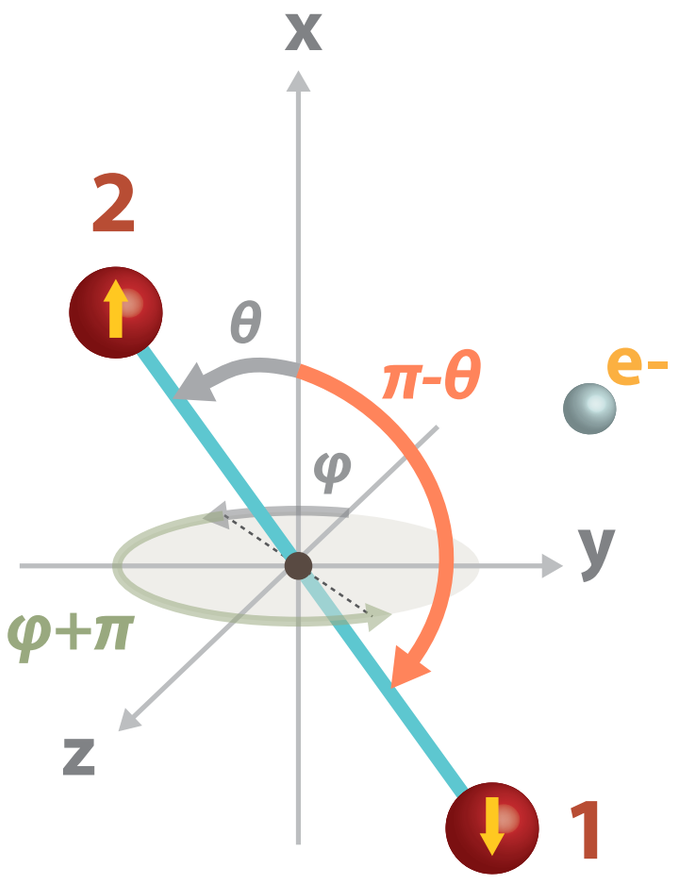
$z = \cos\theta$

$-z = \cos(-\theta)$

$Y_{Jm} \sim z^J$

$J = 1,3,5, \ldots$

$J = 0,2,4, \ldots$



(12) $\phi_r = -\phi_r$

(12) $\phi_r = \phi_r$

total

electronic vibrational rotational nuclear spin

$$\psi = \phi_e \phi_v \phi_r \phi_{ns}$$

totally symmetric — totally symmetric

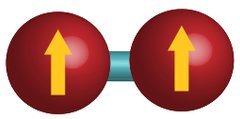
nuclear spin

$$\phi_{ns} = \left\{ |\uparrow\uparrow\rangle \;\; |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \;\; |\downarrow\downarrow\rangle \right\}$$

(12) $\phi_{ns} = \phi_{ns}$

ortho

ortho H_2



$mI = 1, 0, -1$
$gI = 3$

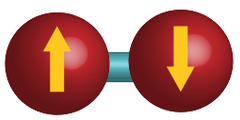
$I = 1/2 + 1/2 = 1$

$$|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$$

(12) $\phi_{ns} = -\phi_{ns}$

para

para H_2



$mI = 0$
$gI = 1$

$I = 1/2 - 1/2 = 0$

total

electronic vibrational rotational nuclear spin

$$\Psi = \Phi_e \Phi_v \Phi_r \Phi_{ns}$$

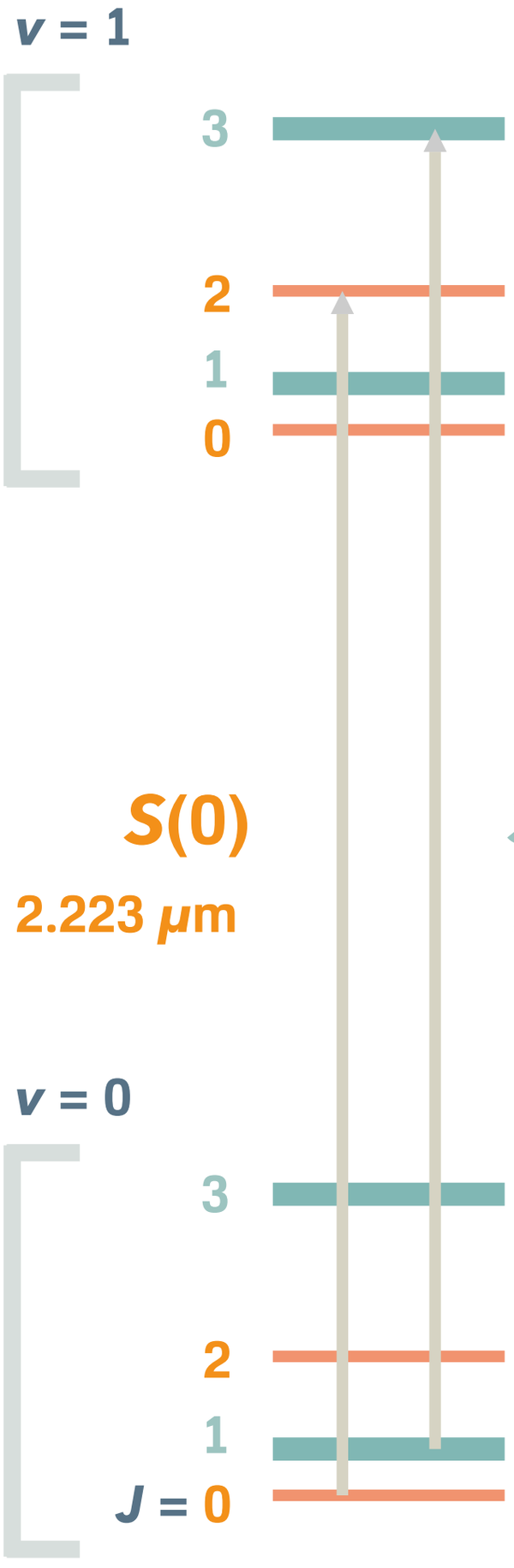
totally symmetric — totally symmetric

$$(12)\ \Psi = -\Psi$$

coupling must be

J = 0,2,4, $(12)\ \Phi_r = \Phi_r$ ortho $(12)\ \Phi_{ns} = \Phi_{ns}$

J = 1,3,5, $(12)\ \Phi_r = -\Phi_r$ para $(12)\ \Phi_{ns} = -\Phi_{ns}$



2 para H_2 ⟷ ortho H_2

behave as if they are

different species of molecules

rather than different excitation states of a molecule

	g_J	g_I	g_{IxJ}
3	7	3	21
2	5	1	5
1	3	3	9
J =0	1	1	1

2 Why para H_2 ⇄ ortho H_2

What kind of **shape** is your **wavefunction**?

		E	(12)	E*	(12)*
			permutation	inversion	permutation × inversion
Σ_g^+	A_1	1	1	1	1
Σ_u^-	A_2	1	1	-1	-1
Σ_g^-	B_1	1	-1	-1	1
Σ_u^+	B_2	1	-1	1	-1

1 : operation leaves sign same $E^*\phi = \phi$

-1 : operation flips sign $(12)\ \phi = -\phi$

		E	(12)	E*	(12)*
Σ_g^+	A_1	1	1	1	1
Σ_u^-	A_2	1	1	-1	-1
Σ_g^-	B_1	1	-1	-1	1
Σ_u^+	B_2	1	-1	1	-1

permutation inversion permutation × inversion

$$(12)\ \phi_r(\theta, \phi) = \phi_r(\pi-\theta, \phi+\pi) = (-1)^J \phi_r(\theta, \phi)$$

$$E^*\ \phi_r(\theta, \phi) = \phi_r(\pi-\theta, \phi+\pi) = (-1)^J \phi_r(\theta, \phi)$$

rotational

ϕ_r

$J = 0,2,4, \ldots$ A_1

$J = 1,3,5, \ldots$ B_1

		E	(12)	E*	(12)*
Σ_g^+	A_1	1	1	1	1
Σ_u^-	A_2	1	1	-1	-1
Σ_g^-	B_1	1	-1	-1	1
Σ_u^+	B_2	1	-1	1	-1

permutation

inversion

permutation +inversion

nuclear spin

$$\phi_{ns} = \left\} \begin{array}{l} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{array} \right.$$

$E^*\phi_{ns} = \phi_{ns}$

$(12)\ \phi_{ns} = \phi_{ns}$

A_1

ortho

$$|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$$

$E^*\phi_{ns} = \phi_{ns}$

$(12)\ \phi_{ns} = -\phi_{ns}$

B_2

para

electric dipole moment?

$$\mu_e = \Sigma e r$$

1. **permutation** does not change μ_e

   only **labeling** changed

2. **inversion** does

   because $r \rightarrow -r$

$$A_2$$

	E	(12)	E*	(12)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

What **group theory** gives us for free

	E	(12)	E*	(12)*
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

1 as long as functions are basis of symmetry representation

$f^{A1} \times f^{A2}$ 1x1, 1x1, 1x-1, 1x-1

1 1 -1 -1 $= f^{A2}$

$f^{A2} \times f^{B1}$ 1x1, 1x-1, -1x-1, -1x1

1 -1 1 -1 $= f^{B2}$

this is why we spent so much time for group theory

2 when we integrate whole space, only f^{A1} has non-zero value

(12) $\phi_r(\theta, \phi) = (-1)^J \phi_r(\theta, \phi)$

E* $\phi_r(\theta, \phi) = (-1)^J \phi_r(\theta, \phi)$

J = 0,2,4, … A_1

J = 1,3,5, … B_1

	E	(12)	E*	(12)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

to have permitted transition $\langle \phi_r' | \mu_e | \phi_r'' \rangle = A_1$

$\phi_r : A_1$

$A_1 \; A_2 \; X = A_1 \rightarrow X = A_2$

$\phi_r : B_1$

$B_1 \; A_2 \; X = A_1 \rightarrow X = B_2$

1 -1 1 -1 B_2

Both not allowed

electric quadrupole moment?

$$\mu_4 : A_1$$

$\phi_r : A_1$

$$A_1\ A_1\ X = A_1 \rightarrow X = A_1$$

$\phi_r : B_1$

$$B_1\ A_1\ X = A_1 \rightarrow X = B_1$$

END13