Group theory

Definition: group $\mathcal{G}$ is a set $\mathcal{G} = \{a, b, c, \ldots\}$ with a product $\cdot$

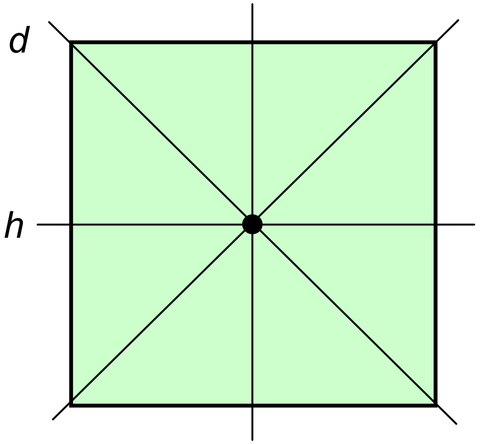
$$\begin{array}{l} a \in \mathcal{G} \\ b \in \mathcal{G} \end{array} \;\Rightarrow\; a \cdot b \in \mathcal{G}$$

associative $(a \cdot b) \cdot c = a \cdot (b \cdot c)$

identity $E \in \mathcal{G}$ with $E \cdot a = a \cdot E = a$

inverse $a \in \mathcal{G} \Rightarrow a^{-1} \in \mathcal{G}$ with $a^{-1} \cdot a = a \cdot a^{-1} = E$

Example: C_{4v} symmetry operation of square



$$C_{4v} = \{E, C_4, C_4^{-1}, C_2, \sigma_h, \sigma_h', \sigma_d, \sigma_d'\}$$

$$C_4 \cdot C_4 = C_2 \qquad \underbrace{\sigma_h \cdot C_4 = \sigma_d' \qquad C_4 \cdot \sigma_h = \sigma_d}_{\sigma_h \cdot C_4 \neq C_4 \cdot \sigma_h}$$

non-abelian

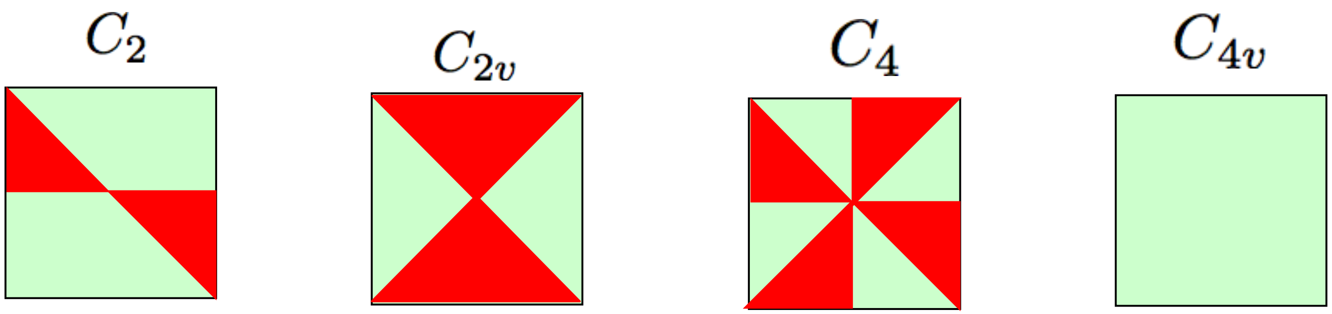
Group theory

subgroup: group $\mathcal{G}'$ subset of $\mathcal{G}$

$$\mathcal{G}' \subset \mathcal{G}$$

examples:

$$\left.\begin{array}{l} C_4 = \{E, C_4, C_4^{-1}, C_2\} \\ C_{2v} = \{E, C_2, \sigma_h, \sigma_h'\} \\ C_2 = \{E, C_2\} \end{array}\right\} \subset C_{4v}$$



number of elements: $|\mathcal{G}'|$ devides $|\mathcal{G}|$

Group theory representations

Representation of a group

represent elements of group as linear operations on a vector space

n-dimensional vector space $\mathcal{V} = \{|1\rangle, |2\rangle, \ldots, |n\rangle\}$

operation: $g \in \mathcal{G} \longmapsto \hat{S}_g$ with $\hat{S}_g|k\rangle = |k\rangle'$

$$gg' \longmapsto \hat{S}_g\hat{S}_{g'} = \hat{S}_{gg'} \quad \text{and} \quad \hat{S}_E = \hat{1}$$

linear operation as matrix representation in $\mathcal{V}$ (dependent on basis)

$$|k\rangle' = \hat{S}_g|k\rangle = \sum_j |j\rangle\langle j|\hat{S}_g|k\rangle = \sum_j M_{kj}(g)|j\rangle$$

$$g'' = gg' \longmapsto \langle j|\hat{S}_{g''}|k\rangle = \sum_m \langle j|\hat{S}_g|m\rangle\langle m|\hat{S}_{g'}|k\rangle \quad \text{and} \quad \langle j|\hat{S}_E|k\rangle = \delta_{jk}$$

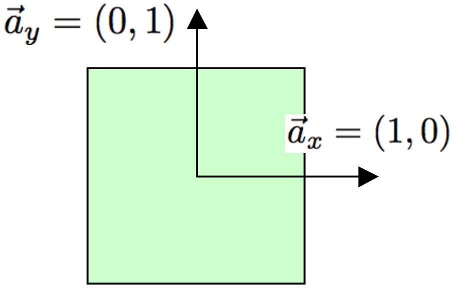
character: $\chi(g) = \sum_j \langle j|\hat{S}_g|j\rangle$ basis independent

Group theory — representations

irreducible representation: independent of basis $\{\hat{M}(g)\}$ connects whole $\mathcal{V}$

trivial representation: $n = 1$ $\quad g \rightarrow \hat{M}(g) = 1$

example: C_{4v} $\quad \hat{M}$ transformation of $\{\vec{a}_x, \vec{a}_y\}$



$$E \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad C_4 \rightarrow \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad C_4^{-1} \rightarrow \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad C_2 \rightarrow \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma_h \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_h' \rightarrow \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad \sigma_d \rightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_d' \rightarrow \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

character table

	E	C_4	C_4^{-1}	C_2	σ_h	σ_h'	σ_d	σ_d'	basis function
A_1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1	-1	-1	$xy(x^2-y^2)$
B_1	1	-1	-1	1	1	1	-1	-1	x^2-y^2
B_2	1	-1	-1	1	-1	-1	1	1	xy
E	2	0	0	-2	0	0	0	0	$\{x, y\}$

Group theory representations & quantum mechanics

vector space $\rightarrow$ Hilbert space $\{|\psi_1\rangle, |\psi_2\rangle, \ldots\}$

group of symmetry operation $\mathcal{G} = \{\hat{S}_1, \hat{S}_2, \ldots\}$

Hamiltonian: $\mathcal{H}$ $\rightarrow$ $[\hat{S}_j, \mathcal{H}] = 0$ invariant under symmetry operation

stationary states: $\mathcal{H}|\phi_n\rangle = \epsilon_n|\phi_n\rangle$

$[\hat{S}, \mathcal{H}] = 0$ $\rightarrow$ $\mathcal{H}\hat{S}|\phi_n\rangle = \hat{S}\mathcal{H}|\phi_n\rangle = \epsilon_n\hat{S}|\phi_n\rangle$

$|\phi_n\rangle$ and $|\phi'_n\rangle = \hat{S}|\phi_n\rangle$ degenerate

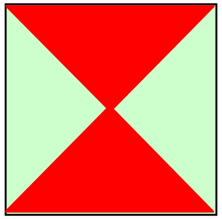
$$|\phi'_n\rangle = \hat{S}|\phi_n\rangle = \sum_m |\phi_m\rangle\langle\phi_m|\hat{S}|\phi_n\rangle$$

within the subspace of degenerate states

Group theory — representations & quantum mechanics

symmetry lowering $C_{4v} \rightarrow C_{2v}$

C_{2v}



	E	C_2	σ_h	σ_h'	basis
A_1'	1	1	1	1	1
A_2'	1	-1	1	-1	x
B_1'	1	1	-1	-1	xy
B_2'	1	-1	-1	1	y

Compatibility relation

C_{4v}	C_{2v}
A_1	A_1'
A_2	B_1'
B_1	A_1'
B_2	B_1'
E	$A_2' \oplus B_2'$

splitting of degeneracy through symmetry lowering