Motivation

Interaction of matter with incident wave (represented by a perturbation *H'*):

transition matrix element for, e.g., absorption from state $m \rightarrow n$:

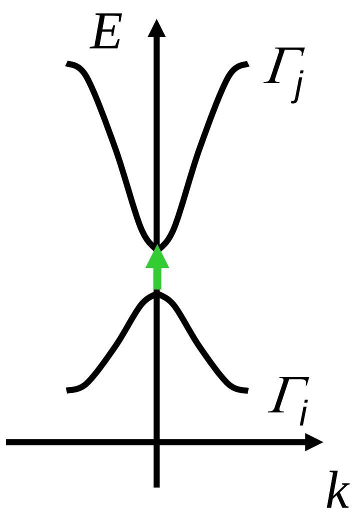
$$H'_{ji}(t) = \int_V \phi_j^*(\boldsymbol{r}) H' \phi_i(\boldsymbol{r}) d^3\boldsymbol{r} = \langle j | H' | i \rangle$$

Using symmetry considerations, we can determine if matrix element vanishes or not (transition forbidden / allowed) $\Rightarrow$ selection rules

$$\langle j | H' | i \rangle = \begin{cases} \neq 0 & \text{if } \Gamma_j \in \Gamma_s \otimes \Gamma_i \Leftrightarrow \Gamma_1 \in \Gamma_j \otimes \Gamma_s \otimes \Gamma_i \\ = 0 & \text{otherwise (for symmetry reasons)} \end{cases}$$

Γ_j Γ_s Γ_i

Note: In this case the matrix element could still be „coincidentally" = 0



i.e., initial state i with symmetry Γ_i, final state j with symmetry Γ_j

perturbation H' has symmetry Γ_s

$\Rightarrow$ group theory!

Further applications (see later):

- band structure (degeneracy of electronic states)
- matrix elements in general

Group theory – general remarks

Consider Noether's theorem again:

From the invariance of the Hamiltonian towards a transformation follows a conserved quantity, e.g.:

a) H invariant for infinitesimal shifts in time: $H(t) = H(t + dt)$

$\Rightarrow$ total energy is conserved: E_{total} = const.

b) H invariant for infinitesimal shifts in space: $H(x) = H(x + dx)$

$\Rightarrow$ momentum is conserved: p_x = const.

c) H invariant for infinitesimal rotations around some axis: $H(f) = H(f + df)$

$\Rightarrow$ angular momentum is conserved: $\boldsymbol{L}$ = const.

In a crystal:

a) still satisfied

b) H is only invariant for translation about a lattice vector

$\Rightarrow$ $\hbar\boldsymbol{k}$ is only conserved for shifts about a reciprocal lattice vector $\hbar\boldsymbol{G}$

c) H is at most invariant for specific rotation angles $\Rightarrow$ $\boldsymbol{L}$ is not conserved

$\Rightarrow$ **Bands cannot be characterized by angular momentum quantum numbers**

$\Rightarrow$ **Replacement for charact. of bands / derivation of selection rules etc.: symm. prop.**

Group theory – basics

Definition: group (G, "•"):

Set of elements $\{x_i\}$ and operations with the following properties:

1) Closure: $\forall\, x, y \in G$ follows $x \cdot y = z \in G$

2) Associativity: $\forall\, x, y, z \in$ G follows $x \cdot (y \cdot z) = (x \cdot y) \cdot z$

3) Identity / neutral element $E \in$ G, $\forall\, x \in G$ follows $E \cdot x = x \cdot E = x$

4) Inverse element: $\forall\, x, E \in G\ \exists\, x^{-1} \in G\ \therefore\ x^{-1} \cdot x = x \cdot x^{-1} = E$

- Number of elements $x_i \in G$ is called order g of the group
- There are finite and infinite groups

Definition: Abelian group G:

$\forall\, x, y \in G$ follows $x \cdot y = y \cdot x$

Examples:

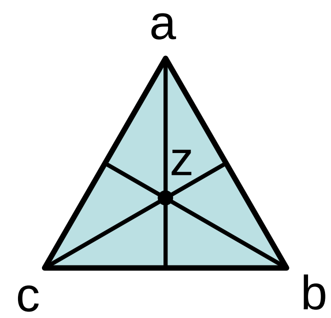
1) {0, ±1, ±2, …, "+"}: infinite, Abelian group of integer numbers (Z, +)

2) Rational numbers (Q, ·): infinite Abelian group with E = 1, inverse: $(p/q)^{-1} = (q/p)$

3) {{1, -1, i, -i}, ·): finite Abelian group, $g = 4$

4) All symmetry operations that convert a equilateral triangle back to itself

Group theory – example: Group D_3



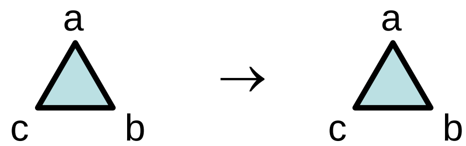
D_3 is finite and *not* abelian

↑

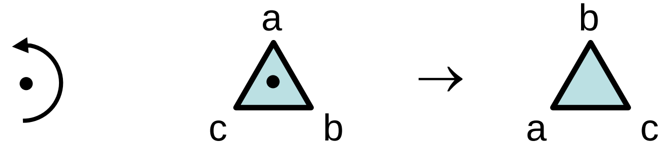
Schönflies notation, 3 denotes 3-fold symmetry axis

Operations:

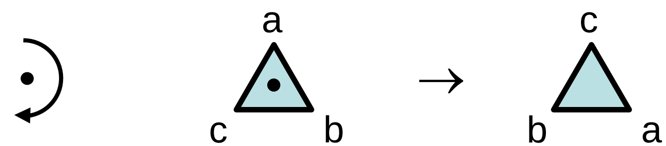
E: ± 0°



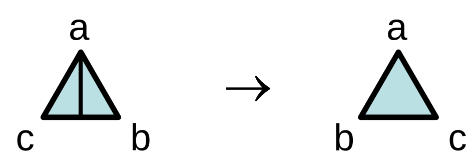
Rotations: *J*: + 120° around z



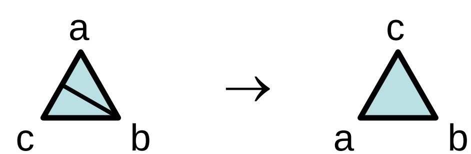
K: - 120° around z



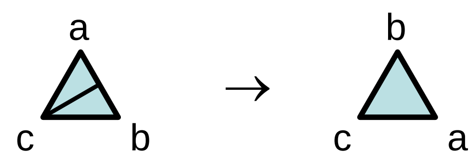
Reflections: *L*: ± 180° about a-axis



M: ± 180° about b-axis



N: ± 180° about c-axis

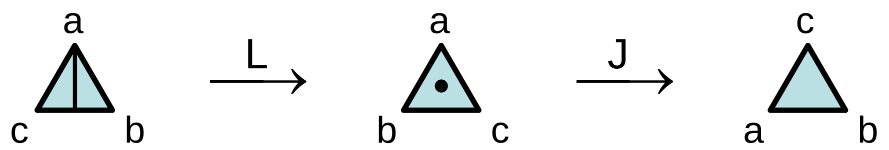


Group theory – example: D_3

Why not abelian?

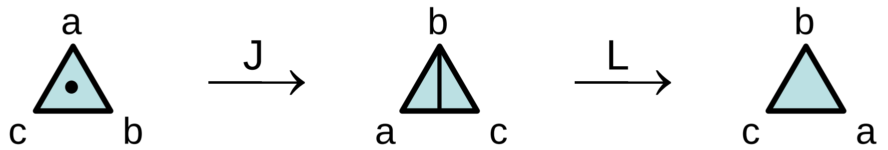
$J \bullet L$:

(First L, then J)



$= M$

but $L \bullet J$:



$= N$

$$\Rightarrow \quad J \bullet L \neq L \bullet J$$

Group theory – example: D_3

Multiplication table (group table):

	E	**J**	**K**	**L**	**M**	**N**
E	*E*	*J*	*K*	*L*	*M*	*N*
J	*J*	*K*	*E*	*M*	*N*	*L*
K	*K*	*E*	*J*	*N*	*L*	*M*
L	*L*	*N*	*M*	*E*	*K*	*J*
M	*M*	*L*	*N*	*J*	*E*	*K*
N	*N*	*M*	*L*	*K*	*J*	*E*

Read:
First column, then row
e.g., $J \bullet L = M$

In every row and column, each element exists only once!

(otherwise, e.g., $K \cdot L = K \cdot M$; multiply by K^{-1} $\Rightarrow L = M$)

$\Rightarrow$ For groups of order 6 exist only two tables:

C_6: 6-fold axis, only rotations

D_3: rotations and reflections

All other groups are isomorphic to C_6 or D_3

Group theory – some definitions

Definition: isomorphism

Bijective transformation of elements $x_i \in G$ to elements $x_i' \in G'$ while keeping the multiplication table

$$\Rightarrow \qquad g = g'$$

$$x_i \rightarrow x_i' \qquad \Rightarrow \qquad x_i' \rightarrow x_i$$

$$\begin{matrix} x_i \rightarrow x_i' \\ x_j \rightarrow x_j' \\ x_k \rightarrow x_k' \end{matrix} \quad \text{with} \quad x_i \bullet x_j = x_k \quad \Rightarrow \quad x_i' \bullet x_j' = x_k'$$

Example: the group of permutations of three elements is isomorphic to D_3

(abc),	(cab),	(bac),	(acb),	(cba),	(bca)
↓	↓	↓	↓	↓	↓
E	K	N	L	M	J

C_6 is not isomorphic to D_3 !

Group theory – some definitions

Definition: homomorphism

Similar to isomorphism, however $g \geq g'$, i.e., not bijective (no one-to-one correspondence)

e.g.: $E \rightarrow 1$, $J \rightarrow 1$, $K \rightarrow 1$, $L \rightarrow -1$, $M \rightarrow -1$, $N \rightarrow -1$

Definition: sub-group

Subset of *G*, which is itself a group

Examples:

- {*G*}: trivial sub group
- {*E*}: trivial sub group
- {*E*, *J*, *K*}
- {*E*, *L*}

	E	***J***	***K***	***L***	***M***	***N***
E	*E*	*J*	*K*	*L*	*M*	*N*
J	*J*	*K*	*E*	*M*	*N*	*L*
K	*K*	*E*	*J*	*N*	*L*	*M*
L	*L*	*N*	*M*	*E*	*K*	*J*
M	*M*	*L*	*N*	*J*	*E*	*K*
N	*N*	*M*	*L*	*K*	*J*	*E*

Group theory – some definitions

Definition: adjoint

The elements A and $B \in G$ are adjoint, if there exists at least one element $X \in G$ ∴

$$B = X^{-1} \bullet A \bullet X \text{ (similarity transformation)}$$

e.g., in D_3, L and M are adjoint: $M = N^{-1} \bullet L \bullet N$ with $N^{-1} = N$

Definition: self-adjoint

An element $A \in G$ is called self-adjoint, if $\forall X \in G$ follows: $X^{-1} \bullet A \bullet X = A$

e.g., E: $X^{-1} \bullet E \bullet X = E$

Definition: class

All elements of a group, that are adjoint, form a class.

e.g., for D_3: three classes

$$C_1 = \{E\}, \quad C_2 = \{L, M, N\} \text{ (reflections)}, \quad C_3 = \{J, K\} \text{ (120° rotations)}$$

Group theory – some definitions

Definition: outer / direct product of two groups

G'' = $G \otimes G'$ is a group of all ordered pairs (x_i, x_j') with $x_i \in G$ and $x_j' \in G'$

Product:

$$(x_i, x_j') \bullet (x_k, x_l') = (x_i \bullet x_k, x_j' \bullet x_l')$$

Order of G'': $g'' = g \bullet g'$

e.g.

$H_1 = \{E, J, K\}$ and $H_2 = \{E, L\}$

$\Rightarrow H_1 \otimes H_2 = \{\{E, E\}, \{E, L\}, \{J, E\}, \{J, L\}, \{K, E\}, \{K, L\}\}$

$= C_6$

not isomorphic to D_3

Group theory – representations

Definition: representation Γ_α

- Γ_α is (in the narrower sense) a set of matrices that fulfills the multiplication table of the group
- $\Gamma_\alpha(R)$ is a matrix out of Γ_α, that represents the group element R
- $\Gamma_\alpha(R)_{ij}$ is the ij-element (i^{th} row, j^{th} column) of the matrix $\Gamma_\alpha(R)$
- n_α is the dimension of the ($n_\alpha \times n_\alpha$) matrices of the representation Γ_α (same for all matrices)

Matrix multiplication: $$\sum_l \Gamma_\alpha(K)_{il}\,\Gamma_\alpha(L)_{lj} = \Gamma_\alpha(K \cdot L)_{ij}$$

e.g.

E	$= 1$	or $= 1$
J	$= 1$	$= 1$
K	$= 1$	$= 1$
L	$= 1$	$= -1$
M	$= 1$	$= -1$
N	$= 1$	$= -1$

trivial representation

The number of representations for each group is infinite!

If Γ_α is a representation of a group G and X a

non-singular matrix (i.e., det $X \neq 0$)

$\Rightarrow \{X^{-1} \cdot \Gamma_\alpha \cdot X\}$ (i.e., $X^{-1} \cdot \Gamma_\alpha(R) \cdot X \;\; \forall\, R \in G$) is also a representation

Group theory – example: D_3

Example: one representation of the group D_3: $\Gamma_3^{(1)}$

$$\Gamma_3^{(1)}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \Gamma_3^{(1)}(J) = \begin{pmatrix} 0 & 1 \\ -1 & -1 \end{pmatrix} \qquad \Gamma_3^{(1)}(K) = \begin{pmatrix} -1 & -1 \\ 1 & 0 \end{pmatrix}$$

$$\Gamma_3^{(1)}(L) = \begin{pmatrix} 1 & 0 \\ -1 & -1 \end{pmatrix} \qquad \Gamma_3^{(1)}(M) = \begin{pmatrix} -1 & -1 \\ 0 & 1 \end{pmatrix} \qquad \Gamma_3^{(1)}(N) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$\Gamma_3^{(1)}$ fulfills the multiplication table of D_3:

e.g., $\Gamma_3^{(1)}(J) \cdot \Gamma_3^{(1)}(N) = \Gamma_3^{(1)}(J \bullet N) = \Gamma_3^{(1)}(L)$

Group theory – representations

Definition: reducible representation

Given is a set of matrices Γ_α. If one can find one non-singular matrix X, such that *all* matrices from Γ_α obtain block-diagonal format under the transformation $X^{-1} \cdot \Gamma_\alpha(R) \cdot X$, then the representation is called *reducible.*

$$\begin{pmatrix} \Gamma_1(R) & 0 & 0 \\ 0 & \Gamma_2(R) & 0 \\ 0 & 0 & \Gamma_3(R) \end{pmatrix} = \Gamma_1(R) \oplus \Gamma_2(R) \oplus \Gamma_3(R) \qquad \forall R$$

- During matrix multiplication the blocks are multiplied with each other without mixing into other blocks. This means each set of blocks is again a representation.
- The reducible matrix is equivalent to a *direct sum* of several matrices:

$$\Gamma_1(R) \oplus \Gamma_2(R) = \begin{pmatrix} \Gamma_1(R) & 0 \\ 0 & \Gamma_2(R) \end{pmatrix}$$

Definition: *Irreducible Representation*

If a representation cannot be reduced further through the transformation above, it is called *irreducible.*

Example: Representations of the group D_3

	E	J	K	L	M	N
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
$\Gamma_3^{(a)}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & -1 \\ 3 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & -3 \\ 1 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & 3 \\ 1 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & 3 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$

$\Gamma_3^{(b)}$ is equivalent to $\Gamma_3^{(1)}$ with $X = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$

reducible represent. $\Gamma_1 \oplus \Gamma_3^{(a)}$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -1/2 \\ 0 & 3/2 & -1/2 \end{pmatrix} \quad \cdots \quad \cdots \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Definition:

Two irreducible representations Γ_α and Γ_β are called *equivalent*, if $\exists$ matrix X $\therefore$

$X^{-1} \cdot \Gamma_\alpha(R) \cdot X = \Gamma_\beta(R)\ \forall\ R \in G$.

Group theory – Orthogonality relations

There is an orthogonality relation for irreducible representations. It follows from the lemmas of Schur:

1. Lemma of Schur

A representation Γ_α is irreducible $\Leftrightarrow$ the only matrices M, that commutes with $\Gamma_\alpha(R)\ \forall\ R$ (i.e., $M \cdot \Gamma = \Gamma \cdot M$), are scalar matrices $M_{ij} = M_0 \delta_{ij}$.

2. Lemma of Schur

Given are Γ_α and Γ_β as irreducible representations and a matrix M with $M \cdot \Gamma_\alpha(R) = \Gamma_\beta(R) \cdot M\ \forall\ R \in G$, then it follows:

a) if $n_\alpha \neq n_\beta$, then $M = 0$ (matrices not square-shaped)

b) if $n_\alpha = n_\beta$, then $M = 0$ or

M is not singular, i.e., Γ_α and Γ_β are equivalent.

Group theory – Orthogonality relations

$\Rightarrow$ Orthogonality relation for irreducible representations:

$$\sum_R \Gamma_\alpha(R)_{ip} \cdot \Gamma_\beta(R^{-1})_{qj} = \frac{g}{n_\alpha}\delta_{\alpha\beta}\delta_{ij}\delta_{pq} \quad , \; R \in G$$

with $$\delta_{\alpha\beta} = \begin{cases} 0 & \text{if } \Gamma_\alpha \text{ and } \Gamma_\beta \text{ are not equivalent} \\ 1 & \text{if } \Gamma_\alpha \text{ and } \Gamma_\beta \text{ are identical} \\ \text{undefined} & \text{if } \Gamma_\alpha \text{ and } \Gamma_\beta \text{ are equivalent} \end{cases}$$

Group theory - Characters

For each representation exists a set of characteristic values $\chi_\alpha(R)$ with

$$\chi_\alpha(R) = \sum_i \Gamma_\alpha(R)_{ii} = \text{Trace}(R)$$

Definition: *Character*

$\{\chi_\alpha(R)\}$ is called the character of the representation Γ_α

- Two representations Γ_α and Γ_β are equivalent $\Leftrightarrow$ they have the same character since Trace $\Gamma_\alpha(R)$ = Trace $X^{-1} \cdot \Gamma_\alpha(R) \cdot X$ = Trace $\Gamma_\beta(R)$.

- The character value of E indicates the dimension n_α of the representation

- Elements of the same class have the same trace, since the elements of a class are adjoint to each other.

- Characters make our life easier, see below …

Group theory – Characters: Example

Example: D_3

	E	J	K	L	M	N
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
$\Gamma_3^{(1)}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & -1 \\ 3 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & -3 \\ 1 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & 3 \\ 1 & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & 3 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$

	E	***J***	***K***	***L***	***M***	***N***
χ_1	1	1	1	1	1	1
χ_2	1	1	1	-1	-1	-1
χ_3	2	-1	-1	0	0	0

classes

Different character values show that group elements belong to different classes (in this case, identity, rotations, reflections)

Group theory – Characters: Example

It is sufficient to list the character values of the classes (same values within one class):

$C_1 = \{E\}$, $C_2 = \{J, K\}$, $C_3 = \{L, M, N\}$

$\Rightarrow$ Character table of D_3

number of elements

	C_1	$2\ C_2$	$3\ C_3$
χ_1	1	1	1
χ_2	1	1	-1
χ_3	2	-1	0

h_i : number of elements in class C_i
r : number of classes in G

Group theory – Characters: Orthogonality relations etc.

$$\sum_{i=1}^{r} h_i \chi_\alpha(C_i)\chi_\beta^*(C_i) = g\delta_{\alpha\beta}$$ Different representations

$$\sum_{\alpha=1}^{r} h_i \chi_\alpha(C_i)\chi_\alpha(C_j) = g\delta_{ij}$$ Different classes

- Criterion for irreducibility: Γ_α irreducible $\Leftrightarrow \sum_R |\chi_\alpha(R)|^2 = g$
- Number of irreducible representations of a group equal to number of classes, and

$$\sum_{\alpha=1}^{r} n_\alpha^2 = g$$

Group theory – Reduction of a representation

Given: Reducible representation Γ of a group G

$\Rightarrow$ Transformation in block form and reduction into direct sum of given (non-equivalent) irreducible representations Γ_α possible, but how?

Easy to accomplish with character $\chi(R)$ of Γ:

$$\Gamma = p_1\Gamma_1 \oplus \cdots \oplus p_n\Gamma_n \qquad \text{with} \qquad p_\alpha = \frac{1}{g}\sum_R \chi(R)\chi_\alpha^*(R) \qquad (*)$$

Example: 4-dimensional reducible representation Γ of group D_3 given as

	C_1	$2\,C_2$	$3\,C_3$
χ	4	1	0

$$p_1 = \frac{1}{6}\left(4\cdot 1 + 2(1\cdot 1) + 3(0\cdot 1)\right) = \frac{6}{6} = 1$$

$$p_2 = 1 \qquad p_3 = 1$$

$$\Rightarrow \quad \Gamma = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3$$

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad K = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \qquad \cdots$$

Block-diagonal representation equivalent to original reducible representation

Group theory – Direct product

Definition: direct product of two representations

$$\Gamma_\alpha(R)\otimes\Gamma_\beta(R)=\begin{pmatrix}\Gamma_\alpha(R)_{11}\cdot\Gamma_\beta(R) & \cdots & \Gamma_\alpha(R)_{m1}\cdot\Gamma_\beta(R)\\ \vdots & & \vdots\\ \Gamma_\alpha(R)_{1m}\cdot\Gamma_\beta(R) & \cdots & \Gamma_\alpha(R)_{mm}\cdot\Gamma_\beta(R)\end{pmatrix}$$

dimension: $n_\alpha \cdot n_\beta$

$$\Gamma_3(E)\otimes\Gamma_3(E)=\begin{pmatrix}1\cdot\begin{pmatrix}1&0\\0&1\end{pmatrix} & 0\cdot\begin{pmatrix}1&0\\0&1\end{pmatrix}\\ 0\cdot\begin{pmatrix}1&0\\0&1\end{pmatrix} & 1\cdot\begin{pmatrix}1&0\\0&1\end{pmatrix}\end{pmatrix}=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}$$

Remarks:

- Direct product of irreducible representations Γ_α and Γ_β is commutative: $\Gamma_\alpha \otimes \Gamma_\beta = \Gamma_\beta \otimes \Gamma_\alpha$
- Direct product of two representations yields another representation.
- Resulting representation can be written as direct sum of irreducible representations.

Group theory – Character of a direct product representation

For the character of the direct product follows: $\chi(\Gamma_\alpha \otimes \Gamma_\beta) = \chi_\alpha \cdot \chi_\beta$ (**)

$$\Rightarrow \quad \Gamma_\alpha \otimes \Gamma_\beta = \sum_\gamma g_{\alpha\beta\gamma} \Gamma_\gamma$$

with Γ_γ irreducible representation

and $$g_{\alpha\beta\gamma} = \frac{1}{g} \sum_R \chi_\alpha(R) \cdot \chi_\beta(R) \cdot \chi_\gamma(R)$$

(combine formula (*), page 21 with (**) above)

Example: multiplication table for irreducible representations of D_3

$\otimes$	$\boldsymbol{\Gamma_1}$	$\boldsymbol{\Gamma_2}$	$\boldsymbol{\Gamma_3}$
$\boldsymbol{\Gamma_1}$	Γ_1	Γ_2	Γ_3
$\boldsymbol{\Gamma_2}$	Γ_2	Γ_1	Γ_3
$\boldsymbol{\Gamma_3}$	Γ_3	Γ_3	$\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3$

Remark: Worked out tables in literature

(Non-trivial) example:

$$\Gamma_2 \otimes \Gamma_3 = g_{231}\Gamma_1 \oplus g_{232}\Gamma_2 \oplus g_{233}\Gamma_3 \qquad g_{\alpha\beta\gamma} = \frac{1}{g}\sum_R \chi_\alpha(R)\cdot\chi_\beta(R)\cdot\chi_\gamma(R)$$

Resulting representation must be 2-dimensional, since $n_2 = 1$, $n_3 = 2$,
i.e., result must either be (equivalent to) Γ_3, $\Gamma_1 + \Gamma_2$, $2\Gamma_1$, or $2\Gamma_2$.
The last 3 possibilities are obviously wrong. Formal proof:

	E	***J***	***K***	***L***	***M***	***N***
χ_1	1	1	1	1	1	1
χ_2	1	1	1	-1	-1	-1
χ_3	2	-1	-1	0	0	0

$$g_{231} = \frac{1}{6}\left[1\cdot 2\cdot 1 + 1\cdot(-1)\cdot 1 + 1\cdot(-1)\cdot 1 + 0 + 0 + 0\right] = 0$$

$$g_{232} = \frac{1}{6}\left[1\cdot 2\cdot 1 + 1\cdot(-1)\cdot 1 + 1\cdot(-1)\cdot 1 + 0 + 0 + 0\right] = 0$$

$$g_{233} = \frac{1}{6}\left[1\cdot 2\cdot 2 + 1\cdot(-1)\cdot(-1) + 1\cdot(-1)\cdot(-1) + 0 + 0 + 0\right] = 1$$

$$\Rightarrow \quad \Gamma_2 \otimes \Gamma_3 = \Gamma_3$$

How can that be although L, M, N are negated through direct product?
No problem due to special arrangement of results of multiplication table
⇒ Additional sign always cancels out or does not matter !

Connection to physics: Hamiltonian and group theory

Consider wavefunction $\psi(x_1, \cdots, x_n) = \psi(\boldsymbol{r})$ (eigenstate, no spin!)

and coordinate transformation $x_i' = \sum_{j=1}^{n} R_{ij} x_j$ or $\boldsymbol{r}' = \boldsymbol{R} \cdot \boldsymbol{r}$ ($\boldsymbol{R}^{-1}$ exists)

New wavefunction in new coordinate system will be different from ψ,
in general a linear combination of „old“ eigenfunctions with same energy
(and other quantum numbers that remain)

Examples from atomic physics:

- $|p_x>$ will be transformed into $|p_y>$ for a 90° rotation
- States with same energy and given angular momentum l but different m will mix for general rotations (states with different l or E will NOT mix!)

$\Rightarrow$ Define operator $P(R)$ transforming „old“ into „new“ wavefunction, when transformation R is applied:

$$\psi'(\boldsymbol{r}') = \psi(\boldsymbol{R}^{-1} \cdot \boldsymbol{r}') =: P(R)[\psi(\boldsymbol{r})](\boldsymbol{r}')$$

If Hamiltonian H is invariant with respect to R (i.e., R is a symmetry operation):

$$H'(\boldsymbol{r}') = H\left(\boldsymbol{R}^{-1} \cdot \boldsymbol{r}'\right) = H(\boldsymbol{r}')$$

$\Rightarrow P(R)$ *commutates* with H: $P(R)\, H = H\, P(R)$

$\Rightarrow$ Eigenfunctions of Schrödinger equation can be chosen to be simultaneously eigenfunctions of $P(R)$!

$\Rightarrow$ Solutions of Schrödinger equation can be classified according to eigenvalues of $P(R)$ (symmetry properties) !

Holds for all types of symmetry operations
(rotations, reflections, translations by lattice vector)

All symmetry operations leaving H invariant form a group:
Group of the Schrödinger equation

Eigenfunctions and representations

Consider n-fold degenerate solutions of Schrödinger equation $\psi_{\alpha i}$, i = 1,…, $n(\alpha)$ with energy E_α :

$$H\psi_{\alpha i} = E_\alpha \psi_{\alpha i}$$

Then we have: $H[P(R)\psi] = P(R)[H\psi] = P(R)[E\psi] = E[P(R)\psi]$

i.e., $P(R)\,\psi_{\alpha i}$ is again eigenfunction of H with the same eigenvalue E_α

$\Rightarrow$ $P(R)\,\psi_{\alpha i}$ can be written as *linear combination* of $\psi_{\alpha i}$

$$P(R)\psi_{\alpha j} = \sum_{i=1}^{n} \Gamma_\alpha(R)_{ij}\psi_{\alpha i}$$

For all j $\Rightarrow$ Matrix $\Gamma_\alpha(R)$: Transformation matrix written in basis $\psi_{\alpha i}$

For all R $\Rightarrow$ Set of matrices $\{\Gamma_\alpha(R)\}$

$\{\Gamma_\alpha(R)\}$ **is a representation of the group of the Schrödinger equation !**

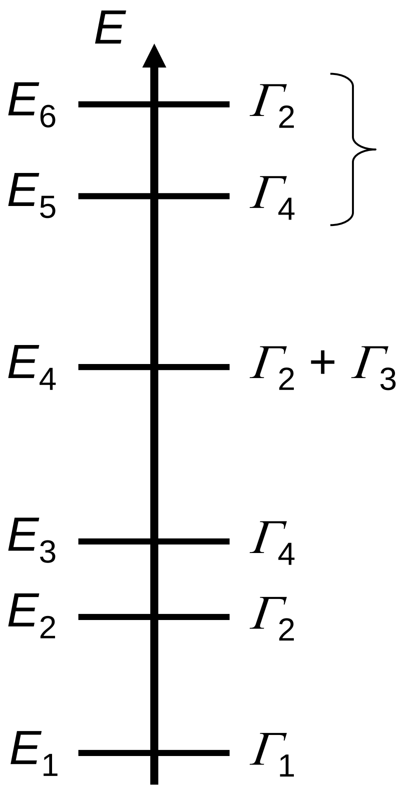
Generally, $\{\Gamma_\alpha(R)\}$ is irreducible

(apart from coincidental, i.e., non-symmetry related degenerate states)

Labeling of eigenfunctions

- Eigenstates are labeled according to their corresponding (irreduc.) representations:
  State (wave function) is said to "transform according to Γ_α" or "have symmetry Γ_α"
- Dimension of Γ_α corresponds to degree of degeneracy

Example:



ground state: E_1

E_6 (Γ_2), E_5 (Γ_4): multiple occurrence of irreducible representations

E_4 ($\Gamma_2 + \Gamma_3$): accidental degeneracy: two eigenvalues that have coincidentally the same value

Construction of basis functions with def. symmetry

Take a random function $f(\mathbf{r})$ and apply projection:

$$O_\alpha^{pq} = \frac{n_\alpha}{g} \sum_R \Gamma_\alpha(R)_{pq}^* P(R)$$

The resulting set of basis functions with fixed q transforms according to Γ_α

Example: group of order 2: inversion

C_i	E	J
Γ_1	1	1
Γ_2	1	-1

$n_\alpha = 1$
$g = 2$

Find functions with symmetry Γ_1 and Γ_2!

$$O_1^{11} f(\boldsymbol{r}) = \frac{1}{2}\left[\Gamma_1(E)_{11}^* P(E) f(\boldsymbol{r}) + \Gamma_1(J)_{11}^* P(J) f(\boldsymbol{r})\right]$$

$$O_2^{11} f(\boldsymbol{r}) = \frac{1}{2}\left[\Gamma_2(E)_{11}^* P(E) f(\boldsymbol{r}) + \Gamma_2(J)_{11}^* P(J) f(\boldsymbol{r})\right]$$

With $\Gamma_1(E) = \Gamma_1(J) = \Gamma_2(E) = 1,\ \Gamma_2(J) = -1$

and $P(E) f(\boldsymbol{r}) = f(\boldsymbol{r})\ ;\ P(J) f(\boldsymbol{r}) = f(-\boldsymbol{r})$

we get:

$$O_1^{11} f(\boldsymbol{r}) = \frac{1}{2}\left[f(\boldsymbol{r}) + f(-\boldsymbol{r})\right] \quad \text{even part}$$

$$O_2^{11} f(\boldsymbol{r}) = \frac{1}{2}\left[f(\boldsymbol{r}) - f(-\boldsymbol{r})\right] \quad \text{odd part}$$

} of function $f(\boldsymbol{r})$

Transformation of wavefunction including spin

Eigenfunctions of z-component of (spatial) angular momentum operator:

$$L_z\psi = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\psi = l_z\psi \;\Rightarrow\; \psi \sim e^{im\varphi}; \quad l_z = m\hbar \quad (-l \le m \le +l)$$

Scalar wavefunction, reproduces after rotation of 2π

Spin operator for spin ½ particle given by Pauli matrices: $\mathbf{s} = \frac{\hbar}{2}\boldsymbol{\sigma}$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Eigenfunctions of z-component of spin:

$$S_z\psi^{spin} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \psi_1^{spin} \\ \psi_2^{spin} \end{pmatrix} = s_z\psi^{spin} \quad \Rightarrow$$

$$\psi_{spin} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad s_z = +\frac{1}{2}\hbar \quad \text{(spin up)}$$

$$\psi_{spin} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad s_z = -\frac{1}{2}\hbar \quad \text{(spin down)}$$

Two-component spinor wavefunction, reproduces only after rotation of 4π !

Transformation according to $D_{1/2}$

Transformation of full wavefunction (including spin):

For eigenstates of s_z : $\psi(\mathbf{r}) = \varphi(\mathbf{r}) \cdot \psi^{spin}$

Product of spatial and spin wavefunction

$\psi(\mathbf{r})$ transforms as point group $\otimes D_{1/2}$

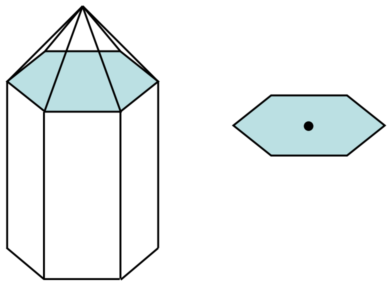
"Double group"

Double group has additional elements and classes compared to point group!

Example: group C_{6v} (symmetry of materials like GaN, ZnO, etc. with hexagonal (wurtzite) crystal structure)

Symmetry of eigenfunctions of the Hamiltonian

Example: C_{6v} (group of a pointy hexagonal pencil)



for instance: CdS, ZnO, CdSe, GaN

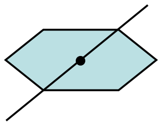
C_{6v}: E

$2\ C_6$: ± 60°

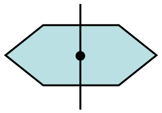
$2\ C_3$: ± 120°

C_2: ± 180°

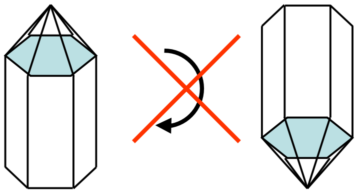
$3\sigma_v$: reflection about diagonal



$3\sigma_d$: reflection about area normal



No reflection on plane perpendicular to pen
since no inversion symmetry!
(double layers of, e.g., Ga and N along axis)



with spin: $\overline{E}$: rotation about 2π (changes sign of wavefunction, different from E)

$2\overline{C}_3$, $2\overline{C}_6$, $\overline{C}_2$, $\overline{\sigma}_v$, $\overline{\sigma}_d$

Applications of group theory – selection rules

Using group theory, we can determine if a matrix element vanishes or not

$\Rightarrow$ **selection rules !**

$$\langle j | H' | i \rangle = \begin{cases} \neq 0 & \text{if } \Gamma_j \in \Gamma_s \otimes \Gamma_i \Leftrightarrow \Gamma_1 \in \Gamma_j \otimes \Gamma_s \otimes \Gamma_i \\ = 0 & \text{else} \end{cases}$$

$$\underset{\Gamma_j}{\langle j} \; \underset{\Gamma_s}{| H' |} \; \underset{\Gamma_i}{i \rangle}$$

Intuitive explanation (mathematical proof possible):

Integrand can be written as integral value / volume (constant average) that transforms according to the trivial representation Γ_1 plus positive / negative deviations with more complicated symmetries that cancel out in the integration

$\Rightarrow$ Integral does not vanish if there is a finite contribution to the integrand that transforms like Γ_1 (the average value) !

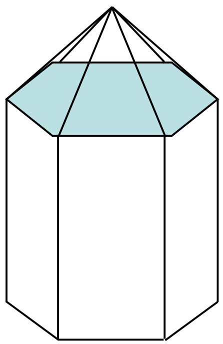
Applications of group theory – selection rules

Example: Electrical dipole transitions

For full rotational symmetry (atomic physics):

- angular momenta good quantum numbers
- selection rules: $\Delta l = \pm 1 \quad ; \quad \Delta m = \pm 1$

In crystal: group theory



Symmetry of perturbation (dipole) operator in wurtzite materials ($C_{6\mathrm{v}}$):

Depends on polarization of light field (see, e.g., tables in Cho)

$$\boldsymbol{E} \parallel \boldsymbol{c} \quad : \; \Gamma_1$$

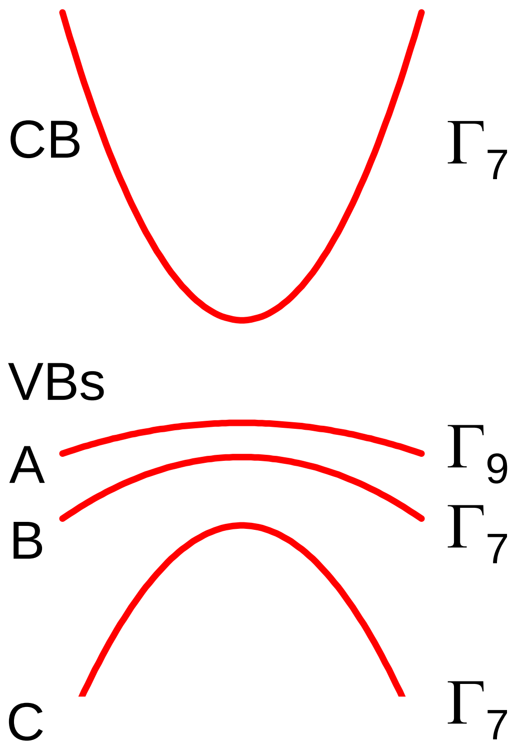
$$\boldsymbol{E} \perp \boldsymbol{c} \quad : \; \Gamma_5$$

Symmetry of wavefunctions at Γ point : from literature
(derivation: start from symmetry of atomic states,
symmetry reduction through crystal structure, see below)

Selection rules for optical transitions in materials with wurtzite crystal structure:

Evaluation of transition matrix elements by group theory!

Optical transitions in materials with wurtzite structure



Band structure including labeling of CB and VBs according to their irreducible representations at the Γ point

Allowed transitions:

- Direct product of representation initial state (VB) with representation of dipole operator must contain representation of final state (CB)
- Use multiplication tables to evaluate direct products

$\boldsymbol{E} \perp \boldsymbol{c}$: symmetry of dipole operator: $\boldsymbol{\Gamma}_5$

$\Gamma_9 \otimes \Gamma_5 = \Gamma_7 \oplus \Gamma_8 \Rightarrow$ Transition VB A to CB allowed

$\Gamma_7 \otimes \Gamma_5 = \Gamma_7 \oplus \Gamma_9 \Rightarrow$ Transition VBs B & C to CB allowed

$\boldsymbol{E} \parallel \boldsymbol{c}$: symmetry of dipole operator: $\boldsymbol{\Gamma}_1$

$\Gamma_9 \otimes \Gamma_1 = \Gamma_9 \Rightarrow$ Transition VB A to CB forbidden

$\Gamma_7 \otimes \Gamma_1 = \Gamma_7 \Rightarrow$ Transition VBs B & C to CB allowed

Wurtzite materials: Coupling of light field to excitons

Product wavefunctions transform according to direct product of individual symmetries (see, e.g., spin states discussed above)

Excitons: $$\phi_{exciton} = \phi_e(\boldsymbol{r_e}) \cdot \phi_h(\boldsymbol{r_h}) \cdot \underbrace{\phi_{envelope}^{nlm}(\boldsymbol{r_e} - \boldsymbol{r_h})}_{H-like}$$

Symmetry of total wavefunction: $\Gamma_{exciton} = \Gamma_e \otimes \Gamma_h \otimes \Gamma_{envelope}$

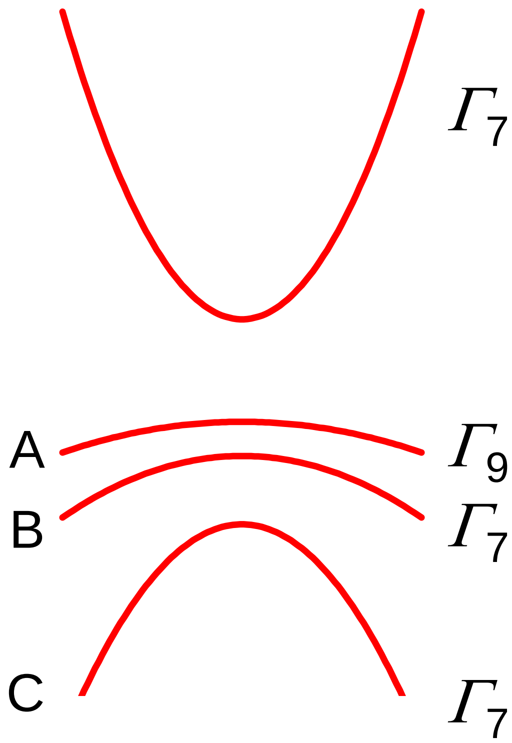
Which excitonic transitions are allowed in emission/absorption?

Transitions from/to ground state (symmetry Γ_1) allowed (matrix element ≠ 0), if direct product of $\Gamma_{exciton}$ with symmetry of dipole operator contains Γ_1

For 1s excitons: $\Gamma_{envelope} = \Gamma_1$

$\Rightarrow$ Exciton does not alter selection rules in this case

Excitons in wurtzite materials: Exciton types



For A exciton (Γ_9 VB) in 1s state
(i.e., n_B = 1 and s-like envelope function)

$$\Gamma_{exciton} = \Gamma_7 \otimes \Gamma_9 \otimes \Gamma_1 = \Gamma_5 \oplus \Gamma_6$$

$\Rightarrow$ Two types of excitons: Γ_5, Γ_6

Γ_5: Total spin = 0: “singlet”

Γ_6: Total spin = 1: “triplet”

Coupling to light field:

$\boldsymbol{E} \parallel \boldsymbol{c}$: $\Gamma_5 \otimes \Gamma_1 = \Gamma_5$ no

$\boldsymbol{E} \perp \boldsymbol{c}$: $\Gamma_5 \otimes \Gamma_5 = \underline{\Gamma_1} \oplus \Gamma_2 \oplus \Gamma_6$ yes

Couples to light field for $\boldsymbol{E} \perp \boldsymbol{c}$:

Singlet ist “bright” exciton !

$\Gamma_6 \otimes \Gamma_1 = \Gamma_6$ no

$\Gamma_6 \otimes \Gamma_5 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$ no

Does not couple to light field

Triplett is “dark” exciton !

For B and C (Γ_7 VB) 1s excitons: $\Gamma_7 \otimes \Gamma_7 \otimes \Gamma_1 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5$

	Γ_1	Γ_2	Γ_5
	Singlet (m_L= 0)	Triplet	Singlet (m_L= ±1)
Couples for	$\boldsymbol{E} \parallel \boldsymbol{c}$		$\boldsymbol{E} \perp \boldsymbol{c}$

- Result consistent with intuitive discussion for electron – hole pairs above, that only excitons with total spin zero can be created by light
- The occurrence of “bright” singlet and “dark” triplet states is a general feature of excitons in any material
- Coupling to light field for wurtzite structure: B and C exciton: *always*, A exciton: *only for* $\boldsymbol{E} \perp \boldsymbol{c}$

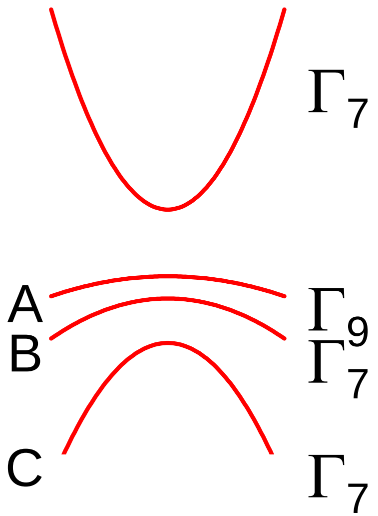
Recap: Linear spectroscopy of excitons: Reflectivity

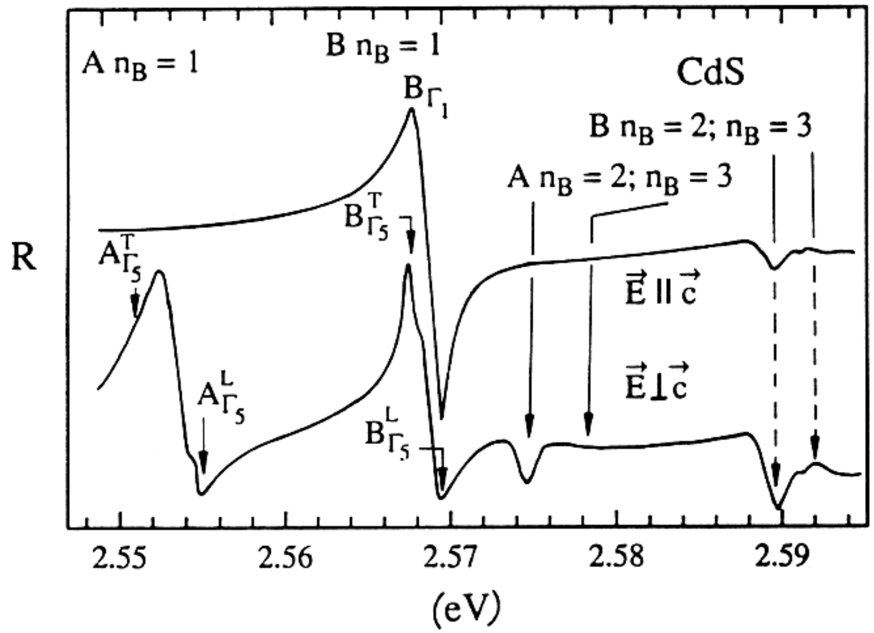
Example: Low-temperature (T ~ 4 K) reflectivity of CdS (wurtzite crystal structure)

- Resonances due to A, B and C excitons at low temperatures (hardly visible at room-temperature due to thermal ionization of excitons)

As expected (see discussion above):

- Polarization dependence:
  A exciton couples only for $\boldsymbol{E} \perp \boldsymbol{c}$





T: transverse
L: longitudinal

Applications of group theory – Perturbation theory

Unperturbed Hamiltonian H^0, assume $E_n{}^0$ is *not* degenerate

$$H^0 \psi_n^0 = E_n^0 \psi_n^0$$

With perturbation: $H = H^0 + H^s$

$$\Rightarrow \quad E_n = E_n^0 + \left\langle \psi_n^0 \middle| H^s \middle| \psi_n^0 \right\rangle$$

From evaluation of matrix element with group theory:

- Does perturbation shift eigenvalue or not ?
- No statement concerning magnitude of shift !

Mixing with other states due to perturbation

$$\psi_n = \psi_n^0 + \sum_{k \neq n} \frac{\left\langle k \middle| H^s \middle| n \right\rangle}{E_n^0 - E_k^0} \psi_k$$

From evaluation of matrix elements with group theory:

- Which states do mix in ?
  $\Rightarrow$ Change in selection rules (forbidden transitions may become allowed)
- No statement concerning strength of mixing !

Degenerate perturbation theory

$$H^0 \psi_{ni}^0 = E_n \psi_{ni}^0$$

With perturbation: $H = H^0 + H^s$

$\Rightarrow$ New eigenfunctions (0th order, “right linear combinations”)

$$\psi_{nj} = \sum_i \alpha_{ni} \psi_{ni}^0$$

New energies from characteristic equation: $\det\left|\langle i | H^s | j \rangle - E\delta_{ij}\right| = 0$

Coefficients from resulting system of equations for these energies

Group theory:

- Is degeneracy lifted, and to which degree?
  (accidental degeneracy despite / due to perturbation possible!)
- No statement concerning magnitude of splitting !

How do we get the Γ_i, e.g., for bands in a solid ?

$\rightarrow$ Properties of atomic orbitals that form bands + compatibility tables

Compatibility tables

Hamiltonian invariant with respect to certain symmetry operations

Symmetry reduction (application of a field, strain, …)

$\Rightarrow$ Less symmetry operations than before, subgroup of previous symmetry group

$\Rightarrow$ Representation of subgroup may be reducible
(although same representation for full group is not)

point group → subgroup

$$\Gamma_i \longrightarrow \Gamma_{f_1} \oplus \Gamma_{f_2} \oplus \ldots$$

- If a representation is mapped onto an *irreducible* representation

$\Rightarrow$ Energy level E_i does *not split*
(since a symmetry operation always exists that maps one state onto the other)

- If a representation is mapped onto a *reducible* representation

⇒ Energy level E_i *splits* (apart from accidental degeneracies), since only some states are connected to each other via symmetry operations (because the representation is block-diagonal)

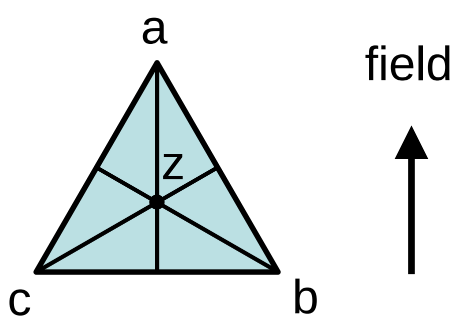
$$E_i \rightarrow \begin{cases} E_{f1} \\ E_{f2} \\ \cdots \end{cases}$$

→ *Compatibility table*:

When a given group representation becomes reducible due to the reduction of number of symmetry elements, what are the resulting irreducible representations of the remaining subgroup?

Example: Group D_3, symmetry reduction through applied field

Rotations and 2 reflections no longer symmetry operations when field is applied !



D_3	Γ_1	Γ_2	Γ_3
C_3	Γ_1	Γ_1	$\Gamma_2 + \Gamma_3$
C_2	Γ_1	Γ_2	$\Gamma_1 + \Gamma_2$

Application of field $\Rightarrow$ $D_3 \rightarrow C_2$

$\Rightarrow$ Γ_3 splits into two energy levels ($\Gamma_1 + \Gamma_2$)

Group theory in solid-state physics

Starting point: Atomic orbitals, radially symmetric potential $V(r)$

Wavefunction: $\phi(\boldsymbol{r}) = \psi(r) \cdot Y_{lm}(\theta, \varphi)$

Angular part of separated Schrödinger equation: Spherical harmonics Y_{lm}

$$\left[\frac{1}{\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_{lm}(\theta,\varphi) = -l(l+1)Y_{lm}(\theta,\varphi)$$

$Y_{lm}(\theta, \varphi)$: Ortho-normal system, basis for full rotation group

For spherical symmetry: Symmetry group is full rotation group

- All rotations with the same angle (but around different axes) belong to one class
- Rotations with arbitrary angles are symmetry elements $\Rightarrow$ *Continuous* group !
- Different representations Γ_{l+1} according to different angular momenta l
- Γ_{l+1} has degeneracy of $2l + 1$ (different m values)

Character table of spherical rotation group

	E 0	$0 \longleftarrow \varphi \longrightarrow 2\pi$
Γ_1	1	
Γ_2		
$\vdots$		
Γ_{l+1}	$(2l+1)$	$\dfrac{\sin(l+1/2)\varphi}{\sin\varphi/2}$
$\vdots$		

Example: Band structure for materials with C_{6v} symmetry

Symmetry of bands at k = 0 for ZnO, GaN, CdS, …?

E.g., for ZnO: 2 outer 4s electrons of Zn are transferred to two empty 2p states of O

$\Rightarrow$ Valence band (highest occupied band) essentially formed by filled p states of O

$\Rightarrow$ Conduction band (lowest empty band) essentially formed by empty s states of Zn

What happens with 4s state in a crystal with C_{6v} symmetry?

Representation of rotation group for l = 0 and positive parity:

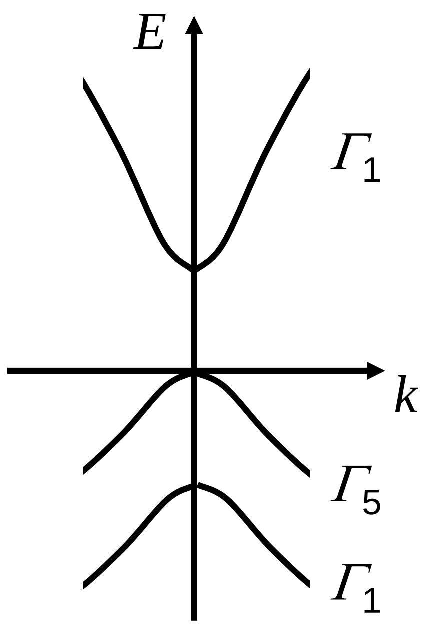
Compatibility table: $D_0^+ \rightarrow \Gamma_1$

What happens with 2p state in a crystal with C_{6v} symmetry?

Representation of rotation group for l = 1 and negative parity:

Compatibility table: $D_1^- \rightarrow \Gamma_1 \oplus \Gamma_5$

⇒ Band structure of C_{6v} materials at k = 0 (still without spin):



- Splitting of valence band into two subbands due to interaction of p-like states with **crystal field** (→ symmetry reduction) !
- Further symmetry reduction for $\boldsymbol{k} \neq 0$
  ⇒ Band structure / labeling only correct for $\boldsymbol{k} = 0$!
- Only labeling of bands with Γ's correct. Labeling of bands using angular momenta is sometimes possible, but only an *approximation !*

$l = 0 \quad D_0^+ \rightarrow \Gamma_1$
$m = 0$

$l = 1 \quad D_1^- \rightarrow \Gamma_1 \oplus \Gamma_5$
$m = 0 \quad m = \pm 1$

$l = 2 \quad D_2^+ \rightarrow \Gamma_1 \oplus \Gamma_5 \oplus \Gamma_6$
$m = 0 \quad m = \pm 1 \quad m = \pm 2$

$l = 3 \quad D_3^- \rightarrow \Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_6$
no identification possible !

Band structure of C_{6v} materials at k = 0 <u>including spin</u>

Transformation of full wavefunction $\psi(\boldsymbol{r}) = \varphi(\boldsymbol{r}) \cdot \psi^{spin}$

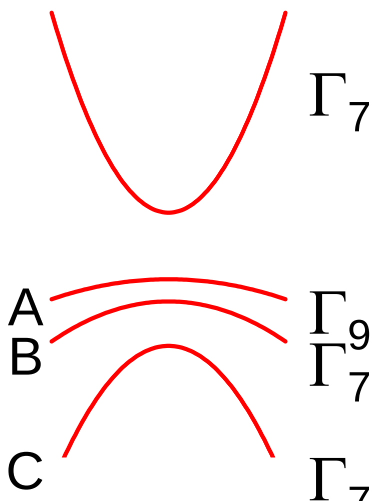
according to symmetry of point group $\otimes D_{1/2}$

Compatibility table for C_{6v} : $D_{1/2} \rightarrow \Gamma_7$

$\Rightarrow$ Symmetries of conduction band (CB) and valence bands (VB):

CB: $\Gamma_1 \otimes \Gamma_7 = \Gamma_7$

VB: $(\Gamma_1 \oplus \Gamma_5) \otimes \Gamma_7 = \Gamma_7 \oplus \Gamma_7 \oplus \Gamma_9$



- Γ_5 VB (single band without spin) splits into Γ_7 and Γ_9 (both two-fold degenerate) when spin is included. Reason: spin-orbit interaction ! (p-like VB states can interact with spin)
- No splitting for CB but two-fold degenerate due to spin (s-like CB states cannot interact with spin)
- Additional crystal field splitting between (Γ_7 , Γ_9) (Γ_5 without spin) and Γ_7
- No direct information on order of bands from group theory !