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5 Exercise - Introduction to Group Theory

5.1 (multiplication table)

We have a look at the multiplication table:

	E	a	b	c	d	f
E	E	a	b	c	d	f
a	a	b	E	d	f	c
b	b	E	a	f	c	d
c	c	d	f	a	E	b
d	d	f	c	b	a	E
f	f	c	d	E	b	a

We first have to check the group properties:
1) closure
The closure condition is fulfilled with the multiplication table. The multiplication operation will not lead out of the group.
2) identity element
We are looking for the identity element I for this group, which fulfills the equation:

$$k \cdot I = I \cdot k = k$$

it seems obvious, that $I = E$.
3) inverse element
The inverse element is defined as the element, which with a operation on the element will lead to the identity. Meaning:

$$k \cdot k^{-1} = k^{-1} \cdot k = I$$

Also we can prove, that if there is a right inverse element β, there is also a left one γ and they are the same $\beta = \gamma$, just the prove for the easier condition, that both of them exist:

$$\gamma = \gamma \cdot I = \gamma \cdot (k \cdot \beta) = (\gamma \cdot k) \cdot \beta = I \cdot \beta = \beta$$

Therefore we have to check, if there is an inverse element for all the elements of the table, while $I = E$. The first three elements are ok:

$$\begin{aligned} E \cdot E &= E \\ a \cdot b &= E \\ b \cdot a &= E \end{aligned}$$

with $a^{-1} = b$ or $b^{-1} = a$ and $E^{-1} = E$.
After that we get the problem that the inverse element isn't the same for both sides anymore, so there is no inverse element for all the elements, therefore the multiplication table doesn't contain a group.

$$
\begin{aligned}
c \cdot d = E &\quad\leftrightarrow\quad f \cdot c = E \\
d \cdot f = E &\quad\leftrightarrow\quad c \cdot d = E \\
f \cdot c = E &\quad\leftrightarrow\quad d \cdot f = E
\end{aligned}
$$

$c^{-1} = d$ but also $c^{-1} = f$, $d^{-1} = f$ and $d^{-1} = c$ and $f^{-1} = c$ and $f^{-1} = d$, what isn't possible.
4) associativity
The associativity holds because of using multiplication, which itself is always associative. Therefore:

$$k \cdot (l \cdot m) = (k \cdot l) \cdot m$$

Conclusion:
The **3)** condition (inverse element) isn't fulfilled, therefore this is no group. If we just use the subset E, a, b the multiplication table becomes:

	E	a	b
E	E	a	b
a	a	b	E
b	b	E	a

and the subset forms a group.

5.2 (crystal field splitting)

We are starting from the characters of the integral order irreducible representation of the full rotation group which are given with:

$$\chi\left(\Gamma^i(\alpha)\right) = \sum_{m=-l}^{l} e^{-im\alpha} = e^{-\frac{i}{\alpha}} \left(\frac{e^{i(2l+1)\alpha} - 1}{e^{i\alpha} - 1}\right) = \frac{\sin\left[\left(l + \frac{1}{2}\right)\alpha\right]}{\sin\left(\frac{\alpha}{2}\right)} \tag{1}$$

Our job is to determine the splitting of s, p, d and f type atomic states in fields of:

a) $SU(2) \rightarrow T$

tetrahedral symmetry T. The character table is given with:

T	E	$4C_3$	$(4C_3)^2$	$3C_2$
A	1	1	1	1
E	1	ε	ε^*	1
	1	ε^*	ε	1
T	3	0	0	-1

with

$$\varepsilon = \exp\left(\frac{2\pi i}{3}\right) = \cos\left(\frac{2\pi}{3}\right) + i \cdot \sin\left(\frac{2\pi}{3}\right) = -0.5 + i\frac{\sqrt{3}}{2}$$

and

$$\varepsilon^* = \exp\left(-\frac{2\pi i}{3}\right) = \cos\left(\frac{2\pi}{3}\right) - i \cdot \sin\left(\frac{2\pi}{3}\right) = -0.5 - i\frac{\sqrt{3}}{2}$$

therefore $\varepsilon + \varepsilon^* = -1$ and $1 + 1 = 2$, hopefully this means:

T	E	$4C_3$	$(4C_3)^2$	$3C_2$
E	2	-1	-1	2

the character table for the orbitals can be obtained by using formula (1):

$$
\begin{aligned}
\chi(E) = \chi(\Gamma(\alpha)) &= 2l + 1 \text{ for } \alpha = 0,\, 2\pi \\
\chi(C_3) = \chi\left(\Gamma\left(\frac{2\pi}{3}\right)\right) &= \begin{cases} 1 & \text{for } l = 0, 3 \\ 0 & \text{for } l = 1 \\ -1 & \text{for } l = 2 \end{cases} \\
\chi(C_3^2) = \chi\left(\Gamma\left(\frac{4\pi}{3}\right)\right) &= \begin{cases} 1 & \text{for } l = 0, 3 \\ 0 & \text{for } l = 1 \\ -1 & \text{for } l = 2 \end{cases} \\
\chi(C_2) = \chi(\Gamma(\pi)) &= \begin{cases} 1 & \text{for } l = 0, 2 \\ -1 & \text{for } l = 1, 3 \end{cases}
\end{aligned}
$$

This leads to:

T	E	$4C_3$	$(4C_3)^2$	$3C_2$
s D_0	1	1	1	1
p D_1	3	0	0	-1
d D_2	5	-1	-1	1
f D_3	7	1	1	-1

This can be decomposed

s D_0	A
p D_1	T
d D_2	$E + T$
f D_3	$A + 2T$

b) $SU(2) \rightarrow D_{6h}$

D_{6h} symmetry. The character table is given with:

D_{6h}	E	$2C_6(z)$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	$\sigma_h(xy)$	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	1
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	-1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	-1
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	1
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0

while we are looking at the full rotation group (well i don't know how to calculate the table for the orbitals, only using formula (1), which only depends on l and α, while you cannot describe all operations by rotations around one axis), the only relevant part therefore is:

D_{6h}	E	$2C_6(z)$	$2C_3$	C_2
A	1	1	1	1
B	1	-1	1	-1
E_1	2	1	-1	-2
E_2	2	-1	-1	2

the character table for the orbitals can be obtained by using formula (1):

$$\begin{aligned}
\chi(E) = \chi(\Gamma(\alpha)) &= 2l+1 \text{ for } \alpha = 0,\, 2\pi \\
\chi(C_6) = \chi\left(\Gamma\left(\frac{\pi}{3}\right)\right) &= \begin{cases} 2 & \text{for } l = 1 \\ 1 & \text{for } l = 0,2 \\ -1 & \text{for } l = 3 \end{cases} \\
\chi(C_3) = \chi\left(\Gamma\left(\frac{2\pi}{3}\right)\right) &= \begin{cases} 1 & \text{for } l = 0,3 \\ 0 & \text{for } l = 1 \\ -1 & \text{for } l = 2 \end{cases} \\
\chi(C_2) = \chi(\Gamma(\pi)) &= \begin{cases} 1 & \text{for } l = 0,2 \\ -1 & \text{for } l = 1,3 \end{cases}
\end{aligned}$$

This leads to:

T	E	$2C_6(z)$	$2C_3$	C_2
s D_0	1	1	1	1
p D_1	3	2	0	-1
d D_2	5	1	-1	1
f D_3	7	-1	1	-1

This can be decomposed

s D_0	A
p D_1	$A + E_1$
d D_2	$A + E_1 + E_2$
f D_3	$A + 2B + E_1 + E_2$

c) $SU(2) \to C_{4v}$

C_{4v} symmetry. The character table is given with:

C_{4v}	E	$2C_4(z)$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

if we only have a look at rotations, this becomes:

C_{4v}	E	$2C_4\,(z)$	C_2
A	1	1	1
B	1	-1	1
E	2	0	-2

the character table for the orbitals can be obtained by the using formula (1):

$$\begin{aligned}
\chi(E) = \chi(\Gamma(\alpha)) &= 2l+1 \text{ for } \alpha = 0,\, 2\pi \\
\chi(C_4) = \chi\left(\Gamma\left(\frac{\pi}{2}\right)\right) &= \begin{cases} 1 & \text{for } l = 0,1 \\ -1 & \text{for } l = 2,3 \end{cases} \\
\chi(C_2) = \chi(\Gamma(\pi)) &= \begin{cases} 1 & \text{for } l = 0,2 \\ -1 & \text{for } l = 1,3 \end{cases}
\end{aligned}$$

C_{4v}	E	$2C_4\,(z)$	C_2
s D_0	1	1	1
p D_1	3	1	-1
d D_2	5	-1	1
f D_3	7	-1	-1

This can be decomposed

s D_0	A
p D_1	$A+E$
d D_2	$A+2B+E$
f D_3	$A+2B+2E$

5.3 (extra - problem from the lecture)

optical, i.e. dipole-allowed transitions in a d-metal, from a 'd' initial to an 'f' final state. The dipole operator transforms as spatial coordinates x, y, z. We consider O symmetry. The initial state transforms as either E or T_2. The final state (an f level) transforms as either A_2, T_1 or T_2.

ψ_f	O	ψ_i	$\psi_f \otimes O \otimes \psi_i$
A_2	T_1	E	$T_1 + T_2$
T_1	T_1	E	$A_1 + A_2 + 2E + 2T_1 + 2T_2$
T_2	T_1	E	$A_1 + A_2 + 2E + 2T_1 + 2T_2$
A_2	T_1	T_2	$A_1 + E + T_1 + T_2$
T_1	T_1	T_2	$A_1 + A_2 + 2E + 3T_1 + 4T_2$
T_2	T_1	T_2	$A_1 + A_2 + 2E + 4T_1 + 3T_2$