Point-group symmetries in bandstructure of crystals

October 15, 2012

1 Simple cubic lattice

$$\mathbf{a}_1 = a\,(1,0,0) \quad \mathbf{a}_2 = a\,(0,1,0) \quad \mathbf{a}_3 = a\,(0,0,1) \tag{1}$$

$$\mathbf{b}_1 = \frac{2\pi}{a}\,(1,0,0) \quad \mathbf{b}_2 = \frac{2\pi}{a}\,(0,1,0) \quad \mathbf{b}_3 = \frac{2\pi}{a}\,(0,0,1) \tag{2}$$

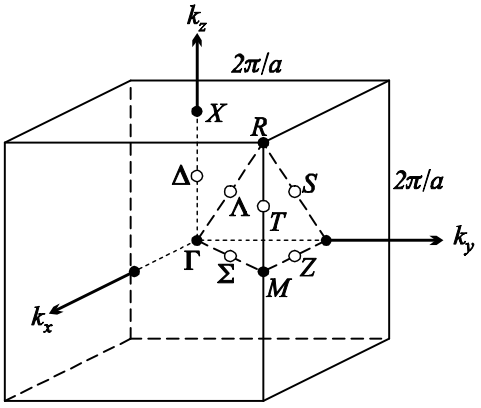

Figure 1: The Brillouin zone of a simple cubic lattice.

Let us investigate the bandstructure along the ΓX line of the Brillouin zone.

$$\Gamma = (0,0,0) \quad X = \frac{\pi}{a}\,(0,0,1) \tag{3}$$

$$\mathbf{k} = \frac{\pi}{a}\,(0,0,\xi) \quad 0 \le k \le 1 \tag{4}$$

2 Empty lattice bandstructure

Free electron bands in a crystal

$$\varphi_{\mathbf{K}}\,(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \tag{5}$$

$$\varepsilon_{\mathbf{K}}\,(\mathbf{k}) = \frac{\hbar^2\,(\mathbf{k}+\mathbf{K})^2}{2m} \tag{6}$$

In particular, in case of sc lattice along the ΓX direction:

$$\varepsilon_0 = \frac{\hbar^2\pi^2}{2ma^2} \tag{7}$$

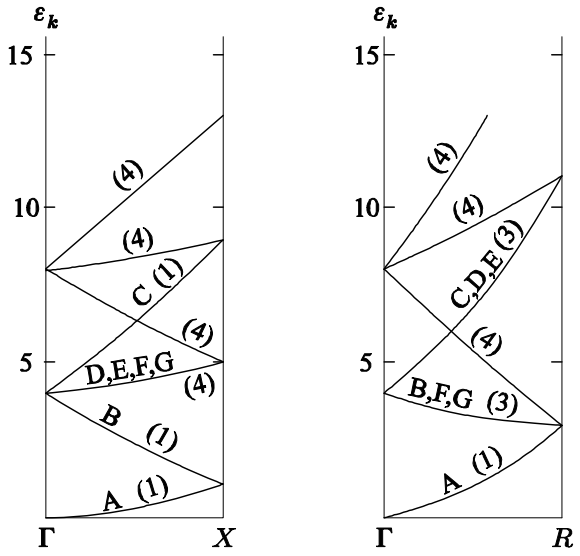

Figure 2: Bandstructure of the empty simple cubic lattice along two directions of the Brillouin zone.

1. band generated by $\mathbf{K} = \frac{2\pi}{a}(0,0,0)$

$$\varepsilon_A(\mathbf{k}) = \varepsilon_0 \xi^2 \tag{8}$$

$$\varphi_A = e^{i\frac{\pi}{a}\xi z} \tag{9}$$

2. band generated by $\mathbf{K} = \frac{2\pi}{a}(0,0,-1)$

$$\varepsilon_B(\mathbf{k}) = \varepsilon_0 (2-\xi)^2 \tag{10}$$

$$\varphi_B = e^{i\frac{\pi}{a}(\xi-2)z} \tag{11}$$

Degeneracy at X:

$$\varepsilon_A(X) = \varepsilon_B(X) \tag{12}$$

3.-6. bands generated by $\mathbf{K} = \frac{2\pi}{a}(\pm 1,0,0), \frac{2\pi}{a}(0,\pm 1,0)$

$$\varepsilon_{D,E,F,G}(\mathbf{k}) = \varepsilon_0 \left(\xi^2 + 4\right) \tag{13}$$

$$\varphi_D = e^{i\frac{\pi}{a}(\xi z+2x)}, \quad \varphi_E = e^{i\frac{\pi}{a}(\xi z+2y)}, \quad \varphi_F = e^{i\frac{\pi}{a}(\xi z-2x)}, \quad \varphi_G = e^{i\frac{\pi}{a}(\xi z-2y)} \tag{14}$$

7. band generated by $\mathbf{K} = \frac{2\pi}{a}(0,0,1)$

$$\varepsilon_C(\mathbf{k}) = \varepsilon_0 (2+\xi)^2 \tag{15}$$

$$\varphi_C = e^{i\frac{\pi}{a}(\xi+2)z} \tag{16}$$

Degeneracy at Γ:

$$\varepsilon_B(\Gamma) = \varepsilon_{D,E,F,G}(\Gamma) = \varepsilon_C(\Gamma) \tag{17}$$

3 Nearly free electron approach

3.1 Lifting of degeneracy at the X-point

Nearly free electron approach:

$$V_{\mathbf{K}} = \frac{1}{\varepsilon_0 v_0} \int_{v_0} d^3 r V(\mathbf{r}) e^{i\mathbf{K}\mathbf{r}} \tag{18}$$

Hamiltonian on the basis of φ_A and φ_B:

$$H_{AA}(\mathbf{k}) = \varepsilon_0 \xi^2 \quad H_{BB}(\mathbf{k}) = \varepsilon_0 (2-\xi)^2 \quad H_{AB}(\mathbf{k}) = H_{BA}(\mathbf{k}) = \varepsilon_0 V_{001} \tag{19}$$

$$\varepsilon(\mathbf{k}) = \varepsilon_0 \lambda \tag{20}$$

First order degenerate perturbation theory

$$\begin{pmatrix} \xi^2 - \lambda & V_{001} \\ V_{001} & (2-\xi)^2 - \lambda \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{21}$$

$$\left(\xi^2 - \lambda\right)\left((2-\xi)^2 - \lambda\right) - V_{001}^2 = 0 \tag{22}$$

$$\lambda^2 - \left[(2-\xi)^2 + \xi^2\right]\lambda + \xi^2 (2-\xi)^2 - V_{001}^2 = 0 \tag{23}$$

Choose $\xi = 1$ and $V_{001} > 0$

$$\lambda_\pm = 1 \pm V_{001} \tag{24}$$

Eigenfunctions:

$$\begin{pmatrix} \mp 1 & 1 \\ 1 & \mp 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{25}$$

$$\psi_+(z) \sim e^{i\frac{\pi}{a}z} + e^{-i\frac{\pi}{a}z} \sim \cos\frac{\pi}{a}z \tag{26}$$

$$\psi_-(z) \sim e^{i\frac{\pi}{a}z} - e^{-i\frac{\pi}{a}z} \sim \sin\frac{\pi}{a}z \tag{27}$$

3.2 Lifting of degeneracy along ΓX

Four basis functions:

$$\varphi_D = e^{i\frac{\pi}{a}(\xi z + 2x)}, \quad \varphi_E = e^{i\frac{\pi}{a}(\xi z + 2y)}, \quad \varphi_F = e^{i\frac{\pi}{a}(\xi z - 2x)}, \quad \varphi_G = e^{i\frac{\pi}{a}(\xi z - 2y)} \tag{28}$$

Matrixelements of the Hamiltonian:

$$H_{DD}(\mathbf{k}) = H_{EE}(\mathbf{k}) = H_{FF}(\mathbf{k}) = H_{GG}(\mathbf{k}) = \varepsilon_0\left(\xi^2 + 4\right) \tag{29}$$

$$H_{DE}(\mathbf{k}) = \varepsilon_0 V_{1\bar{1}0} \quad H_{DF}(\mathbf{k}) = \varepsilon_0 V_{200} \quad H_{DG}(\mathbf{k}) = \varepsilon_0 V_{110} \tag{30}$$

$$H_{EF}(\mathbf{k}) = \varepsilon_0 V_{110} \quad H_{EG}(\mathbf{k}) = \varepsilon_0 V_{020} \quad H_{FG}(\mathbf{k}) = \varepsilon_0 V_{\bar{1}10} \tag{31}$$

A simplification arises from point-group symmetry: for $R \in \mathcal{G}$, where $\mathcal{G}$ is the point-group of the lattice,

$$V_{\mathbf{K}} = \int d^3r\, V(\mathbf{r})\, e^{i\mathbf{K}\mathbf{r}} = \int d^3r\, V\left(R^{-1}\mathbf{r}\right) e^{i\mathbf{K}\cdot R^{-1}\mathbf{r}} = \int d^3r\, V(\mathbf{r})\, e^{iR\mathbf{K}\cdot\mathbf{r}} \Longrightarrow V_{\mathbf{K}} = V_{R\mathbf{K}} \tag{32}$$

Considering the cubic point-group, O_h, the reciprocal lattice vectors $\frac{2\pi}{a}(110)$, $\frac{2\pi}{a}\left(1\bar{1}0\right)$ and $\frac{2\pi}{a}\left(\bar{1}10\right)$, as well as $\frac{2\pi}{a}(200)$ and $\frac{2\pi}{a}(020)$ are equivalent. Thus, only two matrixelements are independent: V_{110}, V_{200}

$$\omega \doteq \left(\xi^2 + 4\right) - \lambda \tag{33}$$

$$\det \begin{pmatrix} \omega & V_{110} & V_{200} & V_{110} \\ V_{110} & \omega & V_{110} & V_{200} \\ V_{200} & V_{110} & \omega & V_{110} \\ V_{110} & V_{200} & V_{110} & \omega \end{pmatrix} = \tag{34}$$

$$\omega^4 + V_{200}^4 + 8\omega V_{110}^2 V_{200} - 4\omega^2 V_{110}^2 - 2\omega^2 V_{200}^2 - 4V_{110}^2 V_{200}^2 \tag{35}$$

$$= \left(\omega^2 - V_{200}^2\right)^2 - 4V_{110}^2 (\omega - V_{200})^2 \tag{36}$$

$$= (\omega - V_{200})^2 (\omega + V_{200})^2 - 4V_{110}^2 (\omega - V_{200})^2 \tag{37}$$

$$= (\omega - V_{200})^2 \left((\omega + V_{200})^2 - 4V_{110}^2\right) = 0 \tag{38}$$

$$\omega_{12} = V_{200} \tag{39}$$
$$\omega_3 = -V_{200} + 2V_{110} \tag{40}$$
$$\omega_4 = -V_{200} - 2V_{110} \tag{41}$$

Eigenvalues:

$$\lambda_{12} = \left(\xi^2 + 4\right) - V_{200} \tag{42}$$
$$\lambda_3 = \left(\xi^2 + 4\right) + V_{200} - 2V_{110} \tag{43}$$
$$\lambda_3 = \left(\xi^2 + 4\right) + V_{200} + 2V_{110} \tag{44}$$

Eigenfunctions:

$$\psi_1 = e^{i\frac{\pi}{a}z}\left(\sin\frac{2\pi x}{a} + \sin\frac{2\pi y}{a}\right) \tag{45}$$
$$\psi_2 = e^{i\frac{\pi}{a}z}\left(\sin\frac{2\pi x}{a} - \sin\frac{2\pi y}{a}\right) \tag{46}$$
$$\psi_3 = e^{i\frac{\pi}{a}z}\left(\cos\frac{2\pi x}{a} - \cos\frac{2\pi y}{a}\right) \tag{47}$$
$$\psi_4 = e^{i\frac{\pi}{a}z}\left(\cos\frac{2\pi x}{a} + \cos\frac{2\pi y}{a}\right) \tag{48}$$

In the doubly degenerate band (12), alternatively, we can take the following eigenbasis:

$$\psi_1 = e^{i\frac{\pi}{a}z}\sin\frac{2\pi x}{a} \tag{49}$$
$$\psi_2 = e^{i\frac{\pi}{a}z}\sin\frac{2\pi y}{a} \tag{50}$$

4 C_{4v} point-group

Little group of the k-points along ΓX: C_{4v}^z

Eight symmetry operations:

E	C_{4z}	C_{4z}^{-1}	C_{2z}	σ_y	σ_x	σ_a	σ_b
x	y	$-y$	$-x$	x	$-x$	$-y$	y
y	$-x$	x	$-y$	$-y$	y	$-x$	x
z	z	z	z	z	z	z	z

(51)

Multiplication table:

	E	C_{4z}	C_{4z}^{-1}	C_{2z}	σ_y	σ_x	σ_a	σ_b
E	E	C_{4z}	C_{4z}^{-1}	C_{2z}	σ_y	σ_x	σ_a	σ_b
C_{4z}	C_{4z}	C_{2z}	E	C_{4z}^{-1}	σ_a	σ_b	σ_x	σ_y
C_{4z}^{-1}	C_{4z}^{-1}	E	C_{2z}	C_{4z}	σ_b	σ_a	σ_y	σ_x
C_{2z}	C_{2z}	C_{4z}^{-1}	C_{4z}	E	σ_x	σ_y	σ_b	σ_a
σ_y	σ_y	σ_b	σ_a	σ_x	E	C_{2z}	C_{4z}^{-1}	C_{4z}
σ_x	σ_x	σ_a	σ_b	σ_y	C_{2z}	E	C_{4z}	C_{4z}^{-1}
σ_a	σ_a	σ_y	σ_x	σ_b	C_{4z}^{-1}	C_{4z}	E	C_{2z}
σ_b	σ_b	σ_x	σ_y	σ_a	C_{4z}	C_{4z}^{-1}	C_{2z}	E

(52)

Conjugate class of $S \in \mathcal{G} : (S) = \{S' : \exists\, R \in \mathcal{G} \;\; RS' = SR\}$. $\{E\}$ is always a conjugate class.
$\mathcal{C}_{4v}^z$ has *5 classes*: $\{E\}, \{C_{2z}\}, \{C_{4z}, C_{4z}^{-1}\}, \{\sigma_x, \sigma_y\}, \{\sigma_a, \sigma_b\}$

$$\forall\, R \in \mathcal{C}_{4v}^z \;\; RC_{2z} = C_{2z}R \tag{53}$$
$$\sigma_y C_{4z}^{-1} = C_{4z}\sigma_y = \sigma_a \tag{54}$$
$$C_{4z}\sigma_y = \sigma_x C_{4z} = \sigma_a \tag{55}$$
$$C_{4z}\sigma_a = \sigma_b C_{4z} = \sigma_x \tag{56}$$

Irreducible representations (irrep): the number of irreps equals the number of classes (r) and

$$\sum_{\mu=1}^{r} d_\mu^2 = g \tag{57}$$

5 irreps . $\rightarrow$ 4 one-dimensional, 1 two-dimensional

Character table (μ, ν and i, j label irreps and conjugate classes, respectively)

$$\sum_{R\in\mathcal{G}} \chi^{(\mu)}(R)^* \chi^{(\nu)}(R) = g\,\delta_{\mu\nu} \tag{58}$$

$$\sum_{R\in\mathcal{G}} \left|\chi^{(\mu)}(R)\right|^2 = g \tag{59}$$

$$\sum_{i=1}^{r} g_i\, \chi_i^{(\mu)*} \chi_i^{(\nu)} = g\,\delta_{\mu\nu} \tag{60}$$

$$\sum_{\mu=1}^{r} \chi_i^{(\mu)*} \chi_j^{(\mu)} = \frac{g}{g_i}\,\delta_{ij} \tag{61}$$

	E	C_{4z}	C_{4z}^{-1}	C_{2z}	σ_y	σ_x	σ_a	σ_b
Δ_1	1	1	1	1	1	1	1	1
Δ_2	1	-1	-1	1	1	1	-1	-1
Δ_2'	1	-1	-1	1	-1	-1	1	1
Δ_1'	1	1	1	1	-1	-1	-1	-1
Δ_5	2	0	0	-2	0	0	0	0

(62)

Let us investigate the action of the symmetry transformation on the basisfunctions $\psi_1, \psi_2, \psi_3, \psi_4$:

E	C_{4z}	C_{4z}^{-1}	C_{2z}	σ_y	σ_x	σ_a	σ_b
1	2	-2	-1	1	-1	-2	2
2	-1	1	-2	-2	2	-1	1
3	-3	-3	3	3	3	-3	-3
4	4	4	4	4	4	4	4

(63)

Comparing with the chracter table, we can immediately see, that ψ_4 belongs to the irrep Δ_1, ψ_3 to Δ_2, while $\{\psi_1, \psi_2\}$ to Δ_5.

4.1 Canonical basis and irreducible representations

Let us take the following orthogonal polinomials (canonical basis): $1, x, y, z, xy, xz, yz, x^2 - y^2, 2z^2 - x^2 - y^2, \ldots$ $(x^2 + y^2 + z^2 = 1)$. Then,

$$1, z, 2z^2 - x^2 - y^2 \rightarrow \Delta_1 \tag{64}$$

On the subspace $\{x, y\}$:

$$D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad D(C_{4z}) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad D\left(C_{4z}^{-1}\right) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad D(C_{2z}) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \tag{65}$$

$$D(\sigma_y) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad D(\sigma_x) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad D(\sigma_a) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \quad D(\sigma_b) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{66}$$

which are the matrices of the Δ_5 irrep, thus:

$$\{x, y\}, \{zx, zy\} \to \Delta_5 \tag{67}$$

Furthermore,

E	C_{4z}	C_{4z}^{-1}	C_{2z}	σ_y	σ_x	σ_a	σ_b
xy	$-xy$	$-xy$	xy	$-xy$	$-xy$	xy	xy
x^2-y^2	$-\left(x^2-y^2\right)$	$-\left(x^2-y^2\right)$	x^2-y^2	x^2-y^2	x^2-y^2	$-\left(x^2-y^2\right)$	$-\left(x^2-y^2\right)$

(68)

Comparing with the character table, yields

$$xy \to \Delta_2' \tag{69}$$

$$x^2 - y^2 \to \Delta_2 \tag{70}$$

4.2 Reduction of a reducible representation

Let us take the representation of the $\mathcal{C}_{4v}$ point group elements on the basisfunctions,

$$\varphi_D = e^{i\frac{\pi}{a}(\xi z + 2x)}, \quad \varphi_E = e^{i\frac{\pi}{a}(\xi z + 2y)}, \quad \varphi_F = e^{i\frac{\pi}{a}(\xi z - 2x)}, \quad \varphi_G = e^{i\frac{\pi}{a}(\xi z - 2y)} \tag{71}$$

and also calculate the corresponding characters:

$$D(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \Longrightarrow \chi(E) = 4 \tag{72}$$

$$D(C_{4z}) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(C_{4z}) = 0 \tag{73}$$

$$D\left(C_{4z}^{-1}\right) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \Longrightarrow \chi\left(C_{4z}^{-1}\right) = 0 \tag{74}$$

$$D(C_{2z}) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(C_{2z}) = 0 \tag{75}$$

$$D(\sigma_y) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(\sigma_y) = 2 \tag{76}$$

$$D(\sigma_x) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \Longrightarrow \chi(\sigma_x) = 2 \tag{77}$$

$$D(\sigma_a) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(\sigma_a) = 0 \tag{78}$$

$$D(\sigma_b) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \Longrightarrow \chi(\sigma_b) = 0 \tag{79}$$

Calculate the *number of occurence* of irrep μ, M_μ, in this reducible representation:

$$M_\mu = \frac{1}{g} \sum_{i=1}^{r} g_i \, \chi_i^{(\mu)*} \chi_i \tag{80}$$

$$M_{\Delta_1} = \frac{1}{8}(4 + 2*1*0 + 1*1*0 + 2*1*2 + 2*1*0) = 1 \tag{81}$$

$$M_{\Delta_2} = \frac{1}{8}(4 + 2*2) = 1 \tag{82}$$

$$M_{\Delta_2'} = \frac{1}{8}(4 - 2*2) = 0 \tag{83}$$

$$M_{\Delta_1'} = \frac{1}{8}(4 - 2*2) = 0 \tag{84}$$

$$M_{\Delta_5} = \frac{1}{8}(2*4) = 1 \tag{85}$$

This means that the four-dimensional representation can be reduced to irreps, $\Delta_1 \otimes \Delta_2 \otimes \Delta_5$, via a unitary transformation.

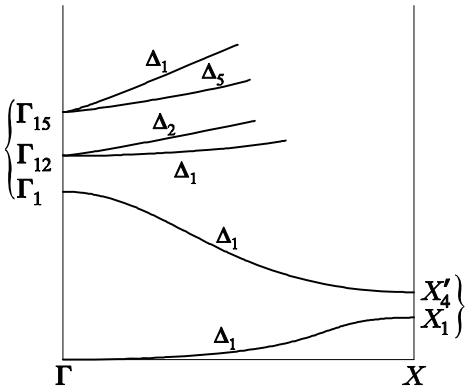

Figure 3: Typical bandstructure of a simple cubic lattice along ΓX.

Projectors of the irreducible basisfunctions:

$$P_i^{(\mu)} = \frac{d_\mu}{g} \sum_{R \in \mathcal{G}} D_{ii}^{(\mu)}(R)^* \cdot D(R) \tag{86}$$

$$\Downarrow$$

$$\psi^{(\Delta_1)} = e^{i\frac{\pi}{a}z}\left(\cos\frac{2\pi x}{a} + \cos\frac{2\pi y}{a}\right) \tag{87}$$

$$\psi^{(\Delta_2)} = e^{i\frac{\pi}{a}z}\left(\cos\frac{2\pi x}{a} - \cos\frac{2\pi y}{a}\right) \tag{88}$$

$$\psi_1^{(\Delta_5)} = e^{i\frac{\pi}{a}z}\sin\frac{2\pi x}{a} \tag{89}$$

$$\psi_2^{(\Delta_5)} = e^{i\frac{\pi}{a}z}\sin\frac{2\pi y}{a} \tag{90}$$

This is exactly that we obtained previously in terms of the nearly free electron approach.

5 Structure of the Hamilton matrix, hybridization

Action of the symmetry operation:

$$R\left[H_{\mathbf{k}}(\mathbf{r})\, u_{\mathbf{k}}(\mathbf{r})\right] = H_{\mathbf{k}}\left(R^{-1}\mathbf{r}\right) u_{\mathbf{k}}\left(R^{-1}\mathbf{r}\right) = \left[\frac{\left(R^{-1}\mathbf{p} + \hbar\mathbf{k}\right)^2}{2m} + V\left(R^{-1}\mathbf{r}\right)\right] u_{\mathbf{k}}\left(R^{-1}\mathbf{r}\right) \tag{91}$$

$$= \left[\frac{\left(\mathbf{p} + \hbar R\mathbf{k}\right)^2}{2m} + V(\mathbf{r})\right] u_{\mathbf{k}}\left(R^{-1}\mathbf{r}\right) = H_{R\mathbf{k}}(\mathbf{r})\, R u_{\mathbf{k}}(\mathbf{r}) \tag{92}$$

consequently,

$$RH_{\mathbf{k}} = H_{R\mathbf{k}}R \tag{93}$$

$$\Downarrow$$

$$H_{R\mathbf{k}}Ru_{\mathbf{k}} = \varepsilon_{\mathbf{k}}Ru_{\mathbf{k}} \tag{94}$$

$$\Downarrow$$

$$\varepsilon_{R\mathbf{k}} = \varepsilon_{\mathbf{k}}$$

and for non-degenerate bands,

$$u_{R\mathbf{k}}(\mathbf{r}) = c\, u_{\mathbf{k}}\left(R^{-1}\mathbf{r}\right) \quad (|c| = 1) \tag{95}$$

$$\psi_{R\mathbf{k}}(\mathbf{r}) = c\, e^{iR\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}\left(R^{-1}\mathbf{r}\right) = R\psi_{\mathbf{k}}(\mathbf{r}) \tag{96}$$

For the little group of $\mathbf{k}$:

$$RH_{\mathbf{k}}(\mathbf{r}) = H_{\mathbf{k}}(\mathbf{r})\, R \tag{97}$$

This implies that $H_{\mathbf{k}}$ and $\{R|R \in \mathcal{G}\}$ have a common basis of eigenfunctions, $\left\{\varphi_i^{\mu,k_\mu}\right\}$, where μ, $k_\mu = 1,\ldots,M_\mu$ and $i = 1,\ldots,d_\mu$ label the irreps, the occurence of irreps and the wavefunctions within an irreducible subset, respectively.

$$H_{\mathbf{k}}\varphi_i^{\mu,k_\mu} = \varepsilon_i^\mu \varphi_i^{\mu,k_\mu} \tag{98}$$

$$\left\langle \varphi_i^{\mu,k_\mu} | \varphi_j^{\mu',k'_{\mu'}} \right\rangle = \delta_{\mu\mu'}\delta_{k_\mu,k'_{\mu'}}\delta_{ij} \tag{99}$$

$$R\varphi_i^{\mu,k_\mu} = \sum_{j=1}^{d_\mu} \varphi_j^{\mu,k_\mu} D_{ji}^\mu(R) \tag{100}$$

Using the "big orthogonality" lemma,

$$\frac{1}{g}\sum_{R\in\mathcal{G}} D_{is}^\mu(R)^*\, D_{rj}^{\mu'}(R) = \frac{g}{d_\mu}\,\delta_{\mu\mu'}\delta_{ij}\delta_{sr}\ , \tag{101}$$

the matrixelements of the Hamiltonian can be expressed as follows,

$$\left\langle \varphi_i^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_j^{\mu',k'_{\mu'}} \right\rangle = \frac{1}{g} \sum_{R\in\mathcal{G}} \left\langle R\varphi_i^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_j^{\mu',k'_{\mu'}} \right\rangle \tag{102}$$

$$= \frac{1}{g} \sum_{s=1}^{d_\mu} \sum_{r=1}^{d_\mu} \sum_{R\in\mathcal{G}} D_{is}^{\mu}(R)^* \left\langle \varphi_s^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_r^{\mu',k'_{\mu'}} \right\rangle D_{rj}^{\mu'}(R) \tag{103}$$

$$= \delta_{\mu\mu'}\delta_{ij} \frac{1}{d_\mu} \sum_{s=1}^{d_\mu} \left\langle \varphi_s^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_s^{\mu,k'_\mu} \right\rangle \ . \tag{104}$$

This means that the blocks of the Hamilton-matrix connecting different irreps are identical to zero, whereas those connecting the same irreps are unit matrices multiplied by a complex number,

$$H_{\mathbf{k}} = \sum_{\mu} \sum_{k_\mu,k'_\mu} h_{\mathbf{k}}^{\mu,k_\mu k'_\mu} \sum_{j=1}^{d_\mu} \left| \varphi_j^{\mu,k_\mu} \right\rangle \left\langle \varphi_j^{\mu,k'_\mu} \right| \tag{105}$$

Corollary 1: If an irrep occurs once in the basis set ($M_\mu = 1$), then it spans an energy subspace and

$$\varepsilon_{\mathbf{k}}^{\mu} = h_{\mathbf{k}}^{\mu} \tag{106}$$

Corollary 2: If the same irrep occurs more than ones ($M_\mu > 1$), than the corresponding eigenvalues are, $\varepsilon_{\mathbf{k}}^{\mu,n}$ $(n = 1, \ldots, M_\mu)$, where n labels the bands related to irrep μ and the eigenfunctions are elements of the tensorial product of the irreducible subspaces. Diagonalizing the $M_\mu \times M_\mu$ matrices, $h_{\mathbf{k}}^{\mu,k_\mu k'_\mu}$,

$$H_{\mathbf{k}} \psi_{\mathbf{k},j}^{\mu,n} = \varepsilon_{\mathbf{k}}^{\mu,n} \psi_{\mathbf{k},j}^{\mu,n} \tag{107}$$

$$(1 \le j \le d_\mu \quad 1 \le n \le M_\mu) \tag{108}$$

$$\psi_{\mathbf{k},j}^{\mu,n} = \sum_{k_\mu=1}^{M_\mu} c_n^{\mu,k_\mu} \varphi_j^{\mu,k_\mu} \tag{109}$$

$$\sum_{k_\mu=1}^{M_\mu} \left| c_n^{\mu,k_\mu} \right|^2 = 1 \tag{110}$$

This is called *hybridization*, which strictly occurs within the sub-spaces of the same irreps!

5.1 Localized (tight-binding) picture

The crystal potential, $V(\mathbf{r})$, can be divided into pieces with respect to atomic cells,

$$V(\mathbf{r}) = \sum_i V(\mathbf{r})\, \Theta_i(\mathbf{r}) \tag{111}$$

where

$$\Theta_i(\mathbf{r}) = \begin{cases} 1 & \text{if} \quad \mathbf{r} \in \Omega_i \\ 0 & \text{if} \quad \mathbf{r} \notin \Omega_i \end{cases} \tag{112}$$

with Ω_i being the Wigner-Seitz cell corresponding to the atomic position $\mathbf{R}_i$,

$$\bigcup_i \Omega_i = 1 \ . \tag{113}$$

The cell-potential is defined as

$$V_i(\mathbf{r}) = V(\mathbf{r})\, \Theta_i(\mathbf{r}) \ , \tag{114}$$

$$V_j(\mathbf{r}-\mathbf{R}_j) = V_i(\mathbf{r}-\mathbf{R}_i) = V_c(\mathbf{r}-\mathbf{R}_i) \tag{115}$$

$$V(\mathbf{r}) = \sum_i V_c(\mathbf{r}-\mathbf{R}_i) \ . \tag{116}$$

Let us introduce spherical atomic potentials,

$$V_a(\mathbf{r}-\mathbf{R}_i) = V_a(|\mathbf{r}-\mathbf{R}_i|) \ , \tag{117}$$

such that

$$V_a(\mathbf{r}-\mathbf{R}_i) = V_a(\mathbf{r}-\mathbf{R}_i)\,\Theta_i(\mathbf{r}) \ , \tag{118}$$

and atomic-like localized wavefunctions, $\varphi_\alpha(\mathbf{r})$, that are solutions of the Schrödinger-equation in a given cell,

$$\left[-\frac{\hbar^2}{2m}\Delta + V_a(\mathbf{r}-\mathbf{R}_i)\right]\varphi_\alpha(\mathbf{r}-\mathbf{R}_i) = \varepsilon_\alpha\varphi_\alpha(\mathbf{r}-\mathbf{R}_i) \tag{119}$$

$$\langle\varphi_\alpha|\varphi_{\alpha'}\rangle = \int d^3r\,\varphi_\alpha(\mathbf{r}-\mathbf{R}_i)^*\,\varphi_\alpha(\mathbf{r}-\mathbf{R}_i) = \delta_{\alpha\alpha'} \ . \tag{120}$$

Apparently, φ_α can be classified according to the irreps of the point-group of continous rotations, $O(3)$,i.e., $\varphi_{n\ell m}$, where $n = 1, 2, \ldots$ is the principal quantum number, ℓ is the orbital quantumnumber and m is the magnetic quantumnumber. Corresponding Bloch functions can be introduced as,

$$\psi_\alpha(\mathbf{k},\mathbf{r}) = \frac{c}{\sqrt{N}}\sum_i e^{i\mathbf{k}\mathbf{R}_i}\varphi_\alpha(\mathbf{r}-\mathbf{R}_i) \tag{121}$$

since

$$\psi_\alpha(\mathbf{k},\mathbf{r}+\mathbf{R}_j) = \frac{c}{\sqrt{N}}\sum_i e^{i\mathbf{k}\mathbf{R}_i}\varphi_\alpha(\mathbf{r}+\mathbf{R}_j-\mathbf{R}_i) \tag{122}$$

$$= e^{i\mathbf{k}\mathbf{R}_j}\psi_\alpha(\mathbf{k},\mathbf{r}) \ . \tag{123}$$

These functions are, however, not orthonormal:

$$\langle\psi_\alpha(\mathbf{k}')\,|\psi_{\alpha'}(\mathbf{k})\rangle = \frac{|c|^2}{N}\sum_{i,j} e^{i\mathbf{k}\mathbf{R}_j - i\mathbf{k}'\mathbf{R}_i}\underbrace{\int d^3r\,\varphi_\alpha(\mathbf{r}-\mathbf{R}_i)^*\,\varphi_{\alpha'}(\mathbf{r}-\mathbf{R}_j)}_{S_{\alpha\alpha'}(\mathbf{R}_j-\mathbf{R}_i)} \tag{124}$$

$$= \delta_{\mathbf{k}\mathbf{k}'}\,|c|^2\,S_{\alpha\alpha'}(\mathbf{k}) \tag{125}$$

with

$$S_{\alpha\alpha'}(\mathbf{k}) = \sum_i e^{i\mathbf{k}\mathbf{R}_i}S_{\alpha\alpha'}(\mathbf{R}_i) \ . \tag{126}$$

Let's simplify matters by supposing

$$S_{\alpha\alpha'}(\mathbf{k}) = \delta_{\alpha\alpha'} \implies c = 1 \tag{127}$$

The eigenfunctions of the system can be looked for as

$$\psi_j(\mathbf{k},\mathbf{r}) = \sum_\alpha c_\alpha^j(\mathbf{k})\,\psi_\alpha(\mathbf{k},\mathbf{r}) \tag{128}$$

$$= \frac{1}{\sqrt{N}}\sum_\alpha c_\alpha^j(\mathbf{k})\sum_i e^{i\mathbf{k}\mathbf{R}_i}\varphi_\alpha(\mathbf{r}-\mathbf{R}_i) \tag{129}$$

$$H\psi_j(\mathbf{k}) = \varepsilon_{\mathbf{k}}^j\psi_j(\mathbf{k}) \tag{130}$$

Then we arrive at a secular equation,

$$\sum_\alpha c_\alpha^j(\mathbf{k})\,H\psi_\alpha(\mathbf{k}) = \varepsilon_{\mathbf{k}}^j\sum_\alpha c_\alpha^j(\mathbf{k})\,\psi_\alpha(\mathbf{k}) \tag{131}$$

$$\sum_{\alpha'}\left[H_{\alpha\alpha'}\left(\mathbf{k}\right)-\varepsilon_{\mathbf{k}}^{j}\delta_{\alpha\alpha'}\right]c_{\alpha'}^{j}=0 \tag{132}$$

$$\det\left(\underline{H}\left(\mathbf{k}\right)-\varepsilon_{\mathbf{k}}^{j}\underline{I}\right)=0\,. \tag{133}$$

The reciprocal-space Hamilton-matrix

$$\begin{aligned}
H_{\alpha\alpha'}\left(\mathbf{k}\right) &= \frac{1}{N}\sum_{i,j}e^{i\mathbf{k}\left(\mathbf{R}_j-\mathbf{R}_i\right)}\int d^3r\,\varphi_\alpha\left(\mathbf{r}-\mathbf{R}_i\right)^*\left(-\frac{\hbar^2}{2m}\Delta+V\left(\mathbf{r}\right)\right)\varphi_{\alpha'}\left(\mathbf{r}-\mathbf{R}_j\right)\\
&= \frac{1}{N}\sum_{i,j}e^{i\mathbf{k}\left(\mathbf{R}_j-\mathbf{R}_i\right)}\int d^3r\,\varphi_\alpha\left(\mathbf{r}-\mathbf{R}_i\right)^*\left(-\frac{\hbar^2}{2m}\Delta+V\left(\mathbf{r}-\mathbf{R}_j\right)\right)\varphi_{\alpha'}\left(\mathbf{r}-\mathbf{R}_j\right)\\
&= \frac{1}{N}\sum_{i,j}e^{i\mathbf{k}\left(\mathbf{R}_j-\mathbf{R}_i\right)}\int d^3r\,\varphi_\alpha\left(\mathbf{r}-\mathbf{R}_i\right)^*\left(-\frac{\hbar^2}{2m}\Delta+V_a\left(\mathbf{r}-\mathbf{R}_j\right)\right)\varphi_{\alpha'}\left(\mathbf{r}-\mathbf{R}_j\right)\\
&+ \frac{1}{N}\sum_{i,j}e^{i\mathbf{k}\left(\mathbf{R}_j-\mathbf{R}_i\right)}\underbrace{\int d^3r\,\varphi_\alpha\left(\mathbf{r}-\mathbf{R}_i\right)^*\left(V\left(\mathbf{r}-\mathbf{R}_j\right)-V_a\left(\mathbf{r}-\mathbf{R}_j\right)\right)\varphi_{\alpha'}\left(\mathbf{r}-\mathbf{R}_j\right)}_{V_{\alpha\alpha'}\left(\mathbf{R}_j-\mathbf{R}_i\right)\left(1-\delta_{\mathbf{R}_i\mathbf{R}_j}\right)+\delta_{\mathbf{R}_i\mathbf{R}_j}\Delta\varepsilon_{\alpha\alpha'}}\\
&= \varepsilon_\alpha\delta_{\alpha\alpha'}+\Delta\varepsilon_{\alpha\alpha'}+\sum_{\mathbf{R}_i\neq 0}e^{i\mathbf{k}\mathbf{R}_i}V_{\alpha\alpha'}\left(\mathbf{R}_i\right)
\end{aligned} \tag{134}$$

$$\varepsilon_{\alpha\alpha'}\equiv\varepsilon_\alpha\delta_{\alpha\alpha'}+\Delta\varepsilon_{\alpha\alpha'}=\int d^3r\,\varphi_\alpha\left(\mathbf{r}\right)^*\left(-\frac{\hbar^2}{2m}\Delta+V\left(\mathbf{r}\right)\right)\varphi_{\alpha'}\left(\mathbf{r}\right) \tag{135}$$

Usual approach (good in case of high symmetry):

$$\varepsilon_{\alpha\alpha'}\simeq\varepsilon_\alpha\delta_{\alpha\alpha'} \tag{136}$$

The hybridization matrix:

$$V_{\alpha\alpha'}\left(\mathbf{R}_i\right)=\int d^3r\,\varphi_\alpha\left(\mathbf{r}\right)^*\left(V\left(\mathbf{r}-\mathbf{R}_i\right)-V_a\left(\mathbf{r}-\mathbf{R}_i\right)\right)\varphi_{\alpha'}\left(\mathbf{r}-\mathbf{R}_i\right) \tag{137}$$

The real-space Hamilton-matrix:

$$H_{\alpha\alpha'}^{ij}=\varepsilon_\alpha\delta_{\alpha\alpha'}\delta_{ij}+V_{\alpha\alpha'}\left(\mathbf{R}_j-\mathbf{R}_i\right)\left(1-\delta_{ij}\right)\,. \tag{138}$$

By using a unitary transformation, the Hamilton-matrix can be written as

$$H_{n\ell i,n'\ell' i'}^{\mu,k}\left(\mathbf{k}\right)\,\delta_{\mu\mu'}\delta_{kk'} \tag{139}$$

where μ and k label the irreps of the little group of $\mathbf{k}$ and the corresponding symmetry-adapted wavefunctions, respectively, while the occurence of irrep μ in the ℓ-th and ℓ'-th irrep of $O\left(3\right)$ is denoted by i and i'. Usually, $n=n'$. Diagonalization of this matrix gives the eigenvalues $\varepsilon_n^{\mu,b}\left(\mathbf{k}\right)$, where b is the bandindex. Thus, basisfunctions with different ℓ values can be mixed to form a band. This is a more common definition of *hyridization*. A well-known example is the $s-d$ $(4s-3d)$ hybridization in $3d$ transition metals.

6 Density of states

Spectral density of states:

$$n_{\mathbf{k}}\left(\varepsilon\right)=\sum_n\delta\left(\varepsilon-\varepsilon_{\mathbf{k}n}\right) \tag{140}$$

$$R \in \mathcal{G} : n_{R\mathbf{k}}(\varepsilon) = n_{\mathbf{k}}(\varepsilon) \tag{141}$$

Total density of states:

$$n(\varepsilon) = \sum_{\mathbf{k}\in BZ} n_{\mathbf{k}}(\varepsilon) = \sum_{R\in\mathcal{G}} \sum_{\mathbf{k}\in IBZ} n_{\mathbf{k}}(\varepsilon) = g \sum_{\mathbf{k}\in IBZ} n_{\mathbf{k}}(\varepsilon) \tag{142}$$

This implies that the total density of states can be calculated by integrating the spectral density of states in the irreducible wedge of the BZ.

Resolution according to irreps

$$H\psi_i = \varepsilon_i \psi_i \tag{143}$$

$$n(\varepsilon) = \sum_i \delta(\varepsilon - \varepsilon_i) \tag{144}$$

The results of the previous sections can be applied here, too:

$$R \in \mathcal{G} : HR = RH \tag{145}$$

$$H\psi_j^{(\mu)i} = \varepsilon^{(\mu)i} \psi_j^{(\mu)i} \tag{146}$$

$$(\mu = 1, \ldots, r \quad j = 1, \ldots, d_\mu) \tag{147}$$

$$n(\varepsilon) = \sum_\mu d_\mu \sum_i \delta\left(\varepsilon - \varepsilon^{(\mu)i}\right) = \sum_\mu n_\mu(\varepsilon) \tag{148}$$

$$n_\mu(\varepsilon) = d_\mu \sum_i \delta\left(\varepsilon - \varepsilon^{(\mu)i}\right) \tag{149}$$

7 Appendix: the cubic point-group, O_h

Rotations: $3C_4, 6C_2, 4C_3 \Longrightarrow 1 + 3\cdot 3 + 6\cdot 1 + 4\cdot 2 = 24$ symmetry oprations. *48 elements* with inversion

10 classes: 4 one-dim., 2 two-dim., 4 three-dim. $(4 + 2\cdot 4 + 4\cdot 9 = 48)$

Irreducible representations → even functions: $A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}$, odd functions: $A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}$

Canonical basis:

$$1 \to A_{1g} \tag{150}$$

$$\{x, y, z\} \to T_{1u} \tag{151}$$

$$\{xy, yz, xz\} \to T_{2g} \tag{152}$$

$$\left\{x^2 - y^2, 2z^2 - x^2 - y^2\right\} \to E_g \tag{153}$$

Splitting of energy levels when reducing symmetry:

	O_h		$C_{4v}^{(z)}$		$C_{2v}^{(xz)}$
p $(\ell = 1)$	$\{x, y, z\}$	$\Longrightarrow$	$\{x, y\}$ z	$\Longrightarrow$	x y z
d $(\ell = 2)$	$\left\{x^2 - y^2, 2z^2 - x^2 - y^2\right\}$ $\{xy, yz, xz\}$	$\Longrightarrow$	$x^2 - y^2$ $2z^2 - x^2 - y^2$ xy $\{yz, xz\}$	$\Longrightarrow$	$x^2 - y^2$ $2z^2 - x^2 - y^2$ xy xz yz

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	O_h		$C_{3v}^{(z)}$		$C_3^{(z)}$
$p\ (\ell=1)$	$\{x,y,z\}$	$\Longrightarrow$	$\begin{matrix}\{x,y\}\\ z\end{matrix}$	$\Longrightarrow$	$\begin{matrix}x+iy\\ x-iy\\ z\end{matrix}$
$d\ (\ell=2)$	$\begin{matrix}\left\{x^2-y^2, 2z^2-x^2-y^2\right\}\\ \{xy,yz,xz\}\end{matrix}$	$\Longrightarrow$	$\begin{matrix}\left\{xy, x^2-y^2\right\}\\ 2z^2-x^2-y^2\\ \{yz,xz\}\end{matrix}$	$\Longrightarrow$	$\begin{matrix}x^2-y^2+2ixy\\ x^2-y^2-2ixy\\ 2z^2-x^2-y^2\\ (x+iy)\,z\\ (x-iy)\,z\end{matrix}$

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8 Appendix: the group $C_3^{(z)}$

Anticlockwise rotation by $\pi/3$:

$$x' = \frac{1}{2}x + \frac{\sqrt{3}}{2}y \tag{156}$$

$$y' = -\frac{\sqrt{3}}{2}x + \frac{1}{2}y \tag{157}$$

$$x' + iy' = \left(\frac{1}{2} - i\frac{\sqrt{3}}{2}\right)x + \left(\frac{\sqrt{3}}{2} + i\frac{1}{2}\right)y = \left(\frac{1}{2} - i\frac{\sqrt{3}}{2}\right)(x+iy) \tag{158}$$

$$= e^{-i2\pi/3}\,(x+iy) \tag{159}$$

$$x' - iy' = \left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)x + \left(\frac{\sqrt{3}}{2} - i\frac{1}{2}\right)y = \left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)(x-iy) \tag{160}$$

$$= e^{i2\pi/3}\,(x-iy) \tag{161}$$

$$2x'y' = -\frac{\sqrt{3}}{2}x^2 + \frac{\sqrt{3}}{2}y^2 - xy = -\frac{1}{2}(2xy) - \frac{\sqrt{3}}{2}\left(x^2-y^2\right) \tag{162}$$

$$x'^2 - y'^2 = \left(\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)^2 - \left(-\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right)^2 = \frac{\sqrt{3}}{2}(2xy) - \frac{1}{2}\left(x^2-y^2\right) \tag{163}$$

$$\begin{pmatrix} 2x'y' \\ x'^2 - y'^2 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 2xy \\ x^2-y^2 \end{pmatrix} \tag{164}$$

$$D(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \quad \chi(C_3) = -1 \tag{165}$$

$$D\left(C_3^{-1}\right) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \quad \chi\left(C_3^{-1}\right) = -1 \tag{166}$$

For one-dimensional irreps (Abelian group):

$$P^{(\mu)} = \frac{1}{g}\sum_{R\in\mathcal{G}} \chi^{(\mu)}(R)^* \cdot D(R) \tag{167}$$

$$\begin{array}{c|ccc} & E & C_3 & C_3^{-1} \\ \hline A & 1 & 1 & 1 \\ {}^1E & 1 & e^{-i2\pi/3} & e^{i2\pi/3} \\ {}^2E & 1 & e^{i2\pi/3} & e^{-i2\pi/3} \end{array} \tag{168}$$

$$P(A) = \frac{1}{3}\left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} + \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}\right] = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \tag{169}$$

$$P\left({}^1E\right) = \frac{1}{3}\left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + e^{-i2\pi/3}\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} + e^{i2\pi/3}\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}\right] = \begin{pmatrix} \frac{1}{2} & \frac{i}{2} \\ -\frac{i}{2} & \frac{1}{2} \end{pmatrix} \tag{170}$$

$$P\left({}^2E\right) = \frac{1}{3}\left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + e^{i2\pi/3}\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} + e^{-i2\pi/3}\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}\right] = \begin{pmatrix} \frac{1}{2} & -\frac{i}{2} \\ \frac{i}{2} & \frac{1}{2} \end{pmatrix} \tag{171}$$