Point-group symmetries in bandstructure of crystals

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1 Electron states in a periodic lattice (brief review)

Periodic potential

$$V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r}) \tag{1}$$

Schrödinger equation

$$\left(\frac{\mathbf{p}^2}{2m} + V(\mathbf{r})\right)\psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}) \tag{2}$$

Bloch state

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}) \tag{3}$$

$$\mathbf{k} \in BZ\,.$$

Alternative form of the Bloch states

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \tag{4}$$

$$u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{\mathbf{k}}(\mathbf{r}) \tag{5}$$

Schrödinger equation for $u_{\mathbf{k}}(\mathbf{r})$

$$e^{-i\mathbf{k}\mathbf{r}}\left(\frac{\mathbf{p}^2}{2m} + V(\mathbf{r})\right)e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}(\mathbf{r})\; u_{\mathbf{k}}(\mathbf{r}) \tag{6}$$

$$\left(\frac{(\mathbf{p}+\hbar\mathbf{k})^2}{2m} + V(\mathbf{r})\right)u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\, u_{\mathbf{k}}(\mathbf{r}) \tag{7}$$

Periodicity in reciprocal space

$$\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}e^{i\mathbf{K}\mathbf{r}}u_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u'_{\mathbf{k}}(\mathbf{r}) \tag{8}$$

$$u'_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{K}\mathbf{r}}u_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \tag{9}$$

$$u'_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u'_{\mathbf{k}}(\mathbf{r})$$

$$\left(\frac{(\mathbf{p}+\hbar\mathbf{k})^2}{2m} + V(\mathbf{r})\right)u'_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}+\mathbf{K}}\, u'_{\mathbf{k}}(\mathbf{r}) \tag{10}$$

$$\Downarrow$$

$$\underline{\varepsilon_{\mathbf{k}+\mathbf{K}} = \varepsilon_{\mathbf{k}}} \tag{11}$$

$$u'_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{K}\mathbf{r}}u_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \tag{12}$$

$$\underline{\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})} \tag{13}$$

Space inversion symmetry

$$V(\mathbf{r}) = V(-\mathbf{r}) \tag{14}$$

$$\psi_{-\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\mathbf{r}} u_{-\mathbf{k}}(\mathbf{r})$$

$$\left(\frac{(\mathbf{p} - \hbar\mathbf{k})^2}{2m} + V(\mathbf{r}) \right) u_{-\mathbf{k}}(\mathbf{r}) = \varepsilon_{-\mathbf{k}}\, u_{-\mathbf{k}}(\mathbf{r}) \tag{15}$$

$$\left(\frac{(\mathbf{p} + \hbar\mathbf{k})^2}{2m} + V(\mathbf{r}) \right) u_{-\mathbf{k}}(-\mathbf{r}) = \varepsilon_{-\mathbf{k}}\, u_{-\mathbf{k}}(-\mathbf{r}) \tag{16}$$

$$\Downarrow$$

$$\underline{\varepsilon_{-\mathbf{k}} = \varepsilon_{\mathbf{k}}} \tag{17}$$

$$u_{-\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(-\mathbf{r}) \tag{18}$$

$$\underline{\psi_{-\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\mathbf{r}} u_{-\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(-\mathbf{r}) = \psi_{\mathbf{k}}(-\mathbf{r})} \tag{19}$$

2 Nearly free-electron model

Free electrons on periodic lattice

$$\psi_{\mathbf{K},\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \qquad (\mathbf{k} \in BZ) \tag{20}$$

$$\int \psi_{\mathbf{K},\mathbf{k}}(\mathbf{r})^* \, \psi_{\mathbf{K}',\mathbf{k}'}(\mathbf{r})\, d^3r = \delta_{\mathbf{k}+\mathbf{K},\mathbf{k}'+\mathbf{K}'} = \delta_{\mathbf{K},\mathbf{K}'}\delta_{\mathbf{k},\mathbf{k}'}$$

$$\varepsilon^0_{\mathbf{K},\mathbf{k}} = \frac{\hbar^2 (\mathbf{k} + \mathbf{K})^2}{2m} \tag{21}$$

General solution

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{K}} c_{\mathbf{K}}(\mathbf{k})\; e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \tag{22}$$

$$\left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) \right) \psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\, \psi_{\mathbf{k}}(\mathbf{r}) \tag{23}$$

$$\Downarrow$$

$$\sum_{\mathbf{K}} \left(\varepsilon^0_{\mathbf{K},\mathbf{k}} + V(\mathbf{r}) \right) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} c_{\mathbf{K}}(\mathbf{k}) = \varepsilon_{\mathbf{k}} \sum_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} c_{\mathbf{K}}(\mathbf{k}) \tag{24}$$

$$\Downarrow$$

$$\underline{\sum_{\mathbf{K}} \left(\varepsilon^0_{\mathbf{K},\mathbf{k}} \delta_{\mathbf{K},\mathbf{K}'} + V_{\mathbf{K},\mathbf{K}'} \right) c_{\mathbf{K}'}(\mathbf{k}) = \varepsilon_{\mathbf{k}} c_{\mathbf{K}}(\mathbf{k})} \tag{25}$$

where

$$V_{\mathbf{K},\mathbf{K}'} = \frac{1}{V} \int d^3r V(\mathbf{r})\, e^{i(\mathbf{K}'-\mathbf{K})\mathbf{r}} = \frac{1}{V_0} \int_{V_0} d^3r V(\mathbf{r})\, e^{i(\mathbf{K}'-\mathbf{K})\mathbf{r}} \tag{26}$$

Hamiltonian matrix

$$H_{\mathbf{K},\mathbf{K}'}(\mathbf{k}) = \varepsilon^0_{\mathbf{K},\mathbf{k}} \delta_{\mathbf{K},\mathbf{K}'} + V_{\mathbf{K},\mathbf{K}'} \tag{27}$$

$$\underline{\underline{H}}(\mathbf{k}) = \left\{ H_{\mathbf{K},\mathbf{K}'}(\mathbf{k}) \right\} \quad \underline{c}(\mathbf{k}) = \{ c_{\mathbf{K}}(\mathbf{k}) \} \tag{28}$$

$$\left(\varepsilon_{\mathbf{k}}\underline{\underline{I}} - \underline{\underline{H}}(\mathbf{k})\right)\underline{c}(\mathbf{k}) = 0 \tag{29}$$

$$\det\left(\varepsilon_{\mathbf{k}}\underline{\underline{I}} - \underline{\underline{H}}(\mathbf{k})\right) = 0 \tag{30}$$

Perturbative solution for non-degenerate Bloch states

$$\varepsilon_{\mathbf{K},\mathbf{k}} \simeq \varepsilon^0_{\mathbf{K},\mathbf{k}} + V_{\mathbf{K},\mathbf{K}} + \sum_{\mathbf{K}'(\neq\mathbf{K})} \frac{\left|V_{\mathbf{K},\mathbf{K}'}\right|^2}{\varepsilon^0_{\mathbf{K}',\mathbf{k}} - \varepsilon^0_{\mathbf{K},\mathbf{k}}} \tag{31}$$

3 Formation of bands on a one-dimensional simple lattice

$$K_l = l\frac{2\pi}{a} \tag{32}$$

$$BZ = \left[-\frac{\pi}{a}, \frac{\pi}{a}\right] \tag{33}$$

$$k = \kappa\frac{\pi}{a} \quad \kappa \in [-1, 1] \tag{34}$$

$$\varepsilon^0_l(\kappa) = \frac{2\hbar^2\pi^2}{ma^2}\left(\frac{\kappa}{2} + l\right)^2 \tag{35}$$

Degeneracies at the center of the BZ

$$\kappa = 0 \quad \varepsilon^0_l(0) = \varepsilon^0_{-l}(0) = \frac{2\hbar^2\pi^2}{ma^2}l^2 \tag{36}$$

and at the boundary of the BZ

$$\kappa = \pm 1 \quad \varepsilon^0_l(\pm 1) = \varepsilon^0_{-l\mp 1}(\pm 1) = \frac{2\hbar^2\pi^2}{ma^2}\left(l \pm \frac{1}{2}\right)^2 \tag{37}$$

Lifting of the degeneracies

$\kappa \simeq 0$

$$\psi^0_l(\kappa; x) = \frac{1}{\sqrt{L}}e^{i\pi(\kappa+2l)x/a} \quad \psi^0_{-l}(\gamma; x) = \frac{1}{\sqrt{L}}e^{i\pi(\kappa-2l)x/a} \tag{38}$$

$$\begin{aligned} V_{ll}(\kappa) &= \int_{-\infty}^{\infty}\psi^0_l(\kappa;x)^*V(x)\,\psi^0_l(\kappa;x)\,dx = \frac{1}{a}\int_{-a/2}^{a/2}e^{-i\pi(\kappa+2l)x/a}V(x)\,e^{i\pi(\kappa+2l)x/a}dx \\ &= \frac{1}{a}\int_{-a/2}^{a/2}V(x)\,dx = V_{00} \end{aligned} \tag{39}$$

$$\begin{aligned} V_{l,-l}(\kappa) &= \int_{-\infty}^{\infty}\psi^0_l(\kappa;x)^*V(x)\,\psi^0_{-l}(\kappa;x)\,dx = \frac{1}{a}\int_{-a/2}^{a/2}e^{-i\pi(\kappa+2l)x/a}V(x)\,e^{i\pi(\kappa-2l)x/a}dx \\ &= \frac{1}{a}\int_{-a/2}^{a/2}V(x)\,e^{-4i\pi lx/a}dx \end{aligned} \tag{40}$$

$$\overline{\varepsilon}_l(\kappa) = \varepsilon_l(\kappa) - V_{00} \tag{41}$$

$$\det\begin{pmatrix} \frac{2\hbar^2\pi^2}{ma^2}\left(\frac{\kappa}{2}+l\right)^2-\overline{\varepsilon}_l(\kappa) & V_{l,-l} \\ V^*_{l,-l} & \frac{2\hbar^2\pi^2}{ma^2}\left(-\frac{\kappa}{2}+l\right)^2-\overline{\varepsilon}_l(\kappa) \end{pmatrix}=0 \tag{42}$$

$$\left(\frac{2\hbar^2\pi^2}{ma^2}\left(\frac{\kappa}{2}+l\right)^2-\overline{\varepsilon}_l(\kappa)\right)\left(\frac{2\hbar^2\pi^2}{ma^2}\left(-\frac{\kappa}{2}+l\right)^2-\overline{\varepsilon}_l(\kappa)\right)-\left|V_{l,-l}\right|^2=0 \tag{43}$$

$$\overline{\varepsilon}_l(\kappa)^2-\overline{\varepsilon}_l(\kappa)\frac{4\hbar^2\pi^2}{ma^2}\left(l^2+\frac{\kappa^2}{4}\right)+\left(\frac{2\hbar^2\pi^2}{ma^2}\right)^2\left(l^2-\frac{\kappa^2}{4}\right)^2-\left|V_{l,-l}\right|^2=0 \tag{44}$$

$$\begin{aligned}\overline{\varepsilon}_l(\kappa) &= \frac{2\hbar^2\pi^2}{ma^2}\left(l^2+\frac{\kappa^2}{4}\right)\pm\sqrt{\left(\frac{2\hbar^2\pi^2}{ma^2}\right)^2\left(l^2+\frac{\kappa^2}{4}\right)^2-\left(\frac{2\hbar^2\pi^2}{ma^2}\right)^2\left(l^2-\frac{\kappa^2}{4}\right)^2+\left|V_{l,-l}\right|^2} \\ &= \frac{2\hbar^2\pi^2}{ma^2}\left(l^2+\frac{\kappa^2}{4}\right)\pm\sqrt{\left(\frac{2\hbar^2\pi^2}{ma^2}\right)^2 l^2\kappa^2+\left|V_{l,-l}\right|^2} \\ &\approx \frac{2\hbar^2\pi^2}{ma^2}\left(l^2+\frac{\kappa^2}{4}\right)\pm\left(\left|V_{l,-l}\right|+\left(\frac{2\hbar^2\pi^2}{ma^2}\right)^2\frac{l^2}{2\left|V_{l,-l}\right|}\kappa^2\right) \\ &\approx \varepsilon^0_l(0)\pm\left|V_{l,-l}\right|\pm\kappa^2\left(\frac{2\hbar^2\pi^2}{ma^2}\right)^2\frac{l^2}{2\left|V_{l,-l}\right|}\end{aligned} \tag{45}$$

$$\underline{\varepsilon_l(0)=\varepsilon^0_l(0)+V_{00}\pm\left|V_{l,-l}\right|} \tag{46}$$

$\kappa \simeq \pm 1$

$$\kappa=\pm(1-\kappa') \quad \kappa'\simeq +0 \tag{47}$$

$$\psi^0_l(\kappa;x)=\frac{1}{\sqrt{L}}e^{i\pi(2l\pm1\mp\kappa')x/a} \quad \psi^0_{-l\mp1}(\kappa;x)=\frac{1}{\sqrt{L}}e^{i\pi(-2l\mp1\mp\kappa')x/a} \tag{48}$$

$$\det\begin{pmatrix} \frac{2\hbar^2\pi^2}{ma^2}\left(l\pm\frac{1}{2}\mp\frac{\kappa'}{2}\right)^2-\overline{\varepsilon}_l(\kappa) & V_{l,-l\mp1} \\ V^*_{l,-l\mp1} & \frac{2\hbar^2\pi^2}{ma^2}\left(l\pm\frac{1}{2}\pm\frac{\kappa'}{2}\right)^2-\overline{\varepsilon}_l(\kappa) \end{pmatrix}=0 \tag{49}$$

$$\underline{\varepsilon_l(\pm1)=\frac{2\hbar^2\pi^2}{ma^2}\left(l\pm\frac{1}{2}\right)^2+V_{00}\pm\left|V_{l,-l\mp1}\right|} \tag{50}$$

4 Band structure in a simple cubic lattice

$$\mathbf{a}_1=a(1,0,0) \quad \mathbf{a}_2=a(0,1,0) \quad \mathbf{a}_3=a(0,0,1) \tag{51}$$

$$\mathbf{b}_1=\frac{2\pi}{a}(1,0,0) \quad \mathbf{b}_2=\frac{2\pi}{a}(0,1,0) \quad \mathbf{b}_3=\frac{2\pi}{a}(0,0,1) \tag{52}$$

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

$$\Gamma=(0,0,0) \quad X=\frac{\pi}{a}(0,0,1) \tag{53}$$

$$\mathbf{k}=\frac{\pi}{a}(0,0,\kappa) \quad 0\le\kappa\le1 \tag{54}$$

4.1 Empty lattice bandstructure

Free electron bands in a crystal are specified by the reciprocal vectors **K:**

$$\varphi_{\mathbf{K},\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \qquad (\mathbf{k} \in BZ) \tag{55}$$

$$\int \varphi_{\mathbf{K},\mathbf{k}}(\mathbf{r})^* \varphi_{\mathbf{K}',\mathbf{k}'}(\mathbf{r})\, d^3r = \delta_{\mathbf{k}+\mathbf{K},\mathbf{k}'+\mathbf{K}'} = \delta_{\mathbf{K},\mathbf{K}'}\delta_{\mathbf{k},\mathbf{k}'}$$

$$\varepsilon_{\mathbf{K}}(\mathbf{k}) = \frac{\hbar^2 (\mathbf{k}+\mathbf{K})^2}{2m} \tag{56}$$

In case of sc lattice along the ΓX direction and by defining

$$\varepsilon_0 = \frac{\hbar^2 \pi^2}{2ma^2} \tag{57}$$

Band A generated by $\mathbf{K} = \frac{2\pi}{a}(0,0,0)$

$$\varepsilon_A(\mathbf{k}) = \varepsilon_0 \kappa^2 \tag{58}$$

$$\varphi_A(\mathbf{r}) = e^{i\frac{\pi}{a}\kappa z} \tag{59}$$

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

$$\varepsilon_B(\mathbf{k}) = \varepsilon_0 (\kappa - 2)^2 \tag{60}$$

$$\varphi_B(\mathbf{r}) = e^{i\frac{\pi}{a}(\kappa-2)z} \tag{61}$$

Degeneracy of bands A and B at the X point:

$$\varepsilon_A(\kappa = 1) = \varepsilon_B(\kappa = 1) = \varepsilon_0 \tag{62}$$

Bands D, E, F, G generated by $\mathbf{K} = \frac{2\pi}{a}(\pm 1, 0, 0), \frac{2\pi}{a}(0, \pm 1, 0)$

$$\varepsilon_{D,E,F,G}(\mathbf{k}) = \varepsilon_0 \left(\kappa^2 + 4\right) \tag{63}$$

$$\varphi_D(\mathbf{r}) = e^{i\frac{\pi}{a}(\kappa z+2x)}, \quad \varphi_E(\mathbf{r}) = e^{i\frac{\pi}{a}(\kappa z+2y)}, \quad \varphi_F(\mathbf{r}) = e^{i\frac{\pi}{a}(\kappa z-2x)}, \quad \varphi_G(\mathbf{r}) = e^{i\frac{\pi}{a}(\kappa z-2y)} \tag{64}$$

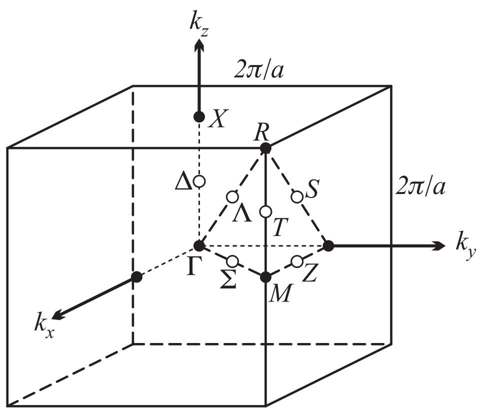

Figure 1: The Brillouin zone of a simple cubic lattice.

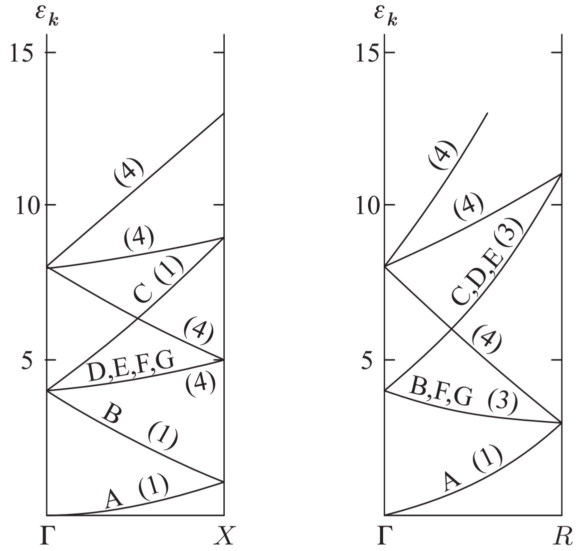

Figure 2: Bandstructure of the empty simple cubic lattice along two directions of the Brillouin zone.

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

$$\varepsilon_C(\mathbf{k}) = \varepsilon_0 (2+\kappa)^2 \tag{65}$$

$$\varphi_C(\mathbf{r}) = e^{i\frac{\pi}{a}(\kappa+2)z} \tag{66}$$

Degeneracy of six bands at the Γ point:

$$\varepsilon_B(0,0,0) = \varepsilon_{D,E,F,G}(0,0,0) = \varepsilon_C(0,0,0) = 4\varepsilon_0 \tag{67}$$

5 Lifting of degeneracies at the Γ point

$B, C \to \mathbf{K} = \frac{2\pi}{a}(0,0,\mp 1)$

$$\varphi_B(\mathbf{r}) = e^{-i\frac{2\pi}{a}z}, \quad \varphi_C(\mathbf{r}) = e^{i\frac{2\pi}{a}z} \tag{68}$$

$D, E, F, G \to \mathbf{K} = \frac{2\pi}{a}(\pm 1,0,0), \frac{2\pi}{a}(0,\pm 1,0)$

$$\varphi_D(\mathbf{r}) = e^{i\frac{2\pi}{a}x}, \quad \varphi_E(\mathbf{r}) = e^{i\frac{2\pi}{a}y}, \quad \varphi_F(\mathbf{r}) = e^{-i\frac{2\pi}{a}x}, \quad \varphi_G(\mathbf{r}) = e^{-i\frac{2\pi}{a}y} \tag{69}$$

$$H_{BB} = H_{CC} = H_{DD} = H_{EE} = H_{FF} = H_{GG} = 4\varepsilon_0 \tag{70}$$

$$\begin{aligned} &H_{BD} = H_{BE} = H_{BF} = H_{BG} = \\ &H_{CD} = H_{CE} = H_{CF} = H_{CG} = \\ &H_{DE} = H_{DG} = H_{EF} = H_{FG} = V_{110} \end{aligned} \tag{71}$$

$$H_{BC} = H_{DF} = H_{EG} = V_{200} \tag{72}$$

$$\omega = 4\varepsilon_0 - \varepsilon \tag{73}$$

Choosing the sequence of states as B, D, E, C, F, G, the Hamiltonian reads as

$$H_\Gamma = \begin{pmatrix} 4\varepsilon_0 & V_{110} & V_{110} & V_{200} & V_{110} & V_{110} \\ V_{110} & 4\varepsilon_0 & V_{110} & V_{100} & V_{200} & V_{100} \\ V_{110} & V_{110} & 4\varepsilon_0 & V_{110} & V_{110} & V_{200} \\ V_{200} & V_{110} & V_{110} & 4\varepsilon_0 & V_{110} & V_{110} \\ V_{110} & V_{200} & V_{110} & V_{110} & 4\varepsilon_0 & V_{110} \\ V_{110} & V_{110} & V_{200} & V_{110} & V_{110} & 4\varepsilon_0 \end{pmatrix} \tag{74}$$

Energy eigenvalues and eigenstates:

$$\varepsilon_1 = 4\varepsilon_0 + V_{200} + 4V_{110} \qquad \left\{ \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \right\} \to \psi_1(\mathbf{r}) = \cos\frac{2\pi}{a}x + \cos\frac{2\pi}{a}y + \cos\frac{2\pi}{a}z$$

$$\varepsilon_2 = 4\varepsilon_0 + V_{200} - 2V_{110} \qquad \left\{ \begin{pmatrix} -1 \\ 1 \\ 0 \\ -1 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} -1 \\ 0 \\ 1 \\ -1 \\ 0 \\ 1 \end{pmatrix} \right\} \to \begin{array}{l} \psi_2^1(\mathbf{r}) = \cos\frac{2\pi}{a}x - \cos\frac{2\pi}{a}z \\ \psi_2^1(\mathbf{r}) = \cos\frac{2\pi}{a}y - \cos\frac{2\pi}{a}z \end{array}$$

$$\varepsilon_3 = 4\varepsilon_0 - V_{200} \qquad \left\{ \begin{pmatrix} -1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ -1 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \right\} \to \begin{array}{l} \psi_3^1(\mathbf{r}) = \sin\frac{2\pi}{a}x \\ \psi_3^2(\mathbf{r}) = \sin\frac{2\pi}{a}y \\ \psi_3^3(\mathbf{r}) = \sin\frac{2\pi}{a}z \end{array}$$

6 Structure of the Hamilton matrix, hybridization

Action of a symmetry operation g:

$$g\left[H_{\mathbf{k}}(\mathbf{r})\, u_{\mathbf{k}}(\mathbf{r})\right] \equiv H_{\mathbf{k}}\left(g^{-1}\mathbf{r}\right) u_{\mathbf{k}}\left(g^{-1}\mathbf{r}\right) = \left[\frac{\left(g^{-1}\mathbf{p} + \hbar\mathbf{k}\right)^2}{2m} + V\left(g^{-1}\mathbf{r}\right)\right] u_{\mathbf{k}}\left(g^{-1}\mathbf{r}\right) \tag{75}$$

$$= \left[\frac{\left(\mathbf{p} + \hbar\, g\mathbf{k}\right)^2}{2m} + V(\mathbf{r})\right] u_{\mathbf{k}}\left(g^{-1}\mathbf{r}\right) = H_{g\mathbf{k}}(\mathbf{r})\; g u_{\mathbf{k}}(\mathbf{r}) \tag{76}$$

consequently,

$$gH_{\mathbf{k}} = H_{g\mathbf{k}}g \tag{77}$$

$$\Downarrow$$

$$gH_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r}) = H_{g\mathbf{k}}(\mathbf{r})\; gu_{\mathbf{k}}(\mathbf{r}) = \varepsilon(\mathbf{k})\, gu_{\mathbf{k}}(\mathbf{r})$$

$$\Downarrow$$

$$\underline{\varepsilon(g\mathbf{k}) = \varepsilon(\mathbf{k})}$$

and for non-degenerate bands,

$$u_{g\mathbf{k}}(\mathbf{r}) = c\, gu_{\mathbf{k}}(\mathbf{r}) = c\, u_{\mathbf{k}}\left(g^{-1}\mathbf{r}\right) \quad (|c| = 1) \tag{78}$$

$$\Downarrow$$

$$\psi_{g\mathbf{k}}(\mathbf{r}) = e^{ig\mathbf{k}\cdot\mathbf{r}} u_{g\mathbf{k}}(\mathbf{r}) = c\, e^{i\mathbf{k}\cdot g^{-1}\mathbf{r}} u_{\mathbf{k}}\left(g^{-1}\mathbf{r}\right) = c\, g\psi_{\mathbf{k}}(\mathbf{r}) \ . \tag{79}$$

For the *little group* of $\mathbf{k}$, $G_{\mathbf{k}} = \{g \in G : g\mathbf{k} = \mathbf{k}\}$

$$gH_{\mathbf{k}}(\mathbf{r}) = H_{\mathbf{k}}(\mathbf{r})\, g \, . \tag{80}$$

Let be $\{\varphi_i^{\mu,k_\mu}\}$ a set of orthonormal functions built up from irreducible subsets, 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:

$$\langle \varphi_i^{\mu,k_\mu} | \varphi_j^{\mu',k'_{\mu'}} \rangle = \delta_{\mu\mu'} \delta_{k_\mu,k'_{\mu'}} \delta_{ij} \tag{81}$$

$$g\, \varphi_i^{\mu,k_\mu} = \sum_{j=1}^{d_\mu} \varphi_j^{\mu,k_\mu} D_{ji}^{\mu}(g) \ . \tag{82}$$

Using the "big orthogonality" lemma,

$$\frac{1}{|G|} \sum_{R\in G} D_{is}^{\mu}(g)^* \, D_{rj}^{\mu'}(g) = \frac{1}{d_\mu} \delta_{\mu\mu'} \delta_{ij} \delta_{sr} \ , \tag{83}$$

the matrixelements of the Hamiltonian can be expressed as follows,

$$\langle \varphi_i^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_j^{\mu',k'_{\mu'}} \rangle = \frac{1}{|G|} \sum_{g\in G} \langle g\, \varphi_i^{\mu,k_\mu} | g\, H_{\mathbf{k}} \varphi_j^{\mu',k'_{\mu'}} \rangle = \frac{1}{|G|} \sum_{g\in G} \langle g\, \varphi_i^{\mu,k_\mu} | H_{\mathbf{k}}\, g\, \varphi_j^{\mu',k'_{\mu'}} \rangle \tag{84}$$

$$= \frac{1}{|G|} \sum_{s=1}^{d_\mu} \sum_{r=1}^{d_{\mu'}} \sum_{g\in G} D_{is}^{\mu}(g)^* \, \langle \varphi_s^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_r^{\mu',k'_{\mu'}} \rangle \, D_{rj}^{\mu'}(g) \tag{85}$$

$$= \delta_{\mu\mu'} \delta_{ij} \frac{1}{d_\mu} \sum_{s=1}^{d_\mu} \langle \varphi_s^{\mu,k_\mu} | H_{\mathbf{k}} \varphi_s^{\mu,k'_\mu} \rangle \ . \tag{86}$$

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, $h_{\mathbf{k}}^{\mu,k_\mu k'_\mu}$,

$$H_{\mathbf{k}} = \sum_{\mu} \sum_{k_\mu, k'_\mu} h_{\mathbf{k}}^{\mu,k_\mu k'_\mu} \sum_{j=1}^{d_\mu} |\varphi_j^{\mu,k_\mu}\rangle \langle \varphi_j^{\mu,k'_\mu}| \ . \tag{87}$$

Because of the hermiticity of $H_{\mathbf{k}}$,

$$h_{\mathbf{k}}^{\mu,k_\mu k'_\mu} = \left(h_{\mathbf{k}}^{\mu,k_\mu k'_\mu}\right)^* \tag{88}$$

and

$$h_{\mathbf{k}}^{\mu,k_\mu k_\mu} \in \mathbb{R} \ . \tag{89}$$

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

$$\varepsilon_{\mathbf{k}}^{\mu} = h_{\mathbf{k}}^{\mu,11} \ . \tag{90}$$

Corollary 2: If the same irrep occurs more than ones ($M_\mu > 1$), than the corresponding eigenvalues are, $\varepsilon^\mu_{\mathbf{k}n}$ $(n = 1, \ldots, M_\mu)$, where n labels the bands related to irrep μ and the eigenfunctions are elements of the direct sum of these irreducible subspaces.

In more details, diagonalizing the $M_\mu \times M_\mu$ matrices, $\underline{\underline{h}}^\mu_{\mathbf{k}} = \{h^{\mu,k_\mu k'_\mu}_{\mathbf{k}}\}$,

$$\underline{\underline{h}}^\mu_{\mathbf{k}}\, \underline{c}^\mu_{\mathbf{k}n} = \varepsilon^\mu_{\mathbf{k}n}\, \underline{c}^\mu_{\mathbf{k}n} \qquad (n = 1, \ldots, M_\mu) \tag{91}$$

$$\underline{c}^\mu_{\mathbf{k}n} = \left(c^{\mu,1}_{\mathbf{k}n}, \ldots, c^{\mu,M_\mu}_{\mathbf{k}n}\right) \ , \ \sum_{k_\mu=1}^{M_\mu} \left|c^{\mu,k_\mu}_{\mathbf{k}n}\right|^2 = 1 \ , \tag{92}$$

we obtain the solution of the eigenproblem of $H_{\mathbf{k}}$,

$$H_{\mathbf{k}}\, u^{\mu,j}_{\mathbf{k}n} = \varepsilon^\mu_{\mathbf{k}n}\, u^{\mu,j}_{\mathbf{k}n} \qquad (j = 1, \ldots, d_\mu) \tag{93}$$

with

$$u^{\mu,j}_{\mathbf{k}n} = \sum_{k_\mu=1}^{M_\mu} c^{\mu,k_\mu}_{\mathbf{k}n}\, \varphi^{\mu,k_\mu}_j \ . \tag{94}$$

The eigenfunctions are linear combinations of basisfunctions corresponding to different subspaces of the same irreps. This can be termed as *hybridization* of orbitals corresponding to the same irrep of the little group of **k**.

7 The C_{4v} point-group

We'd like to derive how the fourfold degenerate energy states along the ΓX line of the Brillouin zone will be split. The little group of these k-points is C^z_{4v}.

It contains 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

(95)

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

(96)

Conjugate class of $g \in G : C(g) = \{g' \in G : \exists\, f \in G \ \rightarrow g' = f\, g\, f^{-1}\}$. $\{E\}$ is always a conjugate class. The C^z_{4v} point group has *5 classes*: $\{E\}, \{C_{2z}\}, \left\{C_{4z}, C_{4z}^{-1}\right\}, \{\sigma_x, \sigma_y\}, \{\sigma_a, \sigma_b\}$

$$\forall\, g \in C^z_{4v} \ \ gC_{2z} = C_{2z}g \tag{97}$$

$$\sigma_y C_{4z}^{-1} \sigma_y = C_{4z} \tag{98}$$

$$C_{4z}\sigma_y C_{4z}^{-1} = \sigma_x \tag{99}$$

$$C_{4z}\sigma_a C_{4z}^{-1} = \sigma_b \ . \tag{100}$$

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

$$\sum_{\mu=1}^{r} d_\mu^2 = |G| \tag{101}$$

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

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

$$\sum_{g \in G} \chi^{(\mu)}(g)^* \chi^{(\nu)}(g) = |G| \; \delta_{\mu\nu} \tag{102}$$

or if the class i has n_i elements:

$$\sum_{i=1}^{r} n_i \, \chi_i^{(\mu)*} \chi_i^{(\nu)} = |G| \; \delta_{\mu\nu} \, . \tag{103}$$

Furthermore

$$\sum_{\mu=1}^{r} \chi_i^{(\mu)*} \chi_j^{(\mu)} = \frac{|G|}{n_i} \delta_{ij} \tag{104}$$

$$\Downarrow$$

	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

(105)

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

(106)

Comparing with the character 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.

7.1 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,

$$1, z, 2z^2 - x^2 - y^2 \rightarrow \Delta_1 \tag{107}$$

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

$$D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad D(C_{4z}) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad D\left(C_{4z}^{-1}\right) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad D(C_{2z}) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \tag{108}$$

$$D(\sigma_y) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad D(\sigma_x) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad D(\sigma_a) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \quad D(\sigma_b) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{109}$$

which are the matrices of the Δ_5 irrep, thus:

$$\{x, y\}, \{zx, zy\} \rightarrow \Delta_5 \tag{110}$$

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	$-(x^2-y^2)$	$-(x^2-y^2)$	x^2-y^2	x^2-y^2	x^2-y^2	$-(x^2-y^2)$	$-(x^2-y^2)$

(111)

Comparing with the character table, yields

$$xy \rightarrow \Delta_2' \tag{112}$$

$$x^2 - y^2 \rightarrow \Delta_2 \tag{113}$$

7.2 Reduction of a reducible representation

Let us take the representation of the C_{4v}^z point group elements on the basisfunctions,

$$\varphi_D = e^{i\frac{\pi}{a}(\kappa z+2x)}, \quad \varphi_E = e^{i\frac{\pi}{a}(\kappa z+2y)}, \quad \varphi_F = e^{i\frac{\pi}{a}(\kappa z-2x)}, \quad \varphi_G = e^{i\frac{\pi}{a}(\kappa z-2y)} \tag{114}$$

and calculate the corresponding characters:

$$D(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \Longrightarrow \chi(E) = 4 \tag{115}$$

$$D(C_{4z}) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(C_{4z}) = 0 \tag{116}$$

$$D\left(C_{4z}^{-1}\right) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \Longrightarrow \chi\left(C_{4z}^{-1}\right) = 0 \tag{117}$$

$$D(C_{2z}) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(C_{2z}) = 0 \tag{118}$$

$$D(\sigma_y) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(\sigma_y) = 2 \tag{119}$$

$$D(\sigma_x) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \Longrightarrow \chi(\sigma_x) = 2 \tag{120}$$

$$D(\sigma_a) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \Longrightarrow \chi(\sigma_a) = 0 \tag{121}$$

$$D(\sigma_b) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \Longrightarrow \chi(\sigma_b) = 0 \tag{122}$$

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

$$M_\mu = \frac{1}{|G|} \sum_{g \in G} \chi^{(\mu)}(g)^* \chi(g) = \frac{1}{|G|} \sum_{i=1}^{r} n_i \, \chi_i^{(\mu)*} \chi_i \tag{123}$$

$$M_{\Delta_1} = \frac{1}{8}(4 + 2*1*0 + 1*1*0 + 2*1*2 + 2*1*0) = 1 \tag{124}$$

$$M_{\Delta_2} = \frac{1}{8}(4 + 2*2) = 1 \tag{125}$$

$$M_{\Delta_2'} = \frac{1}{8}(4 - 2*2) = 0 \tag{126}$$

$$M_{\Delta_1'} = \frac{1}{8}(4 - 2*2) = 0 \tag{127}$$

$$M_{\Delta_5} = \frac{1}{8}(2*4) = 1 \tag{128}$$

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

Projectors of the irreducible basisfunctions:

$$P_i^{(\mu)} = \frac{d_\mu}{|G|} \sum_{R \in G} D_{ii}^{(\mu)}(g)^* \cdot D(g) \tag{129}$$

$$\Downarrow$$

$$\psi^{(\Delta_1)} = e^{i\frac{\pi}{a}\kappa z} \left(\cos\frac{2\pi x}{a} + \cos\frac{2\pi y}{a} \right) \tag{130}$$

$$\psi^{(\Delta_2)} = e^{i\frac{\pi}{a}\kappa z} \left(\cos\frac{2\pi x}{a} - \cos\frac{2\pi y}{a} \right) \tag{131}$$

$$\psi_1^{(\Delta_5)} = e^{i\frac{\pi}{a}\kappa z} \sin\frac{2\pi x}{a} \tag{132}$$

$$\psi_2^{(\Delta_5)} = e^{i\frac{\pi}{a}\kappa z} \sin\frac{2\pi y}{a} \tag{133}$$

This is exactly that can be obtained in terms of the nearly free electron approach.

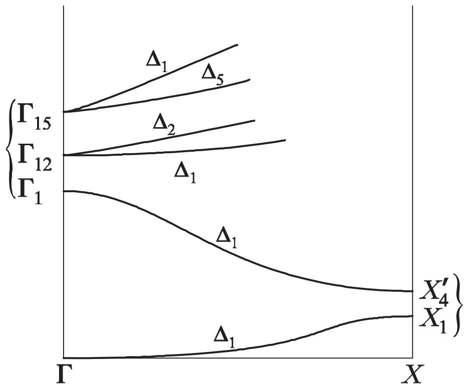

Figure 3: Typical bandstructure of a simple cubic lattice along ΓX.