Lecture 7

Nearly free electrons ⟷ weak potential

Strong interaction but
- Pauli principle
- Screening

Bloch function

$$\psi_k(\bar{r}) = \sum_G C_{\bar{k}-\bar{G}}\, e^{i(\bar{k}-\bar{G})\cdot\bar{r}}$$

with ε, $C_{\bar{k}-\bar{G}}$ given by the central equation

$$\left(\frac{\hbar^2}{2m}(\bar{k}-\bar{G})^2 - \varepsilon\right) C_{\bar{k}-\bar{G}} + \sum_{\bar{G}'} U_{\bar{G}'-\bar{G}}\, C_{\bar{k}-\bar{G}'} = 0$$

define $\varepsilon^0_q = \frac{\hbar^2 q^2}{2m}$

$= 0$ in free el. case

$$U(\bar{r}) = \sum_{\bar{G}} U_{\bar{G}}\, e^{i\bar{G}\cdot\bar{r}}$$ periodic potential

Choise: $U_0 = 0$

$$C_{\bar{k}-\bar{G}} = \frac{\sum_{\bar{G}'} U_{\bar{G}'-\bar{G}}\, C_{\bar{k}-\bar{G}'}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{G}}}$$

NFE:

Small deviations from $\varepsilon = \frac{\hbar^2 k^2}{2m}$

Study case $\bar{k} \approx \frac{\bar{G}_1}{2}$

$$C_{\bar{k}-\bar{G}_1} = \frac{\sum \ldots}{\varepsilon - \frac{\hbar^2}{2m}(\bar{k}-\bar{G}_1)^2}$$ large term

$\varepsilon \approx \frac{\hbar^2 k^2}{2m}$, $\bar{k} \sim \frac{\bar{G}_1}{2}$, $\bar{G}_1 \sim \frac{\bar{G}_1}{2}$

$$C_{\bar{k}} = \frac{\sum \ldots}{\varepsilon - \frac{\hbar^2}{2m}k^2}$$ large term

$$C_{\bar{k}+\bar{G}_1} = \frac{\sum \ldots}{\varepsilon - \frac{\hbar^2}{2m}(\bar{k}+\bar{G}_1)^2}$$ small term ⟶ neglect

all other ⟶ ″ ⟵

Eq :

only term left because $U_0 = 0$

$$\begin{cases} (\varepsilon^0_{\bar{k}-\bar{G}_1} - \varepsilon)\, c_{\bar{k}-\bar{G}_1} + U_{\bar{0}-\bar{G}_1}\, c_{\bar{k}} = 0 \\ (\varepsilon^0_{\bar{k}} - \varepsilon)\, c_{\bar{k}} + U_{\bar{G}_1-\bar{0}}\, c_{\bar{k}-\bar{G}_1} = 0 \end{cases}$$

$$\begin{pmatrix} \varepsilon^0_{\bar{k}-\bar{G}_1} - \varepsilon & U \\ U & \varepsilon^0_{\bar{k}} - \varepsilon \end{pmatrix} \begin{pmatrix} c_{\bar{k}-\bar{G}_1} \\ c_{\bar{k}} \end{pmatrix} = 0$$

cf. (9.24)

$$\begin{vmatrix} \varepsilon^0_{\bar{k}-\bar{G}_1} - \varepsilon & U \\ U & \varepsilon^0_{\bar{k}} - \varepsilon \end{vmatrix} = 0$$

$U_{-\bar{G}_1} = U_{\bar{G}_1} = U$

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crystal with inversion symmetry

$$\varepsilon^0_{\bar{k}-\bar{G}_1}\, \varepsilon^0_{\bar{k}} - \varepsilon\left(\varepsilon^0_{\bar{k}-\bar{G}_1} + \varepsilon^0_{\bar{k}}\right) + \varepsilon^2 - U^2 = 0$$

$$\Longrightarrow \quad \varepsilon = \frac{1}{2}\left(\varepsilon^0_{\bar{k}-\bar{G}} + \varepsilon^0_{\bar{k}}\right) \pm \sqrt{\frac{1}{4}\left(\varepsilon^0_{\bar{k}-\bar{G}} + \varepsilon^0_{\bar{k}}\right)^2 - \frac{4}{4}\left(\varepsilon^0_{\bar{k}-\bar{G}} \cdot \varepsilon^0_{\bar{k}}\right) + U^2}$$

(write $G_1 \to G$)

$(a+b)^2 = a^2 + 2ab + b^2$

$(a-b)^2 = a^2 - 2ab + b^2$

$(a-b)^2 = (a+b)^2 - 4ab$

$$\boxed{\varepsilon = \frac{1}{2}\left(\varepsilon^0_{\bar{k}-\bar{G}} + \varepsilon^0_{\bar{k}}\right) \pm \sqrt{\frac{1}{4}\left(\varepsilon^0_{\bar{k}-\bar{G}} - \varepsilon^0_{\bar{k}}\right)^2 + U^2}}$$

$$\varepsilon^0_{\bar{k}-\bar{G}} = \frac{\hbar^2}{2m}\left(\bar{k}-\bar{G}\right)^2$$

$$\varepsilon^0_{\bar{k}} = \frac{\hbar^2}{2m} k^2$$

At the B.Z. boundary: $\bar{k} = \frac{\bar{G}}{2}$

$$\varepsilon^{\circ}_{\bar{k}-\bar{G}} = \varepsilon^{\circ}_{\bar{k}}$$

$$\Rightarrow \quad \varepsilon_{\pm} = \varepsilon^{\circ}_{\bar{k}} \pm U$$

$$\varepsilon_{+} - \varepsilon_{-} = 2U$$ Energy gap at the B.Z. boundary

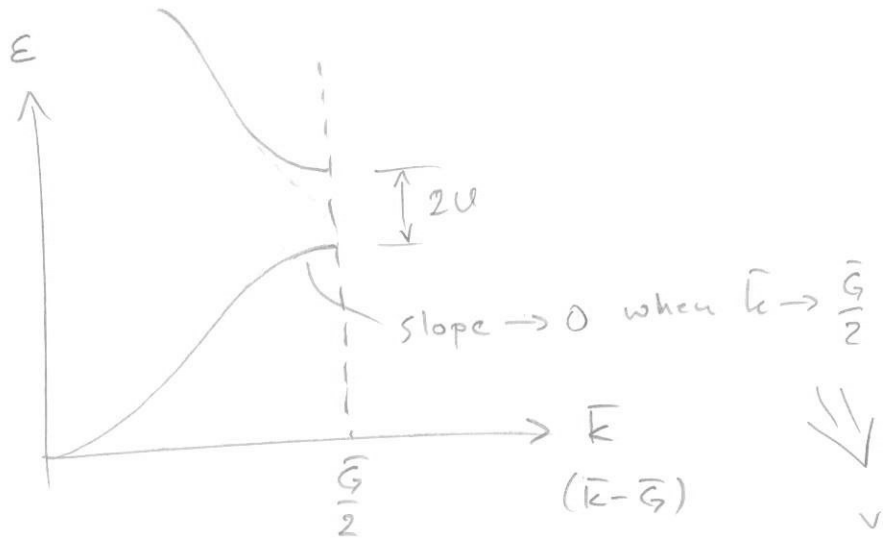
Applies to all zone boundaries

Group velocity at $\bar{k} = \frac{\bar{G}}{2}$:

$$v_g = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k} = \frac{1}{\hbar}\frac{\partial}{\partial k}\left[\frac{1}{2}\left(\varepsilon^{\circ}_{\bar{k}-\bar{G}} + \varepsilon^{\circ}_{\bar{k}}\right) \pm \sqrt{\frac{1}{4}\left(\varepsilon^{\circ}_{\bar{k}-\bar{G}} - \varepsilon^{\circ}_{\bar{k}}\right)^2 + U^2}\right] =$$

$$= \frac{1}{\hbar}\cdot\frac{1}{2}\left[\frac{2\hbar^2(k-G)}{2m} + \frac{2\hbar^2 k}{2m}\right] \pm \frac{\frac{2}{4}\left(\varepsilon^{\circ}_{\bar{k}-\bar{G}} - \varepsilon^{\circ}_{\bar{k}}\right)\cdot\left(\frac{\hbar^2(k-G)}{m} - \frac{\hbar^2 k}{m}\right)}{2\sqrt{\frac{1}{4}(\quad)^2 + U^2}}$$

$$k \to \frac{G}{2}: \quad v_g = \frac{1}{2}\frac{\hbar}{m}\underbrace{\left(-\frac{G}{2} + \frac{G}{2}\right)}_{=0} \pm 0 \quad = 0$$



3D: Constant-energy surfaces @ Bragg plane (BZ boundary) perpendicular to plane

What is the difference between states with ε_+ and ε_- ?

$$\varepsilon_\pm = \varepsilon^\circ_k \pm U$$

NFE: $\psi \approx \psi_{free} = C e^{ikx}$

$\varepsilon \approx \varepsilon_{free} = \frac{\hbar^2 k^2}{2m}$

} except when Bragg reflection occurs, $k = n \cdot \frac{\pi}{a}$

$n = \pm 1, \pm 2, \ldots$

ex. $k = \frac{\pi}{a}$

We then have $e^{i \cdot \frac{\pi}{a} x} \overset{\text{Bragg reflection}}{\rightleftharpoons} e^{-i\frac{\pi}{a}x}$ $\qquad \Delta k = G = \frac{2\pi}{a}$

$$\psi = C_1 e^{i\frac{\pi}{a}x} + C_2 e^{-i\frac{\pi}{a}x}$$

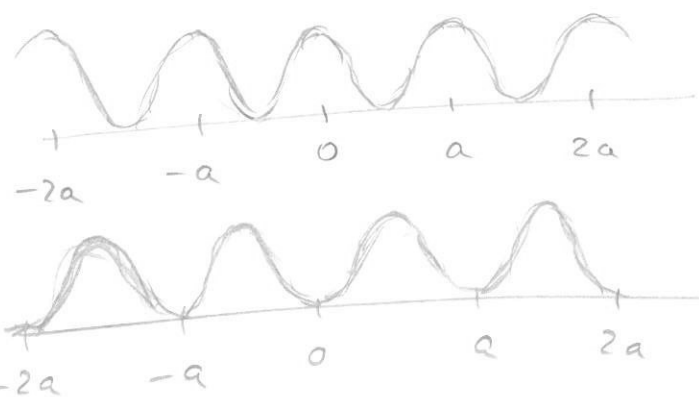
Symmetry: $C_1 = \pm C_2 = C$

$$\psi_+ = C e^{i\frac{\pi}{a}x} + C e^{-i\frac{\pi}{a}x} = 2C \cdot \cos\frac{\pi}{a}x$$

$$\psi_- = C e^{i\frac{\pi}{a}x} - C \cdot e^{-i\frac{\pi}{a}x} = 2iC \sin\frac{\pi}{a}x$$

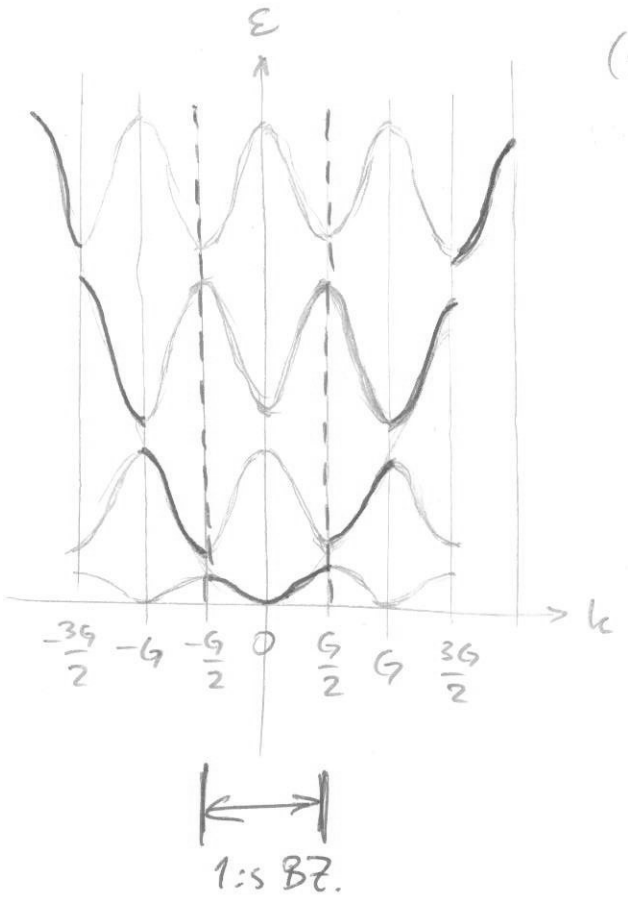
} standing waves

$$-e|\psi|^2 \propto \begin{cases} \cos^2\left(\frac{\pi}{a}x\right) \\ \sin^2\left(\frac{\pi}{a}x\right) \end{cases}$$



Different charge distribution @ ion cores → different pot. energy

⟹ two states with different energy for $k = n\frac{\pi}{a}$

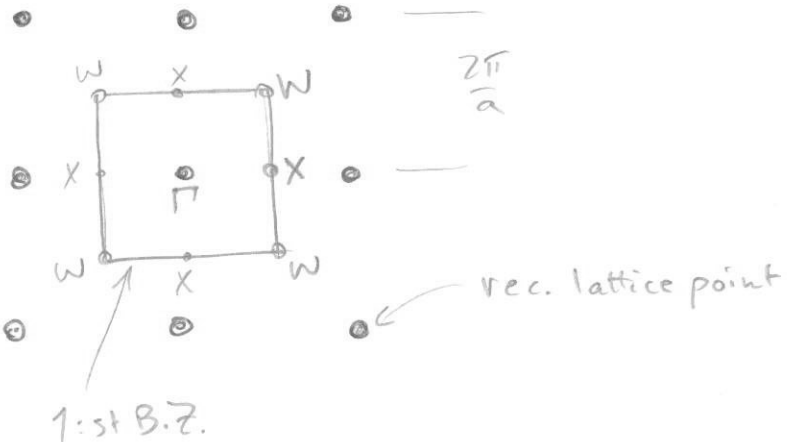


(see p. 160)

Zone schemes

1. Extended zone scheme
   One band in every B.Z.
2. Reduced zone scheme
   All bands in 1:st BZ.
3. Periodic zone scheme
   All bands in all BZ.s.

Symmetry points in 1:st B.Z.:



B.Z. of fcc

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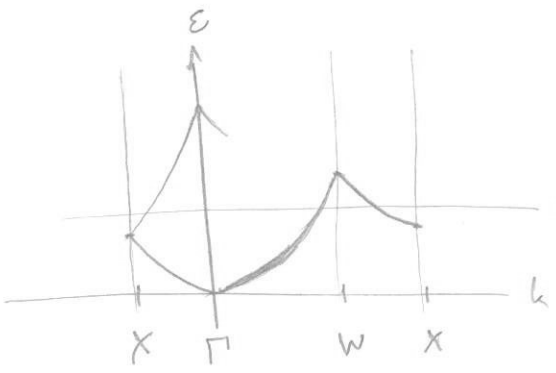
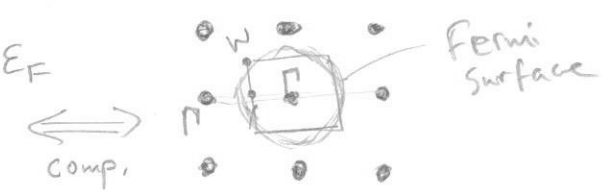
3-dim band structures: slices shown between different points



ex. $\Gamma \rightarrow X \rightarrow W \rightarrow \Gamma$



Geometrical structure factor

We had earlier $S_{\bar{G}} = \sum_j f_j \cdot e^{i\bar{G}\cdot\bar{r}_j}$ sum over cell

and $U(\bar{r}) = \sum_{\bar{G}} U_{\bar{G}} e^{i\bar{G}\cdot\bar{r}}$

The Fourier component $U_{\bar{G}}$ includes $S_{\bar{G}}$ (eq. 9.33)

$\Longrightarrow$ if x-ray diffraction peak vanishes due to cell for some $\bar{G}$, then $U_{\bar{G}}$ vanishes

$\Longrightarrow$ lowest-order splitting of free-el. levels disappears.

Importance of spin-orbit coupling

el in field from $U(\bar{r})$

× Lifting degeneracy of points in k-space of high symmetry

× Increases with atomic number

– Heavy hexagonal metals (hcp)

Tight-binding approximation

Case of overlap of atomic wavefunction being enough to require corrections but not enough to completely destroy atomic description.

- × Partially filled d-shells (transition metals)
- × Insulators

Assume monoatomic crystal $\bar{R}$, one-electron approx.

$U(\bar{r}) = U(\bar{r}+\bar{R})$, Schrödinger $\hat{H}\Psi = \mathcal{E}\Psi$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\bar{r})$$

For free atom, $\bar{R}=0$:

$$\hat{H}_{at}\,\Psi_n(\bar{r}) = \mathcal{E}_n \Psi_n(\bar{r})$$

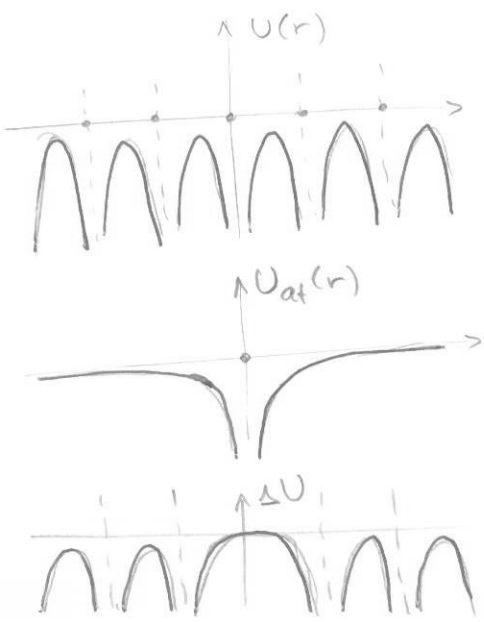
Ψ_n atomic wave function (n ↓ main quantum number)

$$\hat{H}_{at} = -\frac{\hbar^2}{2m}\nabla^2 + U_{at}(\bar{r})$$

(Orthonormal wave functions)

Free atom at other position: $\Psi_n(\bar{r}-\bar{R})$

Write $U(\bar{r}) = U_{at}(\bar{r}) + \Delta U(\bar{r})$



Then we can write

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U_{at}(\bar{r}) + \Delta U(\bar{r})\right]\Psi(\bar{r}) = \mathcal{E}\Psi(\bar{r})$$

i.e.

$$\boxed{\left[H_{at} + \Delta U(\bar{r})\right]\Psi(\bar{r}) = \mathcal{E}\,\Psi(\bar{r})} \qquad (10.2)$$

$$\boxed{\hat{H} = \hat{H}_{at} + \Delta U}$$

We expect wavefunction to be similar to atomic orbital close to any $\bar{R}$ (tight binding approx.) (linear combination)

Thus set

$$\Psi(\bar{r}) = \sum_{\bar{R}} e^{i\bar{k}\cdot\bar{R}} \sum_{n} b_n \Psi_n(\bar{r}-\bar{R})$$

(Ψ_n: linear comb. of atomic orbitals to make Bloch-function)

$$\Psi(\bar{r}+\bar{R}') = e^{i\bar{k}\cdot\bar{R}'}\Psi(\bar{r}) \quad \text{(can be shown easily)}$$

Take Schrödinger and multiply with Ψ_m^*, integrate over space

$$\left[\hat{H}_{at} + \Delta U\right]\Psi = \varepsilon\Psi$$

$$\int \Psi_m^*(\bar{r})\left[\hat{H}_{at} + \Delta U(\bar{r})\right]\Psi(\bar{r})\,d\bar{r} = \int \Psi_m^*(\bar{r})\,\varepsilon\,\Psi(\bar{r})\,d\bar{r}$$

but $\int \Psi_m^* \hat{H}_{at}\Psi\,d\bar{r} = \int (\hat{H}_{at}\Psi_m)^*\Psi\,d\bar{r} = \varepsilon_m \int \Psi_m^*\Psi\,d\bar{r}$

($\hat{H}_{at}$: hermitian)

$$\Rightarrow (\varepsilon_m - \varepsilon)\int \Psi_m^*\Psi\,d\bar{r} + \int \Psi_m^*\,\Delta U\,\Psi\,d\bar{r} = 0$$

$$\boxed{\varepsilon = \varepsilon_m + \frac{\int \Psi_m^*\,\Delta U\,\Psi\,d\bar{r}}{\int \Psi_m^*\Psi\,d\bar{r}}} \quad (10.10)$$

Insert $\Psi(\bar{r})$ and use orthonormality:

$$\int \Psi_m^*(\bar{r})\,\Psi_n(\bar{r})\,d\bar{r} = \delta_{nm}$$

$\Rightarrow$ Equation for $b_n(\bar{k})$ and $\varepsilon(\bar{k})$

$\Psi_n(\bar{r})$ short range $\longrightarrow$ retain only nearest-neighbor terms in sums over $\bar{R}$

Non-degenerate case

s-orbital ψ_0 with energy ε_s

$$\psi(\bar{r}) = \sum_{\bar{R}} e^{i\bar{k}\cdot\bar{R}}\,\psi_0(\bar{r}-\bar{R})$$

gives s-band. Insert $\psi(\bar{r})$

$$\varepsilon = \varepsilon_s + \frac{\int \psi_0^* \Delta U \psi\, d\bar{r}}{\int \psi_0^* \psi\, d\bar{r}} = \varepsilon_s + \frac{\int \psi_0^*(\bar{r})\,\Delta U(\bar{r}) \sum_R e^{i\bar{k}\cdot\bar{R}}\psi_0(\bar{r}-\bar{R})\,d\bar{r}}{\int \psi_0^*(\bar{r}) \sum_R e^{i\bar{k}\cdot\bar{R}}\psi_0(\bar{r}-\bar{R})\,d\bar{r}}$$

ε_s may be different if $\psi_m \neq \psi_0$

$-\beta$ $\qquad\qquad$ $-\gamma(\bar{R})$

$$= \varepsilon_s + \frac{\int \psi_0^*(\bar{r})\,\Delta U\,\psi_0(\bar{r})\,d\bar{r} + \sum_{R\neq 0} e^{i\bar{k}\cdot\bar{R}} \int \psi_0^*(\bar{r})\,\Delta U\,\psi_0(\bar{r}-\bar{R})\,d\bar{r}}{1 + \sum_{R\neq 0} e^{i\bar{k}\cdot\bar{R}} \underbrace{\int \psi_0^*(\bar{r})\,\psi_0(\bar{r}-\bar{R})\,d\bar{r}}_{\alpha(\bar{R})}}$$

$$\boxed{\varepsilon(\bar{k}) = \varepsilon_s - \frac{\beta + \sum_{R\neq 0} e^{i\bar{k}\cdot\bar{R}}\gamma(\bar{R})}{1 + \sum_{R\neq 0} e^{i\bar{k}\cdot\bar{R}}\alpha(\bar{R})}} \quad \text{s-band}$$

often used approx.

- ⊛ $1 + \sum_{R\neq 0} e^{i\bar{k}\cdot\bar{R}}\alpha(\bar{R}) \approx 1$ ← small overlap integrals
- ⊛ $\gamma(\bar{R}) \neq 0$ only for nearest neighbors

$$\Longrightarrow \quad \boxed{\varepsilon(\bar{k}) = \varepsilon_s - \beta - \sum_{\substack{\text{nearest}\\ \text{neighbors}}} e^{i\bar{k}\cdot\bar{R}}\,\gamma_{n.n}}$$

bandwidth/spread proportional to this overlap integral

Small overlap ⇓ Narrow bands

Degenerate case

ex. 3 p-states ψ_m^l

$$\psi(\bar{r}) = \sum_{\bar{R}} e^{i\bar{k}\cdot\bar{R}} \left\{ b_{-1}\,\psi_{-1}'(\bar{r}-\bar{R}) + b_0\,\psi_0'(\bar{r}-\bar{R}) + b_1\,\psi_1'(\bar{r}-\bar{R}) \right\}$$

$\Longrightarrow$ 3 p-band $\varepsilon(\bar{k})$ with different b_m for different $\bar{k}$.

b_m / $-1, 0, +1$