Electrons in a weak periodic potential

We solve

$$\left(-\frac{\nabla^2}{2m} + U(\bar{r})\right)\psi(\bar{r}) = \varepsilon\,\psi(\bar{r})$$

$$U(\bar{r}+\bar{R}) = U(\bar{r})$$

with the boundary conditions $\psi(\bar{r}+N_i\bar{a}_i) = \psi(\bar{r})$

We can expand

$$\psi(r) = \sum_q C_q\, e^{i\bar{q}\bar{r}} \qquad \text{with} \quad q = \sum_i \frac{m_i}{N_i}\vec{b}_i$$

From the periodicity of $U(r)$

$$U(r) = \sum_{\vec{K}} U_{\vec{K}}\, e^{i\vec{K}\vec{r}}$$

$\vec{K}$ - vector of the reciprocal lattice

$$U_{\bar{K}} = \frac{1}{v}\int_{\substack{\text{prim}\\ \text{cell}}} d^3r\, e^{-i\bar{K}\bar{r}}\, U(\bar{r})$$

We choose $U_0 = 0$ and we have $U_{-K} = U_K^*$

The kinetic energy

$$\frac{\hat{p}^2}{2m}\psi = -\frac{\nabla^2}{2m}\psi = \sum \frac{q^2}{2m} C_q\, e^{i\bar{q}\bar{r}}$$

The term in the potential energy

$$U\psi = \left(\sum_k U_k e^{ikr}\right)\left(\sum_q c_q e^{iqr}\right) =$$

$$= \sum_{kq} U_k c_q e^{i(k+q)r} = \sum_{kq'} U_k c_{q'-k} e^{iq'r}$$

$$\sum_q e^{iqr} \left\{ \left(\frac{1}{2m} q^2 - \varepsilon\right) c_q + \sum_{K'} U_{K'} c_{q-K'} \right\} = 0$$

The plane waves in (II) are orthogonal, so

$$\left(\frac{1}{2m} q^2 - \varepsilon\right) c_q + \sum U_{K'} c_{q-K'} = 0$$

$$q \overset{\text{def}}{=} k - \underline{K} \quad , \underline{K'} \to \underline{K'} - \underline{K}$$

$$q - K' \to k - K - (K' - K) = k - K'$$

$$\boxed{\left[\frac{1}{2m} (\vec{k} - \vec{K})^2 - \varepsilon\right] c_{k-K} + \sum_{K'} U_{K'-K} c_{k-K'} = 0}$$

Summation over recip. lat vectors $\vec{K'}$. For fixed $\vec{k}$ there is an eq. for any $\vec{K}$.

The infinitely many solutions for each $\vec{k}$ are labeled with the band index n

$\vec{k}$ is in the first Brillouin zone.

In the free electron case

$$(\varepsilon^0_{k-K} - \varepsilon)\, C_{k-K} = 0$$

$$\varepsilon^0_q = \frac{1}{2m} q^2$$

So either $\varepsilon = \varepsilon^0_{k-K}$ or $C_{k-K} = 0$, so

$\varepsilon = \varepsilon_{k-K}$ $\quad \psi_k \propto e^{i(k-K)r}$

(when there is no degeneracies).

Now consider a small U. Fix k, K_1

and assume that for all other $K \neq K_1$

$$| \varepsilon^0_{k-K_1} - \varepsilon^0_{k-K} | \gg U$$

Then

$$[\varepsilon - \varepsilon^0_{k-K_1}]\, C_{k-K_1} = \sum_{K \neq K_1} U_{K-K_1} C_{k-K}$$

$$C_{k-K} = \frac{U_{K_1-K} C_{k-K_1}}{\varepsilon - \varepsilon^0_{k-K}} + \sum_{K' \neq K_1} \frac{U_{K'-K} C_{k-K'}}{\varepsilon - \varepsilon^0_{k-K}}$$

$$= \frac{U_{K_1-K} C_{k-K_1}}{\varepsilon - \varepsilon^0_{k-K}} + O(U^2)$$

$$\left(\varepsilon - \varepsilon^{0}_{k-K_1}\right) C_{k-K_1} = \sum_{K} \frac{U_{K-K_1} U_{K_1-K}}{\varepsilon - \varepsilon^{0}_{k-K}} C_{k-K_1} + O(U^3)$$

$$\boxed{\varepsilon = \varepsilon^{0}_{k-K_1} + \sum_{K} \frac{|U_{K-K_1}|^2}{\varepsilon^{0}_{k-K_1} - \varepsilon^{0}_{k-K}} + O(U^3)}$$

Weakly perturbed non-degenerate levels weakly repel each other (lower levels push ε_{k-K_1} up and higher levels push it down)

Suppose the value of $\vec{k}$ is such that there are recip. lat. vec $K_1, \dots K_m$ such that

$\varepsilon_{k-K_1}, \dots, \varepsilon_{k-K_m}$ are all within U of each other but far apart from the other ε^{0}_{k-K} on the scale of U. In this case we must use a degenerate perturb. theory. Consider the case when only two levels are within U of each other

$$\left(\varepsilon - \varepsilon^{0}_{k-K_1}\right) C_{k-K_1} = U_{K_2-K_1} C_{k-K_2}$$

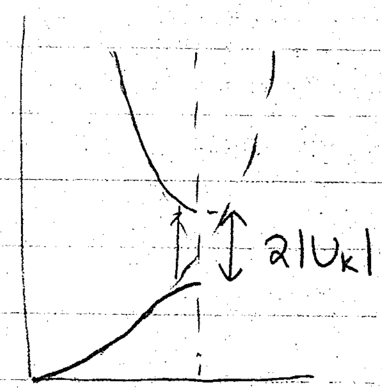
$$\left(\varepsilon - \varepsilon^{0}_{k-K_2}\right) C_{k-K_2} = U_{K_1-K_2} C_{k-K_1}$$

$$q = k - K_1 \qquad K = K_2 - K_1$$

$$\begin{cases} (\varepsilon - \varepsilon_q^0)\, c_q = U_K\, c_{q-K} \\ (\varepsilon - \varepsilon_{q-K}^0)\, c_{q-K} = U_K^*\, c_q \end{cases}$$

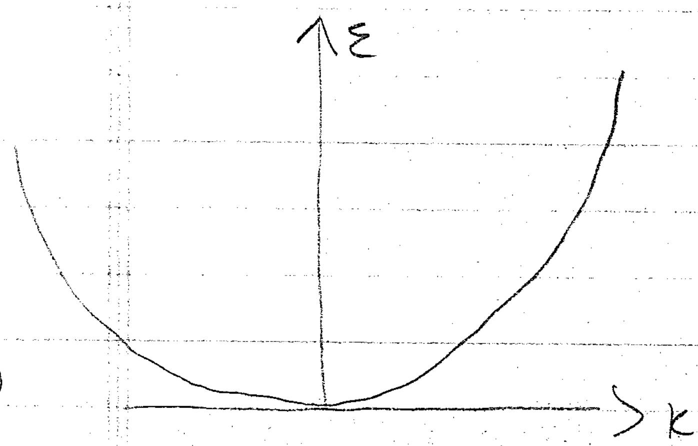
$$\begin{vmatrix} \varepsilon - \varepsilon_q^0 & -U_k \\ -U_k^* & \varepsilon - \varepsilon_{q-k}^0 \end{vmatrix} = 0$$

$$\varepsilon = \frac{1}{2}\left(\varepsilon_q^0 + \varepsilon_{q-K}^0\right) \pm \left[\left(\frac{\varepsilon_q^0 - \varepsilon_{q-K}}{2}\right)^2 + |U_K|^2\right]^{1/2}$$



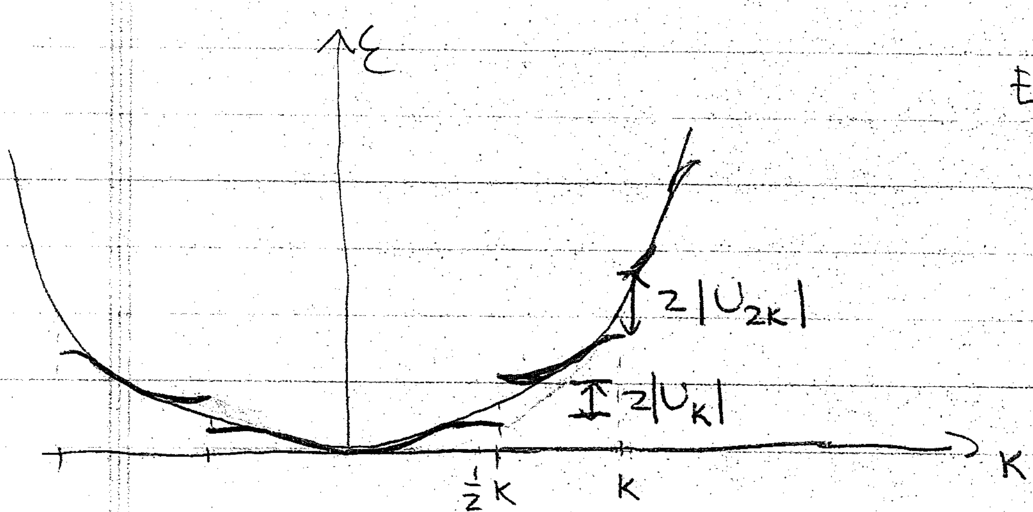
Construction of the band structure in 1d for a weak potential

(a)



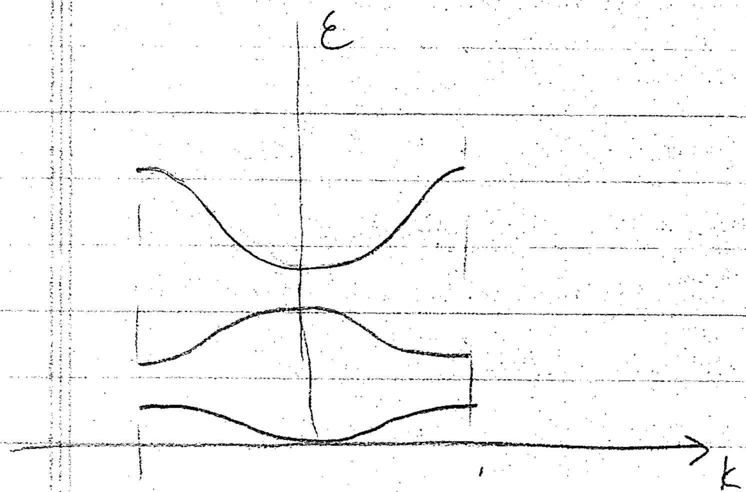
Free electron dispersion

(b)

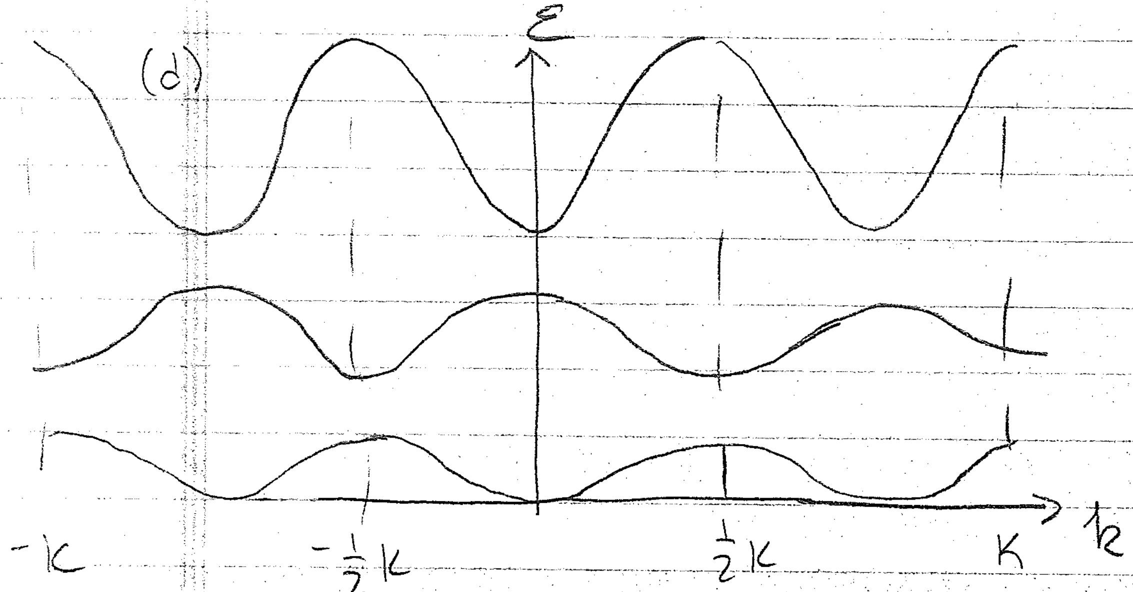


Extended zone scheme

(c)



Reduced zone scheme



Repeated zone scheme