Karlsruhe Institute of Technology
Institute for Theoretical Condensed Matter physics

Condensed Matter Theory I WS 2022/2023

Prof. Dr. A. Shnirman
Dr. D. Shapiro, Dr. H. Perrin

Solutions to sheet 3
Tutorial: 17.11.2020

Category A

1. Nearly free electrons (10 + 10 = 20 points)

The one-dimensional Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\cos^2\left(\frac{\pi x}{a}\right).$$

describes electrons in a periodic $\cos^2$-shaped potential with lattice constant a. We assume in this task that the strength U of the potential is sufficiently small to be treated perturbatively, i.e., within the approximation of nearly free electrons which was discussed in the lecture. We will now derive the band structure $E_{n,k}$ of this model.

(a) Perform perturbation theory to second order for crystal momenta at which the unperturbed solutions are non-degenerate.

(b) Now calculate the leading-order corrections to the electron energies at the degeneracy points in reciprocal space. Draw a sketch of the entire band structure.

Solution:

(a) The Schrödinger equation can be written in Fourier space in the form of Eq. (55) in the lecture notes, whereby the simple potential in this task has only three non-zero Fourier coefficients: $U_{G=0} = \frac{U}{2}$, $U_{G=2\pi/a} = U_{G=-2\pi/a} = \frac{U}{4}$. The Schrödinger equation now reads

$$\begin{aligned} E_k c_{k+G} &= \frac{\hbar^2(k+G)^2}{2m}c_{k+G} + \sum_{G'} U_{G-G'}c_{k+G'} \\ &= \frac{\hbar^2(k+G)^2}{2m}c_{k+G} + \frac{U}{2}\left(c_{k+G} + \frac{1}{2}c_{k+G-2\pi/a} + \frac{1}{2}c_{k+G+2\pi/a}\right) \end{aligned}$$

where we have suppressed the band index n for brevity. In the plane-wave basis, the reciprocal space states $|k\rangle$ with the components $c_k = c_{k+2j\pi/a}$. Then the Hamiltonian has the matrix elements

$$H_{jj'}(k) = \frac{\hbar^2(k+2j\pi/a)^2}{2m}\delta_{j,j'} + \frac{U}{2}\left(\delta_{j,j'} + \frac{1}{2}\delta_{j,j'-1} + \frac{1}{2}\delta_{j,j'+1}\right).$$

Now we call the first term H^0 (free Hamiltonian) and the rest $\tilde{H}$ (perturbation) to rewrite the Schrödinger equation in a way susceptible to standard perturbation theory,

$$\left[H^0(k) + \tilde{H}\right]|k\rangle = E_k\,|k\rangle$$

for all $k \in$ 1st BZ. The free solutions are obviously

$$E^0_{n,k} = \frac{\hbar^2(k + 2n\pi/a)^2}{2m}$$

(now including the band index n again), where the plane-wave basis states are already proper eigenstates $|n, k\rangle_0$. The free-electron bands have degeneracies at the Bragg planes $k \in \frac{\pi}{a}\mathbb{Z}$ and are non-degenerate otherwise. Here we calculate the energy corrections in the latter case. We will return to degeneracies in (b).

First-order corrections:

$$E^1_{n,k} = \langle n, k|_0 \, \tilde{H} \, |n, k\rangle_0 = \tilde{H}_{n,n} = \frac{U}{2} \, . \tag{1}$$

This is the expected shift of the spectrum by $U_0 = U/2$, which equals the mean value of the potential. We could remove this term by changing our energy scale.

Second-order corrections:

$$\begin{aligned} E^2_{n,k} &= \sum_{m \neq n} \frac{\left|\langle m, k|_0 \, H^1 \, |n, k\rangle^0\right|^2}{E^0_{n,k} - E^0_{m,k}} = \sum_{m=n\pm1} \frac{\left|H^1_{m,n}\right|^2}{E^0_{n,k} - E^0_{m,k}} \\ &= \frac{U^2}{16} \left(\frac{1}{E^0_{n,k} - E^0_{n-1,k}} + \frac{1}{E^0_{n,k} - E^0_{n+1,k}} \right) = \frac{U^2 m a^2}{16\hbar^2} \frac{1}{(ak + 2\pi n)^2 - \pi^2} \end{aligned}$$

In total, we obtain the energy

$$E_{n,k} = \frac{\hbar^2}{2m}(k + G_n)^2 + \frac{U}{2} + \frac{U^2 m a^2}{16\hbar^2} \frac{1}{(ak + 2\pi n)^2 - \pi^2} + \mathcal{O}\left(U^3\right) \, .$$

(b) Let $k = j\pi/a$. Then the unperturbed bands $E^0_{n,k}$ and $E^0_{m,k}$ are degenerate if $d =: n - m = 2n + j$ (only two-fold degeneracy is possible). We have to diagonalize H in the degenerate subspace. If $|d| \geq 2$, $\tilde{H}$ does not contribute, such that H is already diagonal. In this case, the corrections are the same as in the non-degenerate case and the degeneracy persists under the perturbation (which is a peculiarity of this specific potential). Now consider $d = \pm 1$. The Hamiltonian in the two-dimensional subspace of energy $E^0_{n,k} = E^0_{n\pm1,k}$ has the matrix form

$$H^0 + \tilde{H} = \begin{pmatrix} E^0_{n,k} + \frac{U}{2} & \frac{U}{4} \\ \frac{U}{4} & E^0_{n,k} + \frac{U}{2} \end{pmatrix}$$

with the eigenvalues

$$E_{1,2} = E^0_{n,k} + \frac{U}{2} \pm \frac{|U|}{4} \, .$$

Thus, at $k = j\pi/a$ with odd j the energetically lowest degeneracy at

$$E^0 = \frac{\hbar^2 \pi^2}{2ma^2}$$

is lifted and the band gap is $\Delta = |U|/2$. A sketch of the overall band structure (extended zone scheme) is shown in Fig. 1.

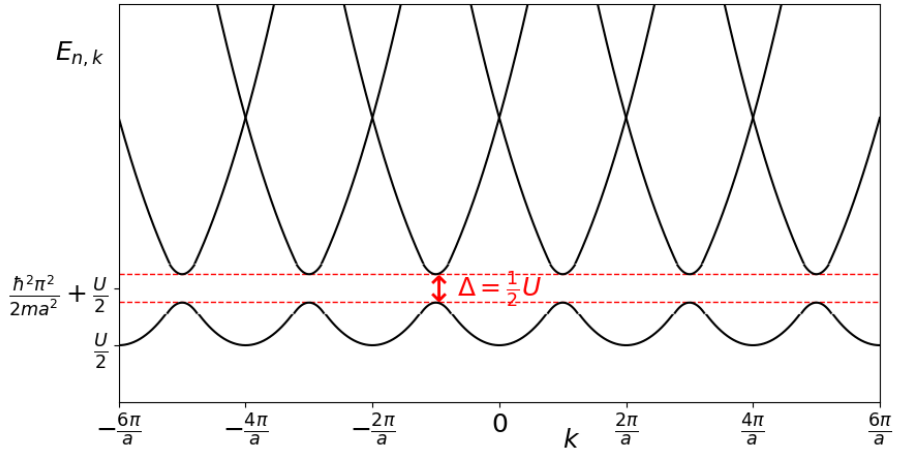

Figure 1: Qualitative sketch of the band structure for nearly free electrons in the $\cos^2$ potential.

Category B

2. $\vec{\mathbf{k}} \cdot \vec{\mathbf{p}}$-Method (10 + 10 = 20 points)

We derived the following Schrödinger equation in the lecture,

$$\left(E_k - \frac{\hbar^2(\vec{k} - i\vec{\nabla})^2}{2m} \right) u_{\vec{k}}(\vec{r}) = U(\vec{r}) u_{\vec{k}}(\vec{r}) \ .$$

Here, $u_{\vec{k}}(\vec{r})$ is the periodic part of the Bloch wave function, $\psi_k(\vec{r}) = u_k(\vec{r}) e^{i\vec{k}\vec{r}}$. The periodic crystal potential is $U(\vec{r}) = U(\vec{r} + \vec{R})$, m is the mass of an electron, and $\vec{k}$ is the quasi-momentum (wave vector) in the first Brillouin zone. We assume that this equation has been solved for a certain quasi-momentum $\vec{k}_0$, i.e., all eigenstates $u_{n,\vec{k}_0}(\vec{r})$ and all eigenenergies $E_{n,\vec{k}_0}$ are known (n is the band index).

We will calculate now the eigenenergies and eigenstates for a state with quasi-momentum $\vec{k} = \vec{k}_0 + \delta\vec{k}$ where $\delta\vec{k}$ is small. Using perturbation theory and assuming no degeneracy at $\vec{k}_0$, calculate:

(a) the group velocity in the band n at the quasi-momentum $\vec{k}_0$;
(b) the effective mass tensor in the band n at the quasi-momentum $\vec{k}_0$.

Solution:

Let us rewrite the Schrödinger equation such that:

$$(H_0 + V_1 + V_2) u_k = E_k u_k,$$

$$\text{with } H_0 = \frac{(\boldsymbol{p} - \boldsymbol{k}_0)^2}{2m} + U(\boldsymbol{r}),\ V_1 = \frac{\delta\boldsymbol{k} \cdot (\boldsymbol{p} + \boldsymbol{k}_0)}{m},\ V_2 = \frac{(\delta\boldsymbol{k})^2}{2m}$$

using $\boldsymbol{p} \equiv -i\hbar\boldsymbol{\nabla}$ und $\delta\boldsymbol{k} \equiv \boldsymbol{k} - \boldsymbol{k}_0$. We suppose that all eigen-functions and energies are known at $\boldsymbol{k}_0$.

$$H_0 u_{n,k_0} = E_{n,k_0} u_{n,k_0}.$$

We have seen in the lecture notes that the bloch states form a complete orthgonal basis states:

$$\int d^3r\, \psi^*_{n_1,k_1}(\boldsymbol{r})\psi_{n_2,k_2}(\boldsymbol{r}) = V\delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}\,\delta_{n_1,n_2},$$

where V the volume of the whole crystal. It follows for the u-functions:

$$\int d^3r\, u^*_{n_1,k_1}(\boldsymbol{r})u_{n_2,k_2}(\boldsymbol{r}) = V\delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}\,\delta_{n_1,n_2},$$

or

$$\int_{E.C.} d^3r\, u^*_{n_1,k_1}(\boldsymbol{r})u_{n_2,k_2}(\boldsymbol{r}) = v\delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}\,\delta_{n_1,n_2},$$

where v is the volume of an elementary cell (E.C.) ist. We should renormalized the u-function such that:

$$\int_{E.C.} d^3r\, u^*_{n_1,k_1}(\boldsymbol{r})u_{n_2,k_2}(\boldsymbol{r}) = \langle u_{n_1,k_1}|u_{n_2,k_2}\rangle = \delta_{\boldsymbol{k}_1,\boldsymbol{k}_2}\,\delta_{n_1,n_2},$$

The energie correction at first order in $\delta\boldsymbol{k}$ is only corrected by the V_1 potential

$$\delta E^{(1)}_n = \langle u_{n,k_0}|V_1|u_{n,k_0}\rangle = \frac{\delta\boldsymbol{k}}{m}\cdot\langle u_{n,k_0}|\boldsymbol{p}+\boldsymbol{k}_0|u_{n,k_0}\rangle.$$

Therefore, we obtain for the group velocity:

$$\boldsymbol{v}_g = \frac{1}{m}\left[\langle u_{n,k_0}|\boldsymbol{p}|u_{n,k_0}\rangle + \boldsymbol{k}_0\right].$$

The second order correction of the energie in $\delta\boldsymbol{k}$ should have one contribution from the potential V_1 up to the second order of the perturbation theory and another contribution from the potential V_2 at first order of the perturbation theory coming (because it is quadratic in $\delta\boldsymbol{k}$):

$$\delta E^{(2)}_n = \frac{1}{m^2}\sum_{n_1\neq n}\frac{\delta k^\alpha\delta k^\beta\langle u_{n,k_0}|p^\alpha+k_0^\alpha|u_{n_1,k_0}\rangle\langle u_{n_1,k_0}|p^\beta+k_0^\beta|u_{n,k_0}\rangle}{E_{n,k_0}-E_{n_1,k_0}} + \frac{(\delta\boldsymbol{k})^2}{2m}.$$

Therefore we obtain for the mass tensor:

$$\left(m^{*-1}\right)_{\alpha,\beta} = \frac{1}{m^2}\sum_{n_1\neq n}\frac{\langle u_{n,k_0}|p^\alpha+k_0^\alpha|u_{n_1,k_0}\rangle\langle u_{n_1,k_0}|p^\beta+k_0^\beta|u_{n,k_0}\rangle}{E_{n,k_0}-E_{n_1,k_0}} + \frac{1}{m}\delta_{\alpha,\beta}.$$

3. Wannier functions (10 points)

The Wannier functions $w_n(\vec{r})$ are given by

$$w_n(\vec{r}) = V_{\rm uc}\int_{1.\rm BZ}\frac{d^3k}{(2\pi)^3}\psi_{n,\vec{k}}(\vec{r})\,,$$

where $\psi_{n,\vec{k}}(\vec{r})$ are Bloch states and $V_{\rm uc}$ is the volume of the unit cell. Show that the Wannier functions $\{w_n(\vec{r}-\vec{R}),\ n=1,2,3,\ldots,\ \vec{R}\in$ Bravais lattice$\}$ form a complete orthonormal system.

Solution: We use that the Bloch functions are a complete orthonormal system.

$$\begin{aligned}
\int d^3r\, w_n^*(\vec{r}-\vec{R})w_{n'}(\vec{r}-\vec{R}') &= V_{\rm uc}^2 \int d^3r \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3}\, \psi^*_{n,\vec{k}}(\vec{r}-\vec{R})\psi_{n',\vec{k}'}(\vec{r}-\vec{R}') \\
&= V_{\rm uc}^2 \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} \underbrace{\int d^3r\, \psi^*_{n,\vec{k}}(\vec{r})\psi_{n',\vec{k}'}(\vec{r})}_{(2\pi)^3\delta_{\vec{k},\vec{k}'}\delta_{n,n'}} e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}'\cdot R'} \\
&= V_{\rm uc}^2 \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\delta_{n,n'} \\
&= V_{\rm uc}\delta_{n,n'}\delta_{\vec{R},\vec{R}'}
\end{aligned}$$

$$\begin{aligned}
\sum_{n,\vec{R}} w_n^*(\vec{r}-\vec{R})w_n(\vec{r}'-\vec{R}) &= V_{\rm uc}^2 \sum_n \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3}\, \psi^*_{n,\vec{k}}(\vec{r})\psi_{n,\vec{k}'}(\vec{r}') \sum_{\vec{R}} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}} \\
&= V_{\rm uc}\, \underbrace{V_{\rm uc} \sum_n \int \frac{d^3k}{(2\pi)^3}\, \psi^*_{n,\vec{k}}(\vec{r})\psi_{n,\vec{k}}(\vec{r}')}_{\delta(\vec{r}-\vec{r}')} \\
&= V_{\rm uc}\delta(\vec{r}-\vec{r}')
\end{aligned}$$