Electrons in a weak periodic potential U

Model can be applied to metals in groups I, II, III, and IV of the periodic table

All contain s-, p- valence electrons

- e cannot go very close to the ion /closed shell/
- conduction electrons screen ions

How to treat a weak potential?

Perturbatively, starting from plane waves - solutions for $U=0$

Second proof of Bloch's theorem

$$\psi(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}$$ Fourier transform

Born-von Karmon BC $\Rightarrow$ $\vec{q} = \sum_{i=1}^{3} \frac{2\pi}{N_i a_i} m_i \hat{e}_i$

$\psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r})$ m_i integer

$\psi(\vec{r}) = \langle \vec{r} | \psi \rangle$ coordinate representation of the eigenstate $|\psi\rangle$

$c_{\vec{q}} = \langle \vec{q} | \psi \rangle$ momentum representation of the eigenstate $|\psi\rangle$

Momentum representation of the Schrödinger equation

$$\frac{\hat{\vec{p}}^2}{2m} \to \frac{\vec{p}^2}{2m} = \frac{\hbar^2 \vec{q}^2}{2m}$$

$$\psi(\vec{r}) \to c_{\vec{q}}$$

$$U(\vec{r}) \cdot \psi(\vec{r}) \xrightarrow{\hspace{2em}} ?$$

Fourier transform

Fourier transform of a periodic potential

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \qquad \vec{R} \in BL$$

$$\boxed{U_{\vec{K}} = \frac{1}{v}\int_{\text{cell}} d\vec{r}\, e^{-i\vec{K}\cdot\vec{r}}\, U(\vec{r})} \qquad (A)$$

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

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

$$\Downarrow$$

$$e^{i\vec{K}\cdot\vec{R}} = 1 \quad \forall\, \vec{R} \in BL$$

$$\Downarrow$$

$$\vec{K} = \sum_{i=1}^{3} n_i \vec{b}_i \quad \in RL$$

Are (A) and (B) consistent ?

$$U_{\vec{K}} \stackrel{?}{=} \int_{\text{cell}} \frac{d\vec{r}}{v}\, e^{-i\vec{K}\cdot\vec{r}} \cdot \sum_{\vec{K}'} U_{\vec{K}'}\, e^{+i\vec{K}'\cdot\vec{r}}$$

$$U_{\vec{K}} = \sum_{\vec{K}'} U_{\vec{K}'} \underbrace{\left[\int_{\text{cell}} \frac{d\vec{r}}{v} e^{i(\vec{K}'-\vec{K})\cdot\vec{r}} \right]}_{\text{must be } \delta_{\vec{K},\vec{K}'}}$$

$$\int_{\text{cell}} \frac{d\vec{r}}{v} \underbrace{e^{i\vec{K}\cdot\vec{r}}}_{\text{periodic function of } \vec{r}} = \begin{cases} \emptyset, & \vec{K} \neq \emptyset \\ 1, & \vec{K} = 0 \end{cases} \qquad \vec{K} \in RL$$

① Potential $U(\vec{r})$ is defined up to an additive constant $\Rightarrow$

We can put

$$\boxed{U_0 = \int_{\text{cell}} \frac{d\vec{r}}{v} U(\vec{r}) = 0}$$

② $U(\vec{r})$ is real: $U^*(\vec{r}) = U(\vec{r}) \Rightarrow$

$$U^*(\vec{r}) = \sum_{\vec{K}} U^*_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} \underset{\vec{K}\to-\vec{K}}{=} \sum_{\vec{K}} U^*_{-\vec{K}} e^{i\vec{K}\cdot\vec{r}}$$

$$\boxed{U^*_{-\vec{K}} = U_{\vec{K}}}$$

③ For simplicity we assume that the crystal has inversion symmetry:

$$U(\vec{r}) = U(-\vec{r})$$

$$U(-\vec{r}) = \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}\, U_{\vec{k}} \underset{\vec{k}\to-\vec{k}}{=} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \cdot U_{-\vec{k}}$$

$$\underbrace{\boxed{U_{-\vec{k}} = U_{\vec{k}}}}_{\vec{r}\to-\vec{r}} = \underbrace{\boxed{U_{-\vec{k}} = U^{*}_{\vec{k}}}}_{U \text{ real}}$$

SEquation:

(i) $$\frac{\hat{p}^2}{2m}\psi(\vec{r}) = -\frac{\hbar^2}{2m}\cdot\vec{\nabla}_r^2 \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} c_{\vec{q}} = \sum_{\vec{q}} \underline{\underline{\frac{\hbar^2 q^2}{2m} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}}}$$

(ii) $$U\psi = \left(\sum_{\vec{k}} U_{\vec{k}}\, e^{i\vec{k}\cdot\vec{r}}\right)\left(\sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} c_{\vec{q}}\right)$$

$$U\psi = \sum_{\vec{k}\vec{q}} U_{\vec{k}}\, c_{\vec{q}}\, e^{i(\vec{k}+\vec{q})\cdot\vec{r}}$$

$$\vec{q} \to \vec{q}\,' = \vec{k}+\vec{q} \qquad \vec{q} = \vec{q}\,'-\vec{k}$$

$$\boxed{U\psi = \sum_{\vec{k}}\sum_{\vec{q}\,'} U_{\vec{k}}\, c_{\vec{q}\,'-\vec{k}}\, e^{i\vec{q}\,'\cdot\vec{r}}}$$

26.5°

SEquation in momentum representation

$$H\psi = \left(\frac{\hat{p}^2}{2m} + U\right)\psi = \varepsilon\psi$$

$$\sum_{\vec{q}} c_{\vec{q}} \cdot \left(\frac{\hbar^2 q^2}{2m} - \varepsilon\right) e^{i\vec{q}\cdot\vec{r}} + \sum_{\vec{q}} \left(\sum_{\vec{K}} U_{\vec{K}} c_{\vec{q}-\vec{K}}\right) e^{i\vec{q}\cdot\vec{r}} = 0$$

$$\boxed{\left[\frac{\hbar^2}{2m}\vec{q}^{\,2} - \varepsilon\right] c_{\vec{q}} + \sum_{\vec{K}} U_{\vec{K}} c_{\vec{q}-\vec{K}} = 0}$$

convolution of Fourier transforms

Some rearrangement

① $\vec{q} = \vec{k} - \vec{K}$ $\quad\quad$ $\vec{K} \in RL$ $\quad\quad$ $\vec{k} \in 1\text{st } BZ$

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

② $\vec{k} - \vec{K} - \vec{K}' = \vec{k} - \vec{K}''$ $\quad\quad$ $\vec{K}'' = \vec{K}' + \vec{K}$

$\vec{K}' \to \vec{K}''$ $\quad\quad$ $\vec{K}' = \vec{K}'' - \vec{K}$

26.5

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

$\vec{k} \in$ 1st BZ $\qquad \vec{K}, \vec{K}' \in RL$

There are N <u>non-equivalent</u> wave vectors $\vec{k}$ in the 1st BZ. Consider arbitrary fixed $\vec{k}$.

(C) shows that the following amplitudes are only coupled:

$c_{\vec{k}} \;\dots\; c_{\vec{k}-\vec{K}''}$ $\qquad \vec{K}'' \in RL$

$\Downarrow$

$\vec{k}-\vec{K}'' \notin$ 1st BZ

Different $\vec{k}, \vec{k}' \in$ 1st BZ:

amplitudes $c_{\vec{k}}$ and $c_{\vec{k}'}$ <u>uncouple</u>

$\Rightarrow$ N <u>independent</u> equations for each $\vec{k}$

$\Rightarrow$ Solutions must be of the form

$$\psi_{\vec{k}} = \sum_{\vec{K}} C_{\vec{k}-\vec{K}}\, e^{i(\vec{k}-\vec{K})\cdot\vec{r}} \qquad (*)$$

$\vec{q}$ can only assume the values $\vec{k}-\vec{K}$

We can rewrite $(*)$:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \cdot \Bigg(\underbrace{\sum_{\vec{K}} C_{\vec{k}-\vec{K}}\, e^{-i\vec{K}\cdot\vec{r}}}_{\equiv\, u_{\vec{k}}(\vec{r})} \Bigg)$$

$$u_{\vec{k}}(\vec{r}+\vec{R}) = \sum_{\vec{K}} C_{\vec{k}-\vec{K}} \cdot e^{-i\vec{K}(\vec{r}+\vec{R})} = u_{\vec{k}}(\vec{r})$$

periodic function

Electrons in a weak periodic potential

$$e: \vec{k} \to \lambda = \frac{2\pi}{k} = \frac{2\pi\hbar}{p}$$

momentum

quantum mechanically: plane waves.

Typical $p \sim p_F \sim \frac{\hbar}{r_s} \sim \frac{\hbar}{a}$ ← lattice spacing

Waves with $k \sim \frac{1}{a}$ in a crystal with lattice spacing a

strong diffraction!

> Bragg planes?
> Effect on electron eigenstates?

Starting point: Schrödinger Equation (SE) in momentum representation

$$U(\vec{r}) \xrightarrow{\text{Fourier transform}} U_{\vec{K}} \qquad \vec{K} \in RL$$