ELECTRONS IN A PERIODIC POTENTIAL: BAND THEORY OF SOLIDS

(I.) Reminder: Bloch's theorem (see A&M ch. 8 for proof and extended discussion)

- Eigenstates ψ of the one-electron Hamiltonian $H = -\hbar^2\nabla^2/2m + U(\vec{r})$ where $U(\vec{r}+\vec{R}) = U(\vec{r})$ for all $\vec{R}$ in the Bravais lattice can be chosen in to have the form

$$\psi_{nk}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{nk}(\vec{r}) \qquad (1)$$

where

$$u_{nk}(\vec{r}+\vec{R}) = u_{nk}(\vec{r}). \qquad (2)$$

- Note that (1) and (2) imply that

$$\psi_{nk}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi_{nk}(\vec{r}) \qquad (3)$$

which is sometimes used as an alternative statement of the theorem.

- In Eq. (1) $\vec{k}$ is known as the "crystal momentum" and n is the band index.

(II) WEAK PERIODIC POTENTIAL

Consider $H = \frac{\hbar^2 \nabla^2}{2m} + U(\vec{r})$ $\qquad U(\vec{r}+\vec{R}) = U(\vec{r})$

H_0 H' "weak" such that H_1 can be treated as a perturbation to H_0.

- First transform to second quantized notation:

$$H_0 = \sum_{k,\sigma} \varepsilon_k c^\dagger_{k\sigma} c_{k\sigma}, \qquad \varepsilon_k = \frac{\hbar^2 k^2}{2m} \tag{4}$$

basis: $\psi_k = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$

$$H' = \sum_{\substack{kk' \\ \sigma\sigma'}} \underbrace{\langle k\sigma | U | k'\sigma' \rangle}_{\downarrow} c^\dagger_{k\sigma} c_{k'\sigma'} \tag{5}$$

$$\frac{1}{V} \delta_{\sigma\sigma'} \int d^3r\, e^{-i\vec{r}(\vec{k}-\vec{k}')} U(\vec{r})$$

- note that due to its periodic property U can be written as

$$U(\vec{r}) = \sum_{\vec{G}} e^{i\vec{r}\cdot\vec{G}} U_{\vec{G}} \tag{6}$$

where $\vec{G}$ are reciprocal lattice vectors satisfying $e^{i\vec{G}\cdot\vec{R}} = 1$ for all $\vec{R}$ in Bravais lattice. (check!)

- We further assume $U_{G=0} = 0$, which only redefines the overall zero of energy.

$$\rightarrow \quad \langle k\sigma | U | k'\sigma' \rangle = \frac{\delta_{\sigma\sigma'}}{V} \int d^3r \sum_G U_G\, e^{-i\vec{r}(\vec{k}-\vec{k}'-\vec{G})} \tag{7}$$

$$= \delta_{\sigma\sigma'} \sum_G U_G\, \delta_{\vec{k}-\vec{k}',\vec{G}}$$

$$H' = \sum_{\substack{kk' \\ \sigma\sigma'}} \delta_{\sigma\sigma'} \sum_G \delta_{\vec{k}-\vec{k}';\vec{G}}\, U_{\vec{G}}\, c^\dagger_{k\sigma} c_{k'\sigma'}$$

$$= \sum_{k,G,\sigma} U_G\, c^\dagger_{k+G\sigma} c_{k\sigma} \tag{8}$$

- In the following we suppress the spin index and focus on a 1D system for simplicity

$$H_0 = \sum_k \varepsilon_k c_k^+ c_k \tag{9}$$

$$H' = \sum_{k,G} U_G c_{k+G}^+ c_k$$

- we now ask how is electron in eigenstate $|k\rangle = c_k^+ |0\rangle$ of H_0 perturbed by H'.

- <u>Zeroth order</u>: $E_k^{(0)} = \varepsilon_k$

- <u>First order</u>: $E_k^{(1)} = \langle k|H'|k\rangle$

$$= \langle k | \sum_{qG} U_G c_{q+G}^+ c_q | k \rangle$$

$$= \langle k | \sum_G U_G c_{k+G}^+ |0\rangle \tag{10}$$

$$= \sum_G U_G \langle k | k+G \rangle$$

$$= U_0 \quad = 0$$

→ to first order in H' there is no effect.

- <u>Second order</u>

$$E_k^{(2)} = \sum_{k'}{}' \frac{|\langle k|H'|k'|^2}{\varepsilon_{k'} - \varepsilon_k} = \sum_{k'}{}' \frac{\langle k|H'|k'\rangle \langle k|H'|k'\rangle^*}{\varepsilon_{k'} - \varepsilon_k} \tag{11}$$

$$\langle k|H'|k'\rangle = \sum_{qG} U_G \langle k | c_{q+G}^+ c_q | k' \rangle \qquad q = k'$$

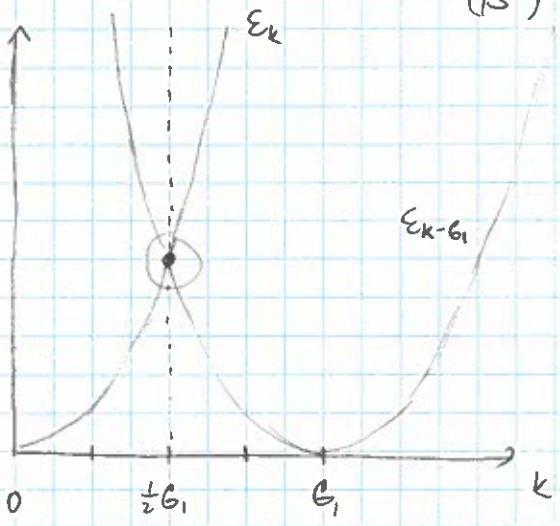
$$= \sum_G U_G \langle k | c_{k'+G}^+ |0\rangle \tag{12}$$

$$= \sum_G U_G \langle k | k'+G \rangle = \sum_G U_G \delta_{k,k'+G}$$

$$E_k^{(2)} = \sum_{k'GG'}{}' \frac{U_G U_{G'}^* \delta_{k,k'+G} \delta_{k,k'+G'}}{\varepsilon_{k'} - \varepsilon_k} \qquad k' = k - G$$

$$= \sum_{GG'}{}' \frac{U_G U_{G'}^* \delta_{GG'}}{\varepsilon_{k+G} - \varepsilon_k}$$

$$= \sum_{G \neq 0} \frac{|U_G|^2}{\varepsilon_{k-G} - \varepsilon_k} \qquad (13)$$



- For small $|U_G|$ this correction to energy will be negligible EXCEPT when $\varepsilon_{k-G} - \varepsilon_k$ is also small. This occurs at specific values of $k = \frac{1}{2}G$. In 3D $\vec{k} = \frac{1}{2}\vec{G}$ defines a "Bragg plane"

- At and near $k = \frac{1}{2}G$ we must apply degenerate perturbation theory (because $E_k^{(2)}$ obtained in Eq. 13 diverges):

  • define two near-degenerate states

$$|1\rangle = |k\rangle, \quad |2\rangle = |k - G_1\rangle \qquad (14)$$

  and construct the Hamiltonian in this basis:

$$\begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix} = \begin{pmatrix} \varepsilon_k & U_{G_1} \\ U_{G_1}^* & \varepsilon_{k-G_1} \end{pmatrix} \qquad (15)$$

  • The perturbed energies are given by eigenvalues of this matrix:

$$\det \begin{pmatrix} \varepsilon_k - E & U_G \\ U_G^* & \varepsilon_{k-G} - E \end{pmatrix} = 0 \qquad (16)$$

We get

$$(\varepsilon_k - E)(\varepsilon_{k-G} - E) - |U_G|^2 = 0$$

$$\rightarrow \boxed{E_k = \frac{1}{2}(\varepsilon_k + \varepsilon_{k-G}) \pm \sqrt{\frac{1}{4}(\varepsilon_k - \varepsilon_{k-G})^2 + |U_G|^2}} \quad (17)$$

- For $\vec{k} = \frac{1}{2}\vec{G}$, i.e. the degeneracy point, we have

$$E_k = \varepsilon_k \pm |U_G| \quad (18)$$

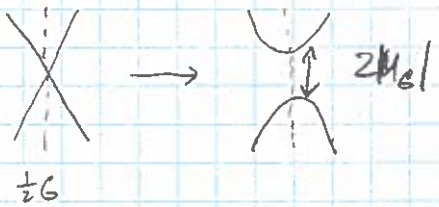
$\Rightarrow$ the energy crossing has been resolved

SUMMARY:

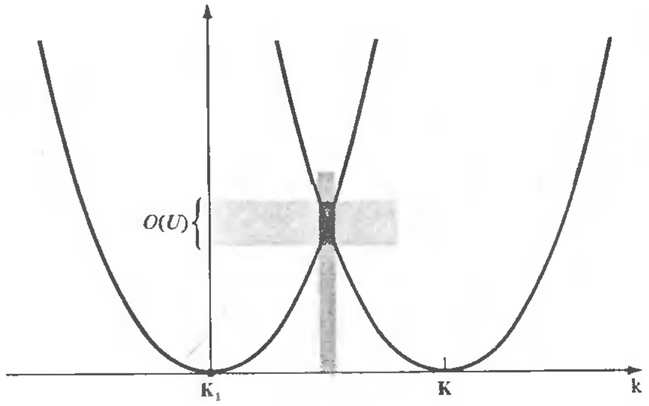
In the weak potential approximation the energy levels (a.k.a. the band structure) of electrons can be obtained in two easy steps:

1) Plot free electron dispersion $\varepsilon_{\vec{k}}$ shifted by all reciprocal lattice vectors $\vec{G}$: $\varepsilon_{\vec{k}-\vec{G}}$

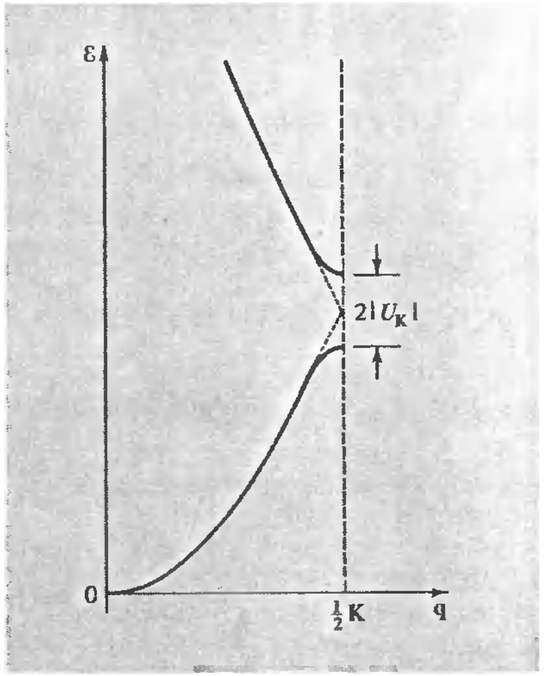
2) Resolve all degeneracies (a.k.a band crossings) according to



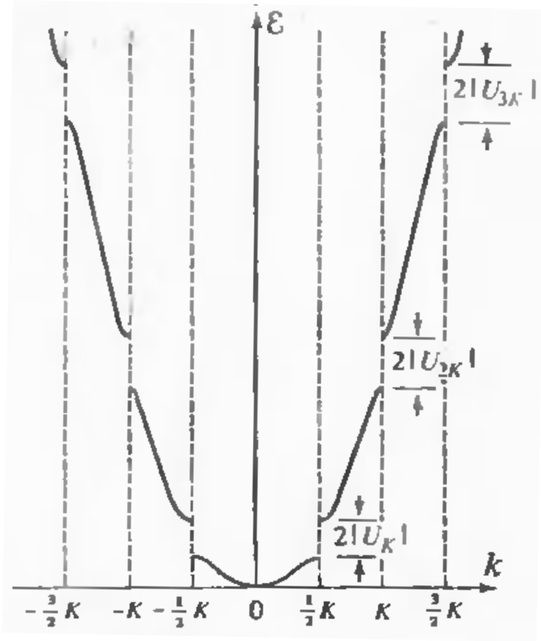
Electrons in weak periodic potential: recap



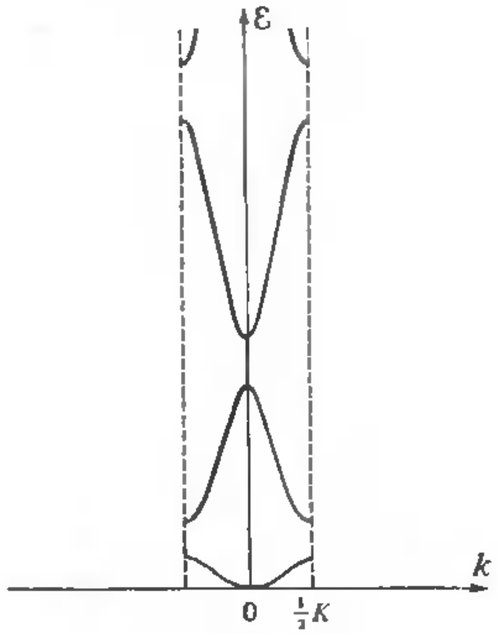
Weak perturbation has no effect except at degeneracy points.



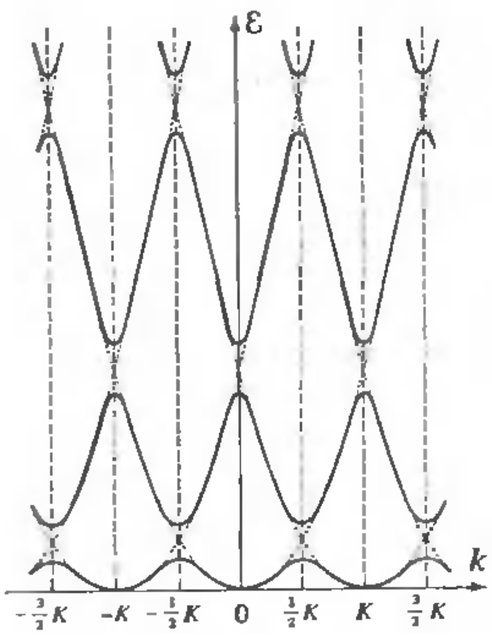
Band structure representations:



“extended zone scheme”



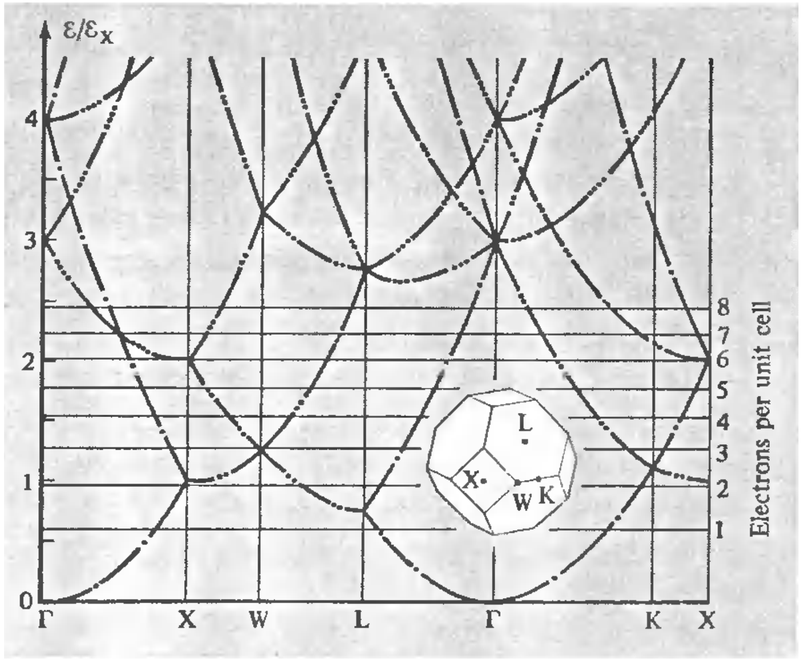
“reduced zone scheme”



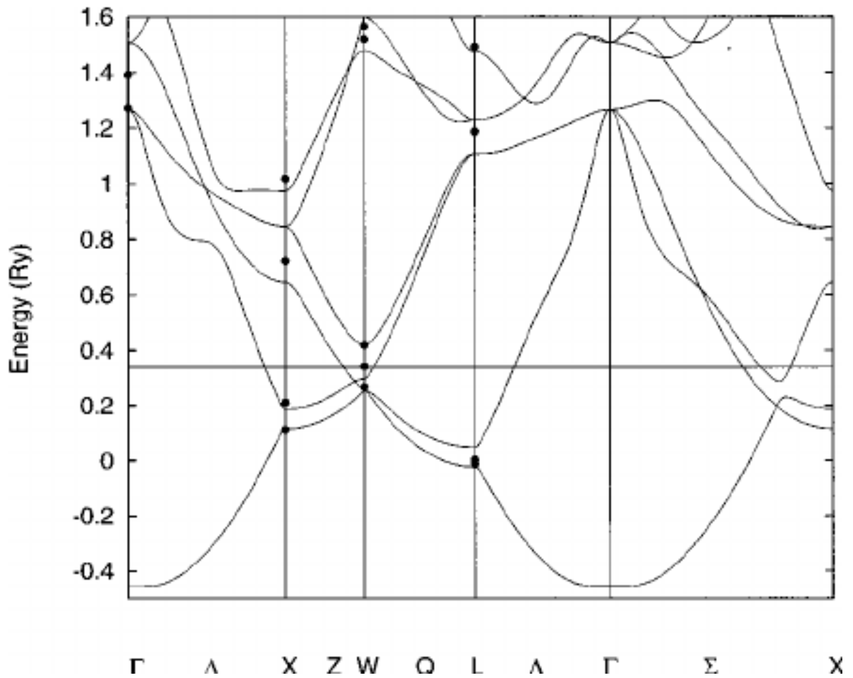
“repeated zone scheme” (redundant)

equivalent

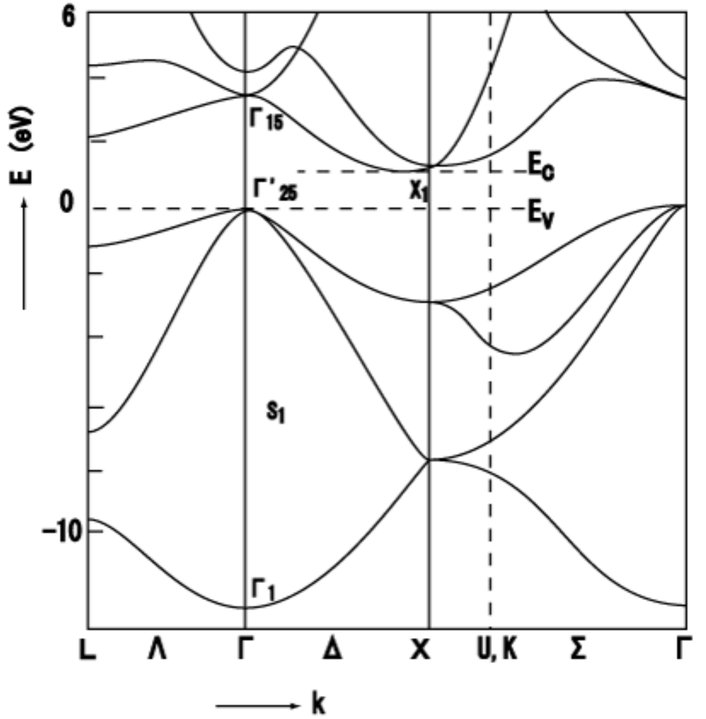
Band structure examples in 3D



Free electron levels in FCC Bravais lattice



Band structure of aluminum
Fermi energy inside the band:
metal



Band structure of silicon
Fermi energy inside the gap:
insulator

Band structure example in 2D:
Graphene