Notice that $\tilde{v}(0)$ can be conventionally absorbed into the definition of the energy. $\Rightarrow$ the first order perturbation vanishes identically.

ii) If $\varepsilon^0_{\vec{k}-\vec{G}_1}$ is degenerate i.e. $|\varepsilon^0_{\vec{k}-\vec{G}_1} - \varepsilon^0_{\vec{k}-\vec{G}_j}| \ll \tilde{v}$ $i = 2, \dots m$

(by construction it always occurs at the edge of BZ since e.g. if $\vec{k} = \frac{\vec{G}}{2} \Rightarrow \vec{k} - \vec{G} = -\frac{\vec{G}}{2} = -\vec{k}$ and $\varepsilon^0_{\vec{k}} = \varepsilon^0_{-\vec{k}}$.)

One obtains a system of m coupled equations

$$\left(\varepsilon - \varepsilon^0_{\vec{k}-\vec{G}_i}\right) c_{\vec{k}-\vec{G}_i} = \sum_{\substack{j=1 \\ j\neq i}}^{m} \tilde{v}(\vec{G}_j - \vec{G}_i)\, c_{\vec{k}-\vec{G}_j}$$

Example: twofold degeneracy $\varepsilon^0_{\vec{k}-\vec{G}_1} \approx \varepsilon^0_{\vec{k}-\vec{G}_2}$

$$\begin{cases} \left(\varepsilon - \varepsilon^0_{\vec{k}-\vec{G}_1}\right) c_{\vec{k}-\vec{G}_1} = \tilde{v}(\vec{G}_2 - \vec{G}_1)\, c_{\vec{k}-\vec{G}_2} \\ \left(\varepsilon - \varepsilon^0_{\vec{k}-\vec{G}_2}\right) c_{\vec{k}-\vec{G}_2} = \tilde{v}(\vec{G}_1 - \vec{G}_2)\, c_{\vec{k}-\vec{G}_1} \end{cases}$$

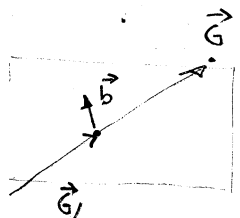
let us set $\vec{q} \equiv \vec{k} - \vec{G}_1$ and $\vec{G}_2 - \vec{G}_1 = \vec{G}$

$$\begin{cases} \left(\varepsilon - \varepsilon^0_{\vec{q}}\right) c_{\vec{q}} = \tilde{v}(\vec{G})\, c_{\vec{q}-\vec{G}} \\ \left(\varepsilon - \varepsilon^0_{\vec{q}-\vec{G}}\right) c_{\vec{q}-\vec{G}} = \tilde{v}^*(\vec{G})\, c_{\vec{q}} \end{cases} \Rightarrow \varepsilon = \frac{\varepsilon^0_{\vec{q}} + \varepsilon^0_{\vec{q}-\vec{G}}}{2} \pm \sqrt{\left|\frac{\varepsilon^0_{\vec{q}} - \varepsilon^0_{\vec{q}-\vec{G}}}{2}\right|^2 + |\tilde{v}(\vec{G})|^2} \qquad (2.49)$$

In particular if $\varepsilon^0_{\vec{q}} = \varepsilon^0_{\vec{q}-\vec{G}} \Leftrightarrow |\vec{q}| = |\vec{q}-\vec{G}| \Rightarrow q^2 = q^2 - 2\vec{q}\cdot\vec{G} + G^2$

$\Rightarrow \vec{G}\cdot(\vec{G} - 2\vec{q}) = 0 \Rightarrow \vec{q} = \frac{\vec{G}}{2} + \vec{b}$ where $\vec{b} \perp \vec{G}$.

In other terms $\vec{q}$ belongs to a Bragg plane.



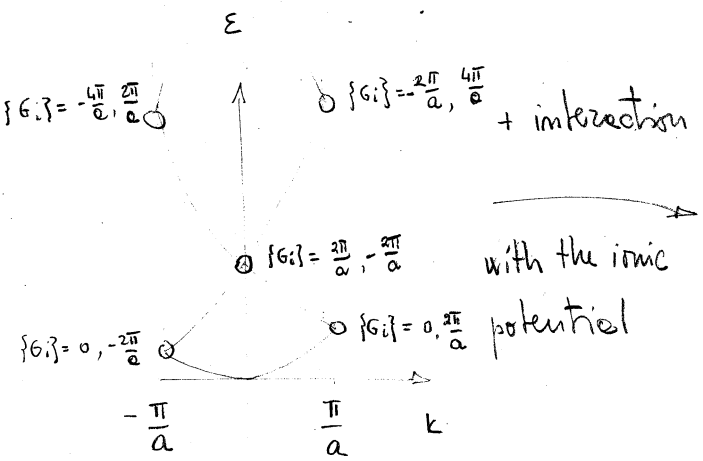
Eq. (2.49) indicates that the degeneracy at the Bragg planes is removed.

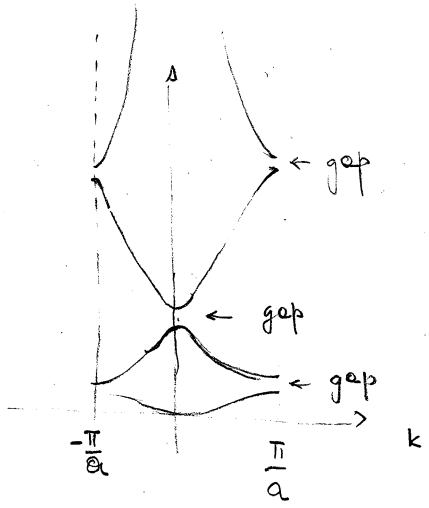
$$\varepsilon(\vec{q}) = \varepsilon^0_{\vec{q}} \pm |\tilde{v}(\vec{G})| \quad \text{if } \vec{q} \in \vec{G}\text{-Bragg plane.} \qquad (2.50)$$

Consequently energy gaps and energy bands are formed.

Notice that degenerate states corresponding to the same $\vec{G}$ are not affected by the previous arguments.

In 1D the maximum is the two-fold degeneracy. To leading order in the potential the free electron description remains correct except at Bragg points.





The 1D are flat at the border of the Brillouin zone. More generally, from (2.49) one obtains that if $\vec{q}$ ∈ Bragg plane defined by $\vec{G}$

$$\vec{\nabla}\,\varepsilon(\vec{q}) = \frac{1}{2}\left(\nabla\varepsilon^{\circ}_{\vec{q}} + \nabla\varepsilon^{\circ}_{\vec{q}-\vec{G}}\right) = \frac{\hbar^2}{4m}\left(2\vec{q} + 2\vec{q} - 2\vec{G}\right) = \frac{\hbar^2}{m}\left(\vec{q} - \frac{\vec{G}}{2}\right) \quad (2.$$

But since $\vec{q} = \frac{\vec{G}}{2} + \vec{b}$ and $\vec{b} \perp \vec{G}$ The group velocity of an electron on a Bragg plane is parallel to the plane itself. The dispersion relation has thus an extremal when calculated along a direction perpendicular to a Bragg plane.

Consequently, for example $\vec{\nabla}\varepsilon(\vec{k})$ vanishes at $\vec{X}, \vec{M}, \vec{R}$ points of the simple cubic lattice example (see page 29). In these points the group velocity vanishes and standing waves are formed.

Full calculation of the gradient of $\mathcal{E}(\vec{q})$ close to a Bragg plane

$$\vec{\nabla}\mathcal{E}(\vec{q}) = \frac{1}{2}\frac{\hbar^2}{2m}\left[\vec{\nabla}q^2 + \vec{\nabla}(\vec{q}-\vec{G})^2\right] \pm \frac{\frac{1}{2}\left|\mathcal{E}^0_{\vec{q}} - \mathcal{E}^0_{\vec{q}-\vec{G}}\right| \frac{\hbar^2}{2m}\left(\vec{\nabla}q^2 - \vec{\nabla}(\vec{q}-\vec{G})^2\right)}{2\sqrt{\left(\mathcal{E}^0_{\vec{q}} - \mathcal{E}^0_{\vec{q}-\vec{G}}\right)^2/4 + |\tilde{V}(\vec{G})|^2}} \quad \Big| \; \vec{q} = \frac{\vec{G}}{2} + \vec{b}$$

$$= \frac{\hbar^2}{2m}\left[\vec{q} + \vec{q} - \vec{G}\right] \pm \frac{\frac{\hbar^2}{2m}\left(\vec{q} - \vec{q} + \vec{G}\right)\left|\mathcal{E}^0_{\vec{q}} - \mathcal{E}^0_{\vec{q}-\vec{G}}\right|}{2\sqrt{\left(\mathcal{E}^0_{\vec{q}} - \mathcal{E}^0_{\vec{q}-\vec{G}}\right)^2/4 + |\tilde{V}(\vec{G})|^2}} \quad \Big| \; \vec{q} = \frac{\vec{G}}{2} + \vec{b}$$

$$= \frac{\hbar^2}{m}\vec{b}\,.$$

The procedure of calculating energy bands in the reduced-zone scheme can be repeated also in 2D or 3D, once the Brillouin zones have been constructed.

2.6 Ground state of Bloch electrons

■ Refresh: FREE ELECTRONS

- The ground state of N_e free electrons is constructed accounting for Pauli exclusion principle: fill energy eigenstates starting from the one with the lowest energy with one electron per level, including spin.
- The highest occupied level is called <u>Fermi level</u> and it is characterized by the Fermi energy ε_F
- Due to the isotropy of the dispersion relation it is possible to identify a Fermi momentum k_F: $\varepsilon(k_F) = \frac{\hbar^2 k_F^2}{2m} = \varepsilon_F$
- The Fermi momentum is connected to the electronic density

$$N_e = 2 \sum_{k<k_F} 1 = 2 \frac{V}{(2\pi)^3} \int d\vec{k}\, \theta(k_F - |\vec{k}|) = \frac{2V}{(2\pi)^3} \frac{4\pi k_F^3}{3}$$

$$\Rightarrow n_e = \frac{N_e}{V} = \frac{k_F^3}{3\pi^2} \qquad (2.52)$$

■ BLOCH ELECTRONS

- The ground state of N_e Bloch electrons is contructed accounting for the Pauli exclusion principle.
- Each band can accomodate, including spin, a total of $2N_{cell}$ electrons
- A Bravais lattice with n atoms per primitive cell consists of $N_{at} = nN_{cell}$ thus contains $\sum_{\alpha=1}^{n} Z_{eff,\alpha} N_{cell}$ valence electrons.

Only two situations can occur:

1. Some bands are completely filled. All others remain empty.
   - the energy difference between the lowest occupied level and the highest occupied one is called BAND-GAP.

- A band gap might occur ONLY if the number of electrons per primitive cell is EVEN

- Filled bands are inert $\Rightarrow$ insulators at $T = 0$

proof:

$$\langle \vec{j}_n \rangle = -\frac{e}{V} \sum_{\vec{k}} \langle n_{\vec{k}} \vec{v}_{n\vec{k}} \rangle = -e \frac{d\vec{k}}{4\pi^3} \int_{1BZ} \nabla_{\vec{k}} \varepsilon_{n\vec{k}} \, d\vec{k} = 0$$

$n_{\vec{k}}$: occupation probability of the state $\vec{k}$

the last equality stems from the fact that $\varepsilon_{n\vec{k}}$ is a periodic function on the reciprocal lattice.

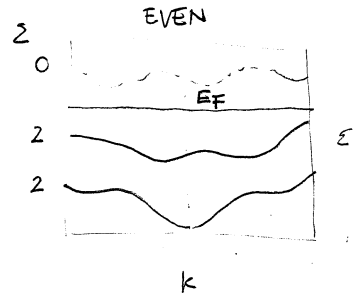
2. A number of bands is partially filled

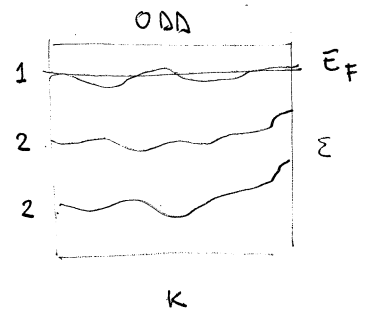
- The energy of the highest occupied level is called Fermi energy. It lies within the energy range of one or more bands.
- The Fermi surface separates filled from unfilled levels

$$\varepsilon_n(\vec{k}) = \varepsilon_F \qquad (2.53)$$

- It always occurs if $z_{el} = \sum_{\alpha=1}^{n} z_{eff,\alpha}$ is odd but not only.

EVEN - ODD rule: narrow bands





Wide bands