

Electrons in periodic potentials; V.M. STOJANOVIĆ

lattice models

In the presence of a periodic potential $V(\vec{r}) = V(\vec{r} + \vec{a})$ the single-electron wavefunction has the form

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}),$$

where $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{a})$, i.e., $u_{\vec{k}}(\vec{r})$ is a periodic function (with the same periodicity as the potential V itself).

In other words, the electron wavefunction can be written as a product of a plane wave and a lattice-periodic function. This is the statement of Bloch's theorem.

For every quasimomentum \vec{k} from the first Brillouin zone the Schrödinger equation for an electron in the periodic potential

$$\hat{H}_e \Psi(\vec{r}) = \mathcal{E} \Psi(\vec{r})$$

$$\hat{H}_e \equiv -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r})$$

has multiple solutions, which are enumerated by the Bloch-band index n :

$$\hat{H}_e \Psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) \Psi_{n\vec{k}}(\vec{r}),$$

where $E_n(\vec{k})$ is the dispersion of the n -th Bloch band. Knowing this, the Bloch theorem can be rewritten as

$$\Psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r}).$$

Another, equivalent, form of the last equation reads

$$\Psi_{n\vec{k}}(\vec{r}+\vec{a}) = e^{i\vec{k}\cdot\vec{a}} \Psi_{n\vec{k}}(\vec{r}) .$$

The eigenvalue problem for the full Bloch wavefunctions

$$\left[\frac{\hat{p}^2}{2m} + V(\vec{r}) \right] \Psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) \Psi_{n\vec{k}}(\vec{r})$$

can be recast (remember Problem sheet 0) as an equivalent eigenvalue problem with $U_{n\vec{k}}(\vec{r})$ playing the role of $\Psi_{n\vec{k}}(\vec{r})$:

$$\hat{H}(\vec{k}) U_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) U_{n\vec{k}}(\vec{r}) ,$$

where

$$\hat{H}(\vec{k}) \equiv \underbrace{\frac{\hat{p}^2}{2m} + V(\vec{r})}_{\hat{H}_e} + \frac{\hbar}{m} \vec{k} \cdot \vec{p} + \frac{\hbar^2 \vec{k}^2}{2m}$$

is a parametric Hamiltonian. Here the relevant parameter is the electron quasimomentum \vec{k} .

(remember the Hellman-Feynman theorem that holds)
(for an arbitrary parametric Hamiltonian!)

The lattice-periodic functions $U_{n\vec{k}}(\vec{r})$ can be expanded in a Fourier series over the reciprocal lattice vectors \vec{G} :

$$U_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k},\vec{G}}^{(n)} e^{i\vec{G}\cdot\vec{r}}$$

Analogously, the full Bloch wave-functions are then

$$\Psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k},\vec{G}}^{(n)} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

It is straightforward to show that the ^{Bloch} eigenvalue problem can then be recast as

$$\left[\frac{\hbar^2}{2m} (\vec{k}+\vec{G})^2 - E_n(\vec{k}) \right] C_{\vec{k},\vec{G}}^{(n)} + \sum_{\vec{G}'} \tilde{V}(\vec{G}-\vec{G}') C_{\vec{k},\vec{G}'}^{(n)}$$

$= 0$, where $\tilde{V}(\vec{G})$ is the Fourier transform of $V(\vec{r})$ evaluated at $\vec{k}=\vec{G}$.

The last equation can also be rewritten as

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m} (\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} + \tilde{V}(\vec{G}-\vec{G}') \right] C_{\vec{k},\vec{G}'}^{(n)} = E_n(\vec{k}) C_{\vec{k},\vec{G}}^{(n)}$$

It is useful to know that all modern electronic structure codes, used for calculating band structures of real materials, are based on solving this type of problem in the truncated plane-wave basis (i.e., truncated basis of reciprocal-lattice vectors).

The truncation criterion is usually given in the form

$$\frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2 \leq \epsilon_{\text{cutoff}}^{\text{kin}},$$

where the actual value of $\epsilon_{\text{cutoff}}^{\text{kin}}$ depends on the constituents (i.e., type of atoms) in the material under consideration; e.g., for a system containing only C and H atoms one typically takes $\epsilon_{\text{cutoff}}^{\text{kin}} = 60 \text{ Ry}$, where $1 \text{ Ry} \equiv 13.606 \text{ eV}$.

Lattice models (tight-binding models)

The tight-binding method (recall Ashcroft-Mermin!) is an approximate, yet often very accurate, approach for calculating band structures. We here will make use of this method cast in the notation of second quantization for electrons on a lattice. Thus our starting point are the tight-binding orbitals

$|\psi_i\rangle \equiv C_{\vec{R}_i}^+ |0\rangle_i$, where $C_{\vec{R}_i}^+$ is a creation operator for electrons on site \vec{R}_i of a lattice (the lattice geometry is as yet unspecified!).

By assumption (tight-binding approximation), such orbitals on different sites have a vanishing overlap

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}.$$

Example 1 single-band tight-binding models ($\sigma = \uparrow, \downarrow$ - spin index)

$$\hat{H} = \epsilon \sum_{i, \sigma} C_{\vec{R}_i \sigma}^\dagger C_{\vec{R}_i \sigma} - t \sum_{i, \vec{\delta}, \sigma} (C_{\vec{R}_i \sigma}^\dagger C_{\vec{R}_i + \vec{\delta}, \sigma} + \text{h.c.})$$

Here $\vec{\delta}$ are ~~the~~ vectors connecting site \vec{R}_i with its nearest neighbors. ϵ is the electron on-site energy, while

$$t_{ij} = - \langle \Psi_i | \hat{H} | \Psi_j \rangle \text{ are the } \underline{\text{hopping integrals}}.$$

In the above Hamiltonian we did not use $t_{i, i+\delta}$ but only one t ; this is a common assumption --- that all nearest-neighbor hopping integrals are the same.

Note that t_{ij} is sometimes defined as $+\langle \Psi_i | \hat{H} | \Psi_j \rangle$, in which case there should also be "+" sign in front of t in the above expression for \hat{H} .

The single-band tight-binding problems are "diagonalized" simply by performing a discrete Fourier transformation

$$C_{\vec{R}_i \sigma} = \frac{1}{\sqrt{N}} \sum_{\vec{k}} C_{\vec{k} \sigma} e^{i\vec{k} \cdot \vec{R}_i}$$

In this manner, we obtain the \vec{k} -space representation of the Hamiltonian \hat{H} above:

$$\hat{H} = \sum_{\vec{k}, \sigma} (\epsilon - z t f_{\vec{k}}) C_{\vec{k} \sigma}^\dagger C_{\vec{k} \sigma},$$

where z is the coordination number (number of nearest neighbors of a given lattice site) and

$$f_{\vec{k}} \equiv \frac{1}{z} \sum_{\vec{\delta}} e^{i\vec{k} \cdot \vec{\delta}}$$

contains all the details (geometry!) of the underlying lattice. This quantity is sometimes called the "structure factor."

In the special case of rectangular lattices (1d lattice, 2d square lattice, and 3d cubic lattice)

$$f_{\vec{k}} = \sum_{i=1}^d \cos k_i \quad \left(\begin{array}{l} \text{we set the} \\ \text{lattice constant } a \\ \text{to } 1 \end{array} \right)$$

$d = 1, 2, \text{ or } 3$ (dimension)

\Rightarrow the tight-binding dispersions for such lattices read

$$E_{\vec{k}} = \varepsilon - 2t \cos k \quad (\text{in 1d}),$$

$$E_{\vec{k}} = \varepsilon - 2t (\cos k_x + \cos k_y) \quad (\text{in 2d}),$$

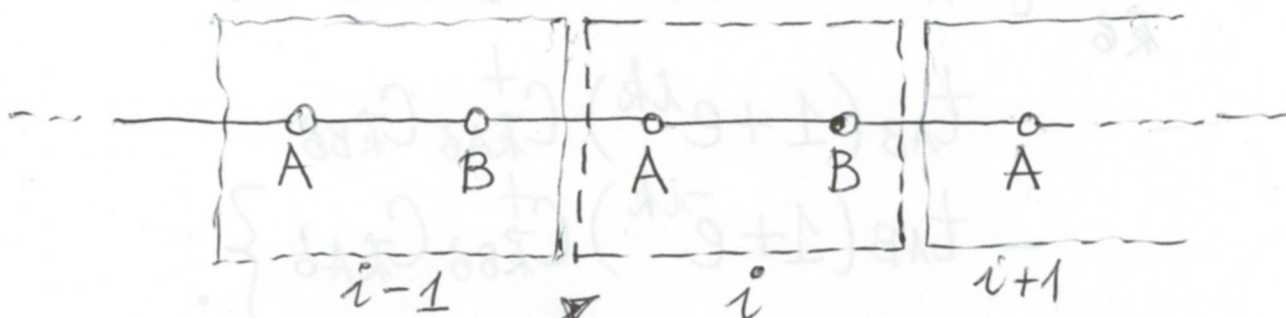
$$E_{\vec{k}} = \varepsilon - 2t (\cos k_x + \cos k_y + \cos k_z) \quad (\text{in 3d}).$$

Thus the bandwidths of these lattices are

$$W = 2zt, \text{ with } z = 2d \Rightarrow \boxed{W = 4dt} \quad \begin{array}{l} \text{e.g., in 1d} \\ W = 4t \end{array}$$

Example 2 - two-band tight-binding models

We will provide an illustration in 1d.



the unit cell of this "AB" lattice

$$\hat{H} = \sum_{i,\sigma} \left\{ \begin{aligned} & \epsilon_A C_{iA\sigma}^\dagger C_{iA\sigma} + \epsilon_B C_{iB\sigma}^\dagger C_{iB\sigma} \\ & - t_{AB} (C_{iA\sigma}^\dagger C_{iB\sigma} + \text{h.c.}) \\ & - t_{AB} (C_{i-1,B\sigma}^\dagger C_{iA\sigma} + \text{h.c.}) \\ & - t_{AB} (C_{iB\sigma}^\dagger C_{i+1,A\sigma} + \text{h.c.}) \end{aligned} \right\}$$

We write such Hamiltonians by first identifying the repeating unit (\equiv unit cell), and then taking into account all hopping processes within the unit cell as well as those between the reference unit cell "i" and its neighbors "i-1" and "i+1".

By performing Fourier transformation to momentum space

$$C_{\vec{k}A\sigma} = \frac{1}{\sqrt{N}} \sum_i C_{iA\sigma} e^{i\vec{k} \cdot \vec{R}_i}; \quad C_{\vec{k}B\sigma} = \frac{1}{\sqrt{N}} \sum_i C_{iB\sigma} e^{i\vec{k} \cdot \vec{R}_i}$$

we find

$$\hat{H} = \sum_{\vec{k} \in \text{BZ}} \left\{ \begin{aligned} &\epsilon_A C_{\vec{k}A0}^\dagger C_{\vec{k}A0} + \epsilon_B C_{\vec{k}B0}^\dagger C_{\vec{k}B0} \\ &- t_{AB} (1 + e^{ik}) C_{\vec{k}A0}^\dagger C_{\vec{k}B0} \\ &- t_{AB} (1 + e^{-ik}) C_{\vec{k}B0}^\dagger C_{\vec{k}A0} \end{aligned} \right\}.$$

Thus after the Fourier transformation we still have a 2×2 problem in \vec{k} -space to solve:

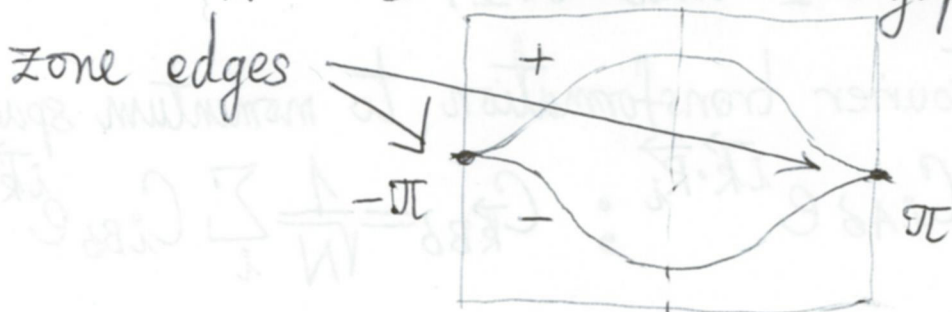
$$\hat{H} = \sum_{\vec{k} \in \text{BZ}} \begin{pmatrix} C_{\vec{k}A0}^\dagger & C_{\vec{k}B0}^\dagger \end{pmatrix} \begin{pmatrix} \epsilon_A & -t_{AB}(1+e^{ik}) \\ -t_{AB}(1+e^{-ik}) & \epsilon_B \end{pmatrix} \begin{pmatrix} C_{\vec{k}A0} \\ C_{\vec{k}B0} \end{pmatrix}$$

by diagonalizing this matrix, one obtains

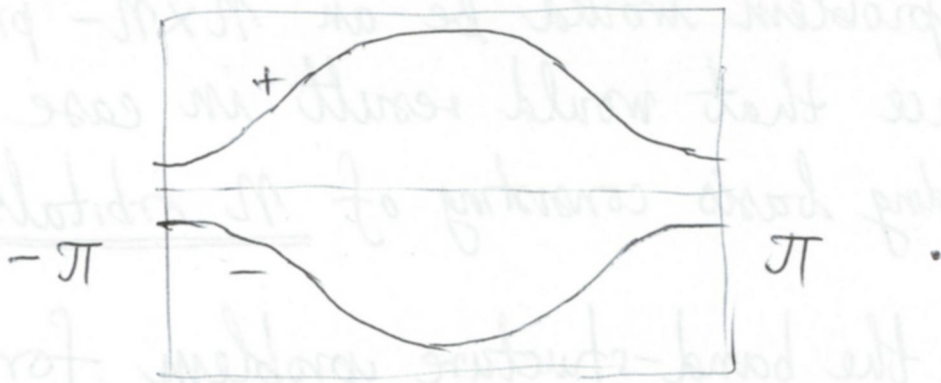
$$\epsilon_{\vec{k}}^\pm = \frac{\epsilon_A + \epsilon_B}{2} \pm \frac{1}{2} \sqrt{(\epsilon_A - \epsilon_B)^2 + 16 t_{AB}^2 \cos^2\left(\frac{k}{2}\right)},$$

the dispersions of the "+" and "-" band.

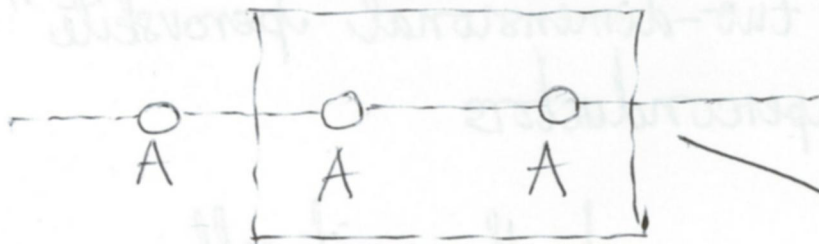
For $\epsilon_A = \epsilon_B$ there is no gap at the Brillouin zone edges



but the gap opens whenever $E_A \neq E_B$

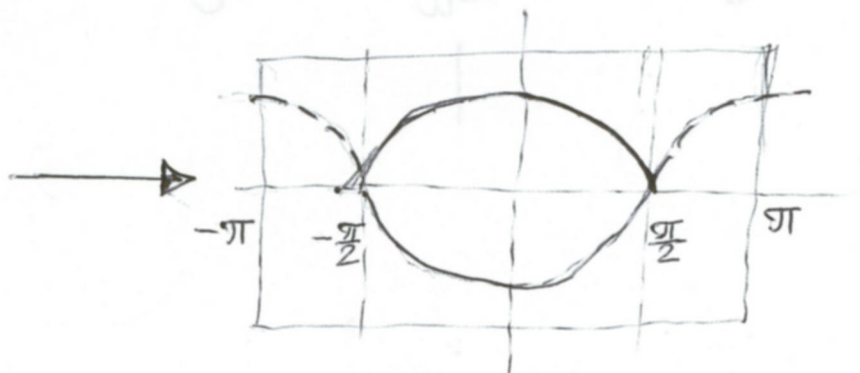
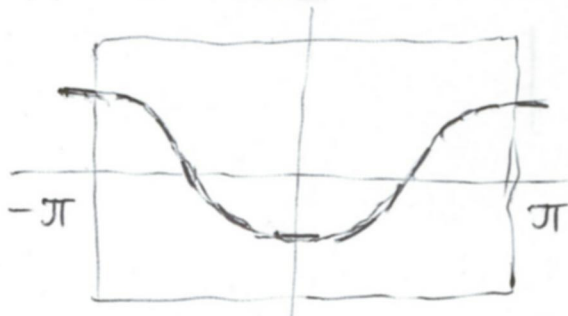


For $E_A = E_B$ we can effectively reduce the problem to the single-band one (the "AA"-lattice!)



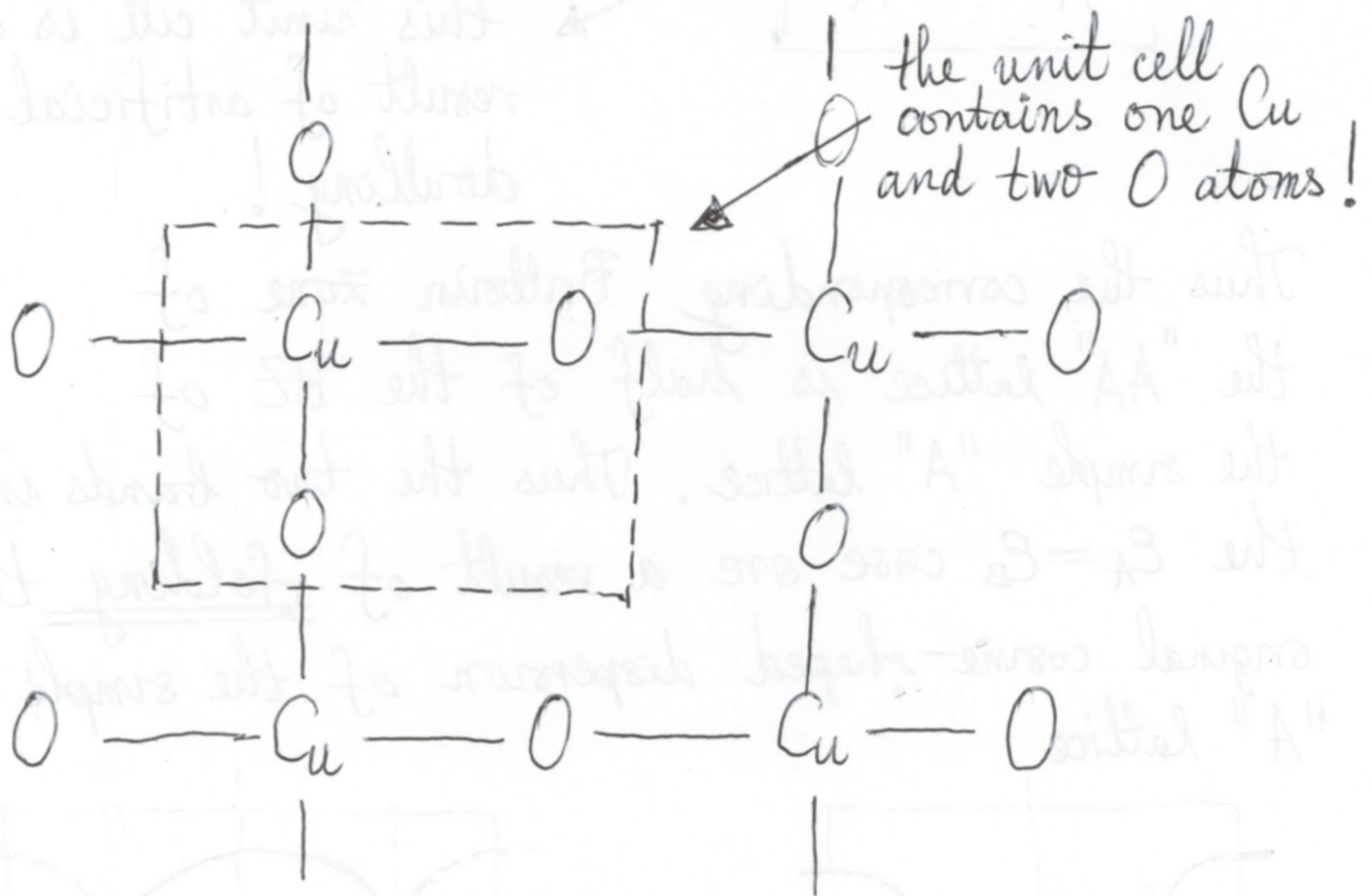
this unit cell is a result of artificial doubling!

Thus the corresponding Brillouin zone of the "AA" lattice is half of the BZ of the simple "A" lattice. Thus the two bands in the $E_A = E_B$ case are a result of folding the original cosine-shaped dispersion of the simple "A" lattice



An obvious generalization of this two-band tight-binding problem would be an $N \times N$ -problem in the k -space that would result in case we had tight binding basis consisting of N orbitals.

But solving the band-structure problem for a given system (material) requires first identifying the unit cell, the repeating unit that defines the discrete translational symmetry. As an example, let us look at the two-dimensional "perovskite" planes of high- T_c superconductors



Density-of-states and critical points (DOS)

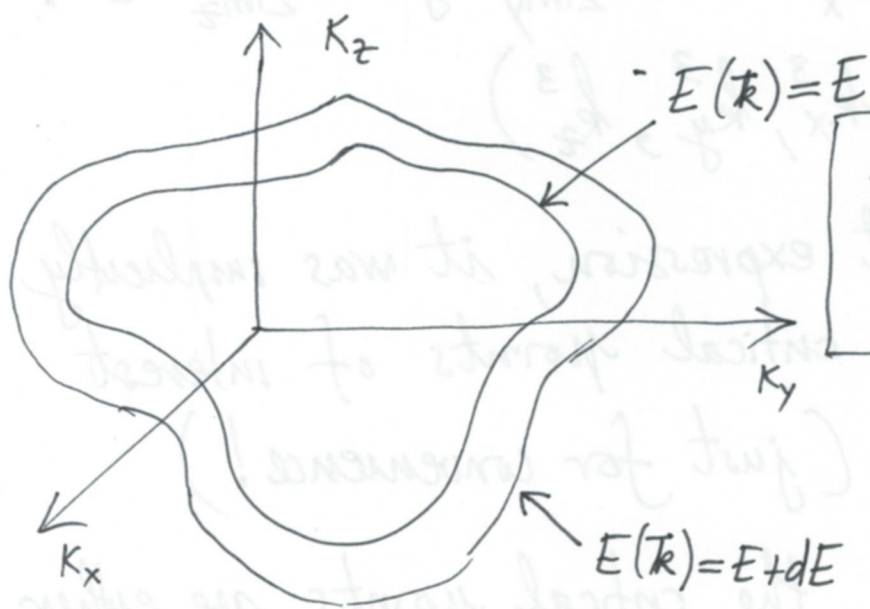
In certain solid-state physics problems it is not necessary to know the detailed \vec{k} -dependence of the band dispersions, but only DOS in certain energy range.

$$D(E) = 2 \sum_{\vec{k} \in \text{BZ}} \delta(E(\vec{k}) - E),$$

accounts for spin degeneracy!

i.e.,
$$D(E) = 2 \int_{\text{BZ}} \frac{\Omega}{(2\pi)^d} \delta(E(\vec{k}) - E) d^d \vec{k}.$$
 (d here is dimension!)

Thus the DOS at energy E counts the band states (if any) such that $E(\vec{k}) = E$.



$$D(E) = 2 \int \frac{V}{(2\pi)^3} \frac{dS}{|\nabla_{\vec{k}} E(\vec{k})|}$$

DOS expressed as a surface integral!

(Ashcroft - Mermin)

$$\left\{ \begin{array}{l} dE = \nabla_{\vec{k}} E(\vec{k}) \cdot d\vec{k} = |\nabla_{\vec{k}} E(\vec{k})| dk \\ \text{is used to arrive at this surface-integral form} \\ \text{for DOS} \end{array} \right\}$$

\Rightarrow the last expression indicates that the singularities in the DOS may appear at those points in \vec{k} -space where

$$\nabla_{\vec{k}} E(\vec{k}) = 0.$$

These are the so-called CRITICAL POINTS!

Near a critical point of a band dispersion (regardless of its actual form!) we have

$$E(\vec{k}) = E_c \pm \frac{\hbar^2}{2m_x} k_x^2 \pm \frac{\hbar^2}{2m_y} k_y^2 \pm \frac{\hbar^2}{2m_z} k_z^2 + \mathcal{O}(k_x^3, k_y^3, k_z^3)$$

In writing the last expression, it was implicitly assumed that the critical points of interest appears at $\vec{k} = 0$ (just for convenience!)

Note that in 1d the critical points are either the maxima or the minima of the band dispersion, while in 2d and 3d saddle points also exist!

Let us find $D(E)$ around the critical points
in the 1d case:

$$D(E) = \frac{L_x}{2\pi\hbar} \int \delta(E_c \pm \frac{\hbar^2}{2m_x} k_x^2 - E) dk_x$$

Recall the formula

$$\delta(f(x)) = \sum_n \frac{\delta(x-x_n)}{|f'(x_n)|},$$

where x_n are the simple zeroes of $f(x)$
(i.e., $f(x_n) = 0$ and $f'(x_n) \neq 0$ for each n).

For convenience, we can first change the integration variable:

$$k_x \rightarrow q_x = \frac{\hbar}{\sqrt{2m_x}} k_x$$

then,

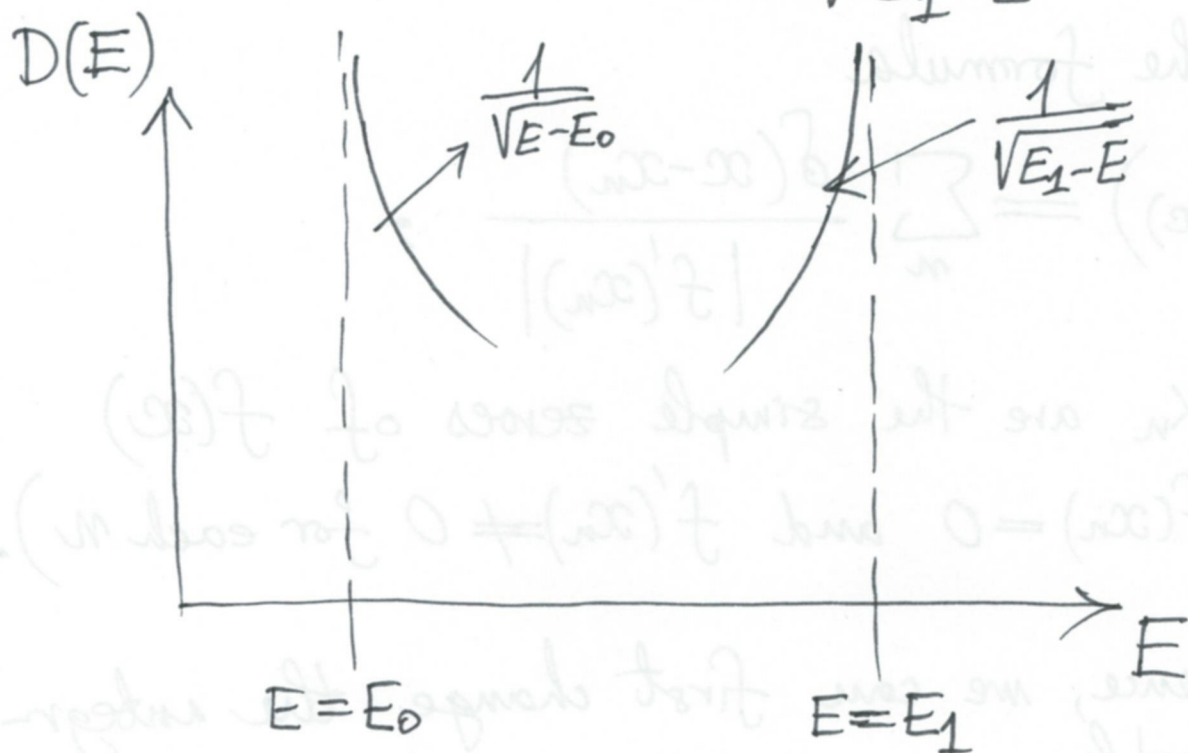
$f(q_x) = E_0 + q_x^2 - E$, if we choose the "+"
sign in the original expression (dispersion minimum
 $E_c = E_0$)

$$f(q_x) = 0 \Rightarrow q_{x_0} = \pm \sqrt{E - E_0}, \quad f'(q_{x_0}) = \pm 2\sqrt{E - E_0}$$

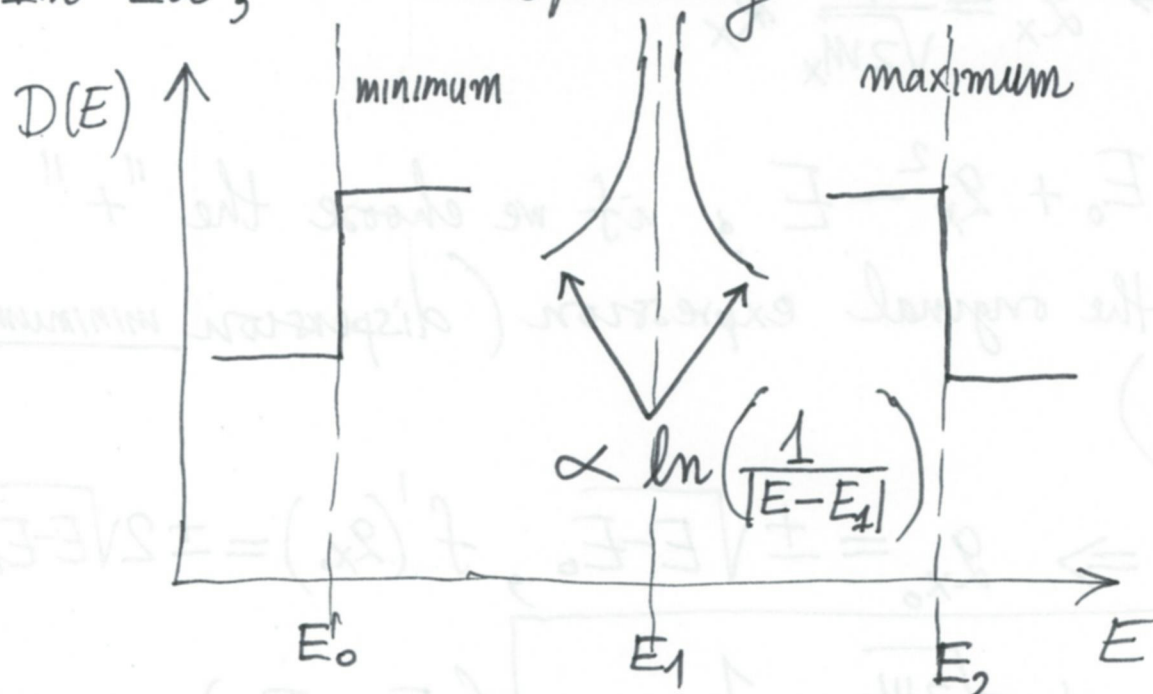
$$\Rightarrow D(E) = L_x \frac{\sqrt{2m_x}}{\pi\hbar} \frac{1}{\sqrt{E - E_0}} \quad (E > E_0)$$

In a similar way, for a dispersion maximum ("-" sign in front of k_x^2 !) we get ($E_0 = E_1$):

$$D(E) = L_x \frac{\sqrt{2m_x}}{\pi \hbar} \frac{1}{\sqrt{E_1 - E}} \quad (E < E_1)$$

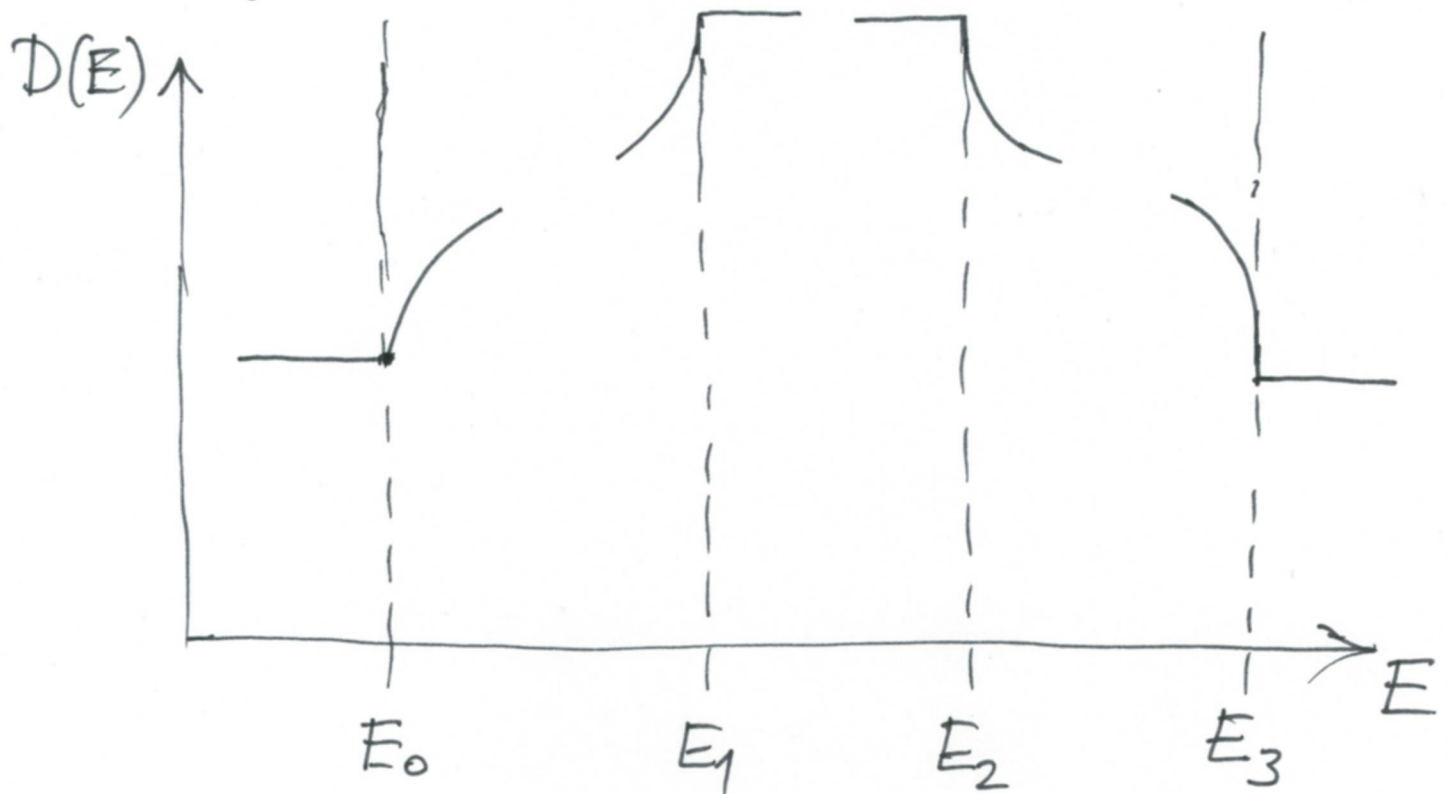


In 2d, the corresponding sketch looks like this:



Thus saddle-points in 2d lead to logarithmic singularities!

Finally, in 3d:



E_0 is minimum, E_3 maximum, while
 E_1 and E_2 are saddle points!

around E_0 : $D(E) = C_0 + V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E - E_0} \quad (E > E_0)$

-||- E_3 : $D(E) = C_0 + V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E_3 - E} \quad (E < E_3)$

-||- E_1 : $D(E) = C_1 - V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E_1 - E} \quad (E < E_1)$

-||- E_2 : $D(E) = C_2 - V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E - E_2} \quad (E > E_2)$