

* Free electron gas model due to Sommerfeld

→ collection of N noninteracting electrons in a volume V

→ wavefunction of each individual particle is a plane wave

$$\phi_{\vec{k}}(\vec{r}) = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}} \quad (\text{spm index suppressed})$$

→ Hamiltonian has only single-particle ~~kinetic~~ kinetic energy terms

$$\hat{H}_0 \phi_{\vec{k}} = -\frac{\hbar^2 \nabla^2}{2m} \phi_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \phi_{\vec{k}}$$

↑ eigenequation defines a dispersion $\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$ (parabolic)

relating wavevector to energy

→ Many-body wavefunction is the fully antisymmetrized Slater Determinant

$$\psi = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \phi_{k_1}(r_{\mathcal{P}1}) \phi_{k_2}(r_{\mathcal{P}2}) \dots \phi_{k_N}(r_{\mathcal{P}N})$$

$$= \frac{1}{\sqrt{N!}} \text{Det} \begin{pmatrix} \phi_{k_1}(r_{\mathcal{P}1}) & \phi_{k_2}(r_{\mathcal{P}1}) & \dots & \phi_{k_N}(r_{\mathcal{P}1}) \\ \phi_{k_1}(r_{\mathcal{P}2}) & \phi_{k_2}(r_{\mathcal{P}2}) & \dots & \phi_{k_N}(r_{\mathcal{P}2}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{k_1}(r_{\mathcal{P}N}) & \phi_{k_2}(r_{\mathcal{P}N}) & \dots & \phi_{k_N}(r_{\mathcal{P}N}) \end{pmatrix}$$

* Alternatively, describe system using abstract state vectors in the Grand Canonical ensemble

→ Hamiltonian expressed in occupation basis: $\hat{H}_0 = \sum_{k,\sigma} \epsilon_k \hat{n}_{k,\sigma}$

↑ measures how many in mode k,σ

(Second quantization $\hat{n}_{k,\sigma} = c_{k,\sigma}^\dagger c_{k,\sigma}$ with fermionic creation and annihilation operators obeying an anti-commutation rule

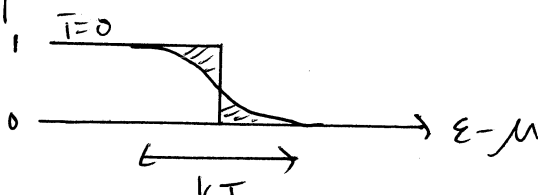
$$\{c_{k,\sigma}, c_{k',\sigma'}^\dagger\} = c_{k,\sigma} c_{k',\sigma'}^\dagger + c_{k',\sigma'}^\dagger c_{k,\sigma} = \delta_{kk'} \delta_{\sigma\sigma'}$$

→ the total particle number N (computed as an ensemble average of $\hat{N} = \sum_{k,\sigma} \hat{n}_{k,\sigma}$) is only fixed on average, and chemical potential μ is the proper thermodynamic variable

→ in thermal equilibrium, all bulk properties follow from populating the modes according to the Fermi function

$$\langle \hat{n}_{k,\sigma} \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$

→ typically, $E_F \gg k_B T$ so thermal effects are related to a small promotion of states across the Fermi level



* Computations take the form of a sum over k -space, where the k dependency enters only through ϵ_k

→ general form
$$\frac{1}{V} \sum_k g(\epsilon_k) \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} = \int \frac{d^3k}{(2\pi)^3} \frac{g(\epsilon_k)}{e^{\beta(\epsilon_k - \mu)} + 1}$$

→ can be reexpressed as

$$\int \frac{d^3k}{(2\pi)^3} \int d\epsilon \delta(\epsilon - \epsilon_k) \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1}$$

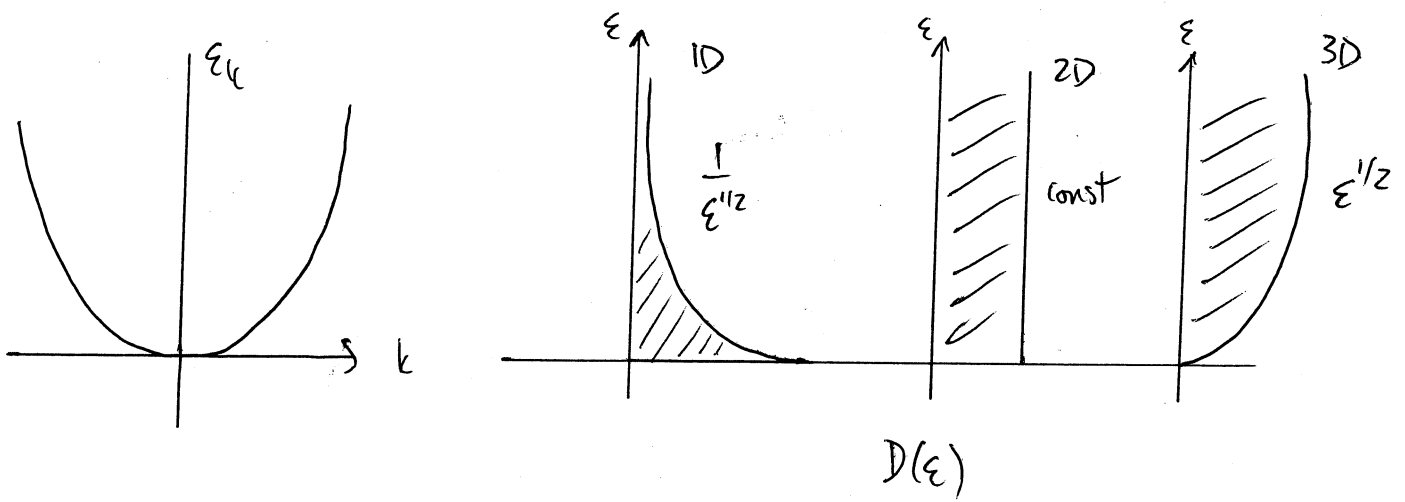
$$= \int d\epsilon \underbrace{\int \frac{d^3k}{(2\pi)^3} \delta(\epsilon - \epsilon_k)}_{\text{density of states}} \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1}$$

in terms of a density of states that counts the number of modes available in the energy window ϵ to $\epsilon + d\epsilon$

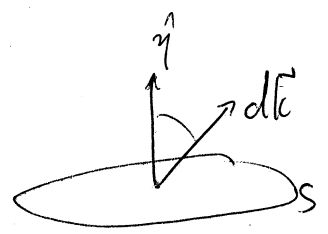
→ DOS turns out to be strongly dependent ~~the~~ on spatial dimensionality:

$$d^d k = \begin{cases} 2dk & d=1 \\ 2\pi k dk & d=2 \\ 4\pi k^2 dk & d=3 \end{cases} \left| \begin{array}{l} \epsilon = \epsilon_k \sim k^2 \Rightarrow k \sim \sqrt{\epsilon} \\ d\epsilon = 2k dk \Rightarrow dk \sim \frac{d\epsilon}{\sqrt{\epsilon}} \end{array} \right.$$

Hence $d^d k \sim k^{d-1} dk \sim \epsilon^{\frac{d-1}{2}} \cdot \frac{d\epsilon}{\sqrt{\epsilon}} \sim \epsilon^{\frac{d-2}{2}}$



- * More possibilities if the dispersion is not strictly parabolic
 - e.g. E_k may not be isotropic in k -space
 - it may not be monotonically increasing in all directions
 - infinitesimal energy change $dE_k = \vec{\nabla} E_k \cdot d\vec{k}$



$$= |\vec{\nabla} E_k| \hat{n} \cdot d\vec{k}$$

↑ unit normal to level surface of the dispersion

$$DOS \sim \int \frac{dS}{|\vec{\nabla} E_k|}$$

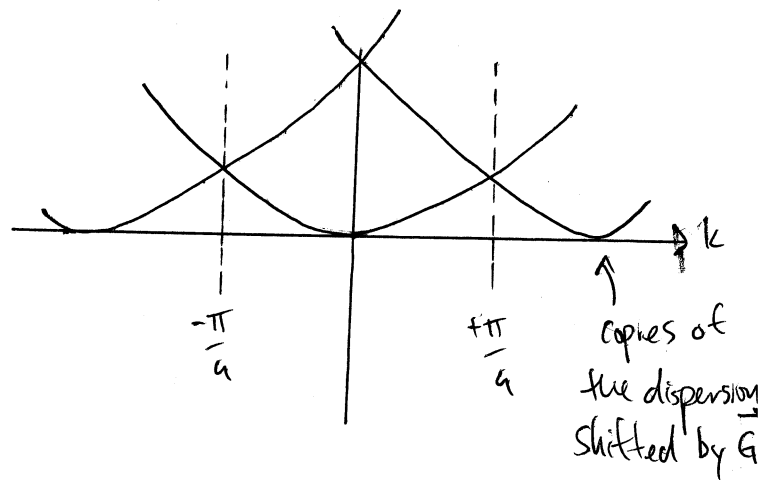
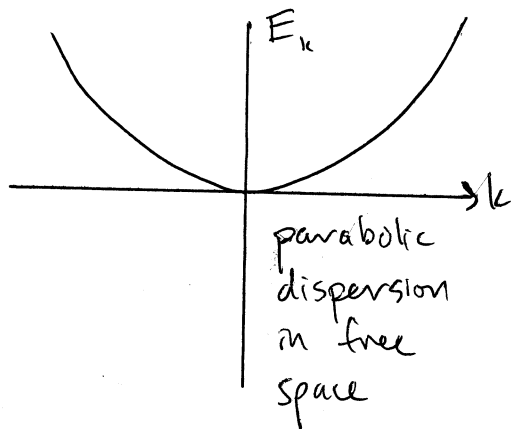
so there is a possibility of a divergent energy profile if the dispersion has regions that are flat (or nearly so) in k -space

→ these are so-called van Hove singularities:



* Next level of realism is to reintroduce the periodic background potential

→ we can already guess what will happen: fold all modes back into the BZ of the underlying Bravais lattice



→ leads to a complicated structure of "energy bands" in the BZ

→ since the potential is periodic, we know it can be expanded in Fourier components that are reciprocal lattice vectors

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

→ the same is true of the single-particle electron density $|\psi_{\vec{k}}(\vec{r})|^2$, which is the physical observable

→ the wavefunction itself has this form, up to an additional phase:

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

$$= e^{i\vec{k}\cdot\vec{r}} u(\vec{r})$$

Bloch's
Theorem
(\Rightarrow)

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

$$\psi_{\vec{k}+\vec{k}'}(\vec{r}) = \psi_{\vec{k}}(\vec{r}) e^{i\vec{k}'\cdot\vec{r}}$$

↑
function periodic
in the lattice

* Single-particle Hamiltonian

$$H = -\frac{\hbar^2 \nabla^2}{2m} + \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

→ stationary solutions to Schrödinger's equation

$$E_{\vec{k}} \psi_{\vec{k}}(\vec{r}) = H \psi_{\vec{k}}(\vec{r})$$

$$= \left(-\frac{\hbar^2 \nabla^2}{2m} + \sum_{\vec{G}'} U_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}} \right) \left(\sum_{\vec{G}''} C_{\vec{G}''} e^{i(\vec{k}+\vec{G}'')\cdot\vec{r}} \right)$$

$$= \sum_{\vec{G}''} \left(\frac{\hbar^2 (\vec{k}+\vec{G}'')^2}{2m} + \sum_{\vec{G}'} U_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}} \right) C_{\vec{G}''} e^{i(\vec{k}+\vec{G}'')\cdot\vec{r}}$$

→ pick out the \vec{G} component

$$\int d^3r e^{-i(\vec{k}+\vec{G})\cdot\vec{r}} E_{\vec{k}} \psi_{\vec{k}}(\vec{r}) = E_{\vec{k}} C_{\vec{G}}$$

$$= \int d^3r e^{-i(\vec{k}+\vec{G})\cdot\vec{r}} \sum_{\vec{G}''} \left(\frac{\hbar^2(\vec{k}+\vec{G}'')^2}{2m} + \sum_{\vec{G}'} U_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}} \right) C_{\vec{G}''} e^{i(\vec{k}+\vec{G}'')\cdot\vec{r}}$$

$$= \sum_{\vec{G}''} \left\{ \frac{\hbar^2(\vec{k}+\vec{G}'')^2}{2m} C_{\vec{G}''} \int d^3r e^{i(\vec{G}''-\vec{G})\cdot\vec{r}} \right.$$

$$\left. + \sum_{\vec{G}'} U_{\vec{G}'} C_{\vec{G}''} \int d^3r e^{i(\vec{G}'+\vec{G}''-\vec{G})\cdot\vec{r}} \right\}$$

$\delta_{\vec{G}, \vec{G}''}$

$\delta_{\vec{G}, \vec{G}'+\vec{G}''}$

* Arrive at an infinite set ~~of~~ of coupled linear equations

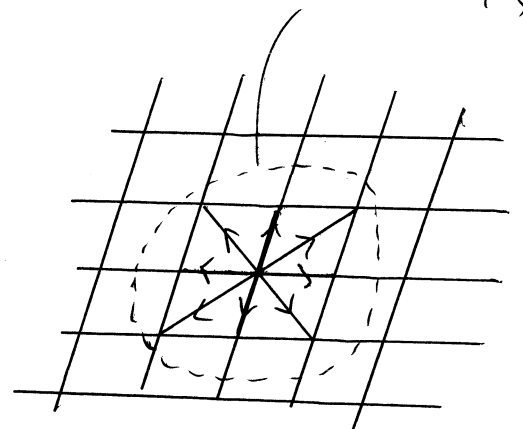
$$E_{\vec{k}} C_{\vec{G}} = E_{\vec{k}+\vec{G}} C_{\vec{G}} + \sum_{\vec{G}'} U_{\vec{G}'} C_{\vec{G}-\vec{G}'}$$

$$\{ \vec{G} : |\vec{G}| < G_{\max} \}$$

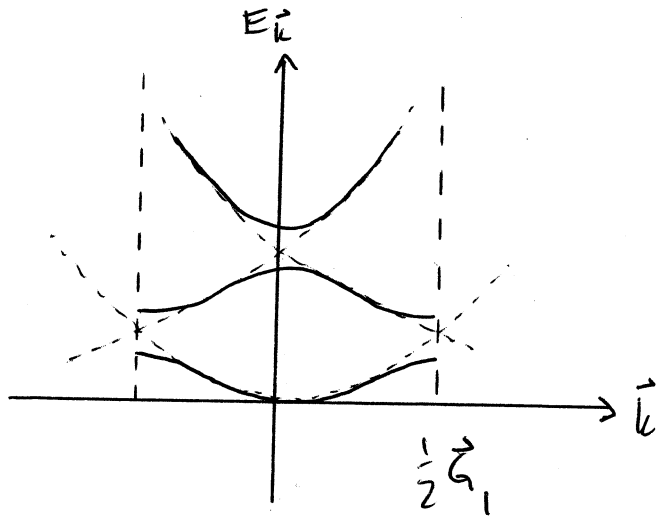
→ solve as a matrix problem
by truncating \vec{G} beyond
some range

(boundedness implies

$$\int d^3r |U(\vec{r})|^2 = \sum_{\vec{G}} |U_{\vec{G}}|^2 < \infty)$$



→ or note that only bands in close proximity can hybridize

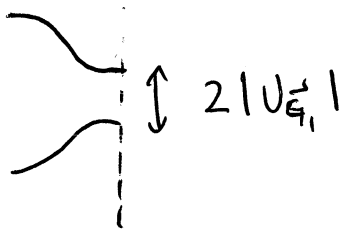


→ avoided level crossings open into band gaps

e.g. where $\varepsilon_{\vec{k}} \approx \varepsilon_{\vec{k}-\vec{G}_1}$ at the zone edge

$$0 = \begin{bmatrix} E - \varepsilon_{\vec{k}} & U_{\vec{G}_1} \\ U_{\vec{G}_1}^* & E - \varepsilon_{\vec{k}-\vec{G}_1} \end{bmatrix} \begin{bmatrix} C_{\vec{0}} \\ C_{-\vec{G}_1} \end{bmatrix}$$

$$\text{or } E_{\vec{k}, \pm} = \frac{1}{2} \left(\varepsilon_{\vec{k}} + \varepsilon_{\vec{k}-\vec{G}_1} \pm \sqrt{(\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}-\vec{G}_1})^2 + 4|U_{\vec{G}_1}|^2} \right)$$



the corresponding Fourier component sets the size of the gap

* 1D example with $g = \frac{2\pi}{a}$ and a BZ edge at $\frac{1}{2}g = \frac{\pi}{a}$

→ evaluate at $k = \frac{\pi}{a} - \delta k$

$$\epsilon_k = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} - \delta k \right)^2 = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} - \frac{2\pi}{a} \delta k + \delta k^2 \right)$$

$$\epsilon_{k-g} = \frac{\hbar^2}{2m} \left(-\frac{\pi}{a} - \delta k \right)^2 = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} + \frac{2\pi}{a} \delta k + \delta k^2 \right)$$

→ take linear combinations

$$\epsilon_k + \epsilon_{k-g} = \frac{\hbar^2}{2m} \left(\frac{2\pi^2}{a^2} + 2\delta k^2 \right)$$

$$\epsilon_k - \epsilon_{k-g} = \frac{\hbar^2}{2m} \left(-\frac{4\pi}{a} \delta k \right)$$

→ substitute

$$E_{\frac{\pi}{a} - \delta k, \pm} = \frac{1}{2} \left(\frac{\hbar^2}{2m} \left(\frac{2\pi^2}{a^2} + 2\delta k^2 \right) \pm \sqrt{\left(\frac{\hbar^2}{2m} \left(-\frac{4\pi}{a} \delta k \right) \right)^2 + 4|U_{\frac{\pi}{a}}|^2} \right)$$

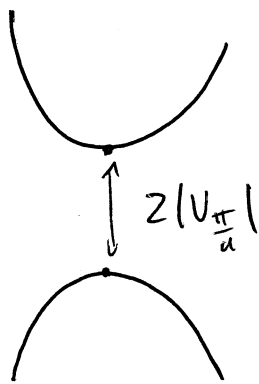
$$= \frac{1}{2} \left(\frac{\hbar^2}{2m} \left(\frac{2\pi^2}{a^2} + 2\delta k^2 \right) \pm 2|U_{\frac{\pi}{a}}| \left(1 + \frac{1}{2} \frac{\left(\frac{\hbar^2}{2m} \right)^2 \left(\frac{4\pi}{a} \delta k \right)^2}{4|U_{\frac{\pi}{a}}|^2} \right) \right)$$

$$= \frac{1}{2} \left(\frac{\hbar^2}{2m} \left(\frac{2\pi^2}{a^2} + 2\delta k^2 \right) \pm 2|U_{\frac{\pi}{a}}| \pm \frac{\left(\frac{\hbar^2}{2m} \right)^2 \left(\frac{4\pi}{a} \delta k \right)^2}{4|U_{\frac{\pi}{a}}|} \right)$$

$$= \frac{\hbar^2 \pi^2}{2ma^2} + \frac{\hbar^2 \delta k^2}{2m} \pm |U_{\frac{\pi}{a}}| \pm \frac{\left(\frac{\hbar^2}{2m}\right)^2 \frac{4\pi^2}{a^2} \delta k^2}{2|U_{\frac{\pi}{a}}|}$$

$$= \frac{\hbar^2 \pi^2}{2ma^2} + \frac{\hbar^2}{2m} \left[1 \pm \frac{\hbar^2}{2m} \cdot \frac{2\pi^2}{|U_{\frac{\pi}{a}}| a^2} \right] \delta k^2 \pm |U_{\frac{\pi}{a}}|$$

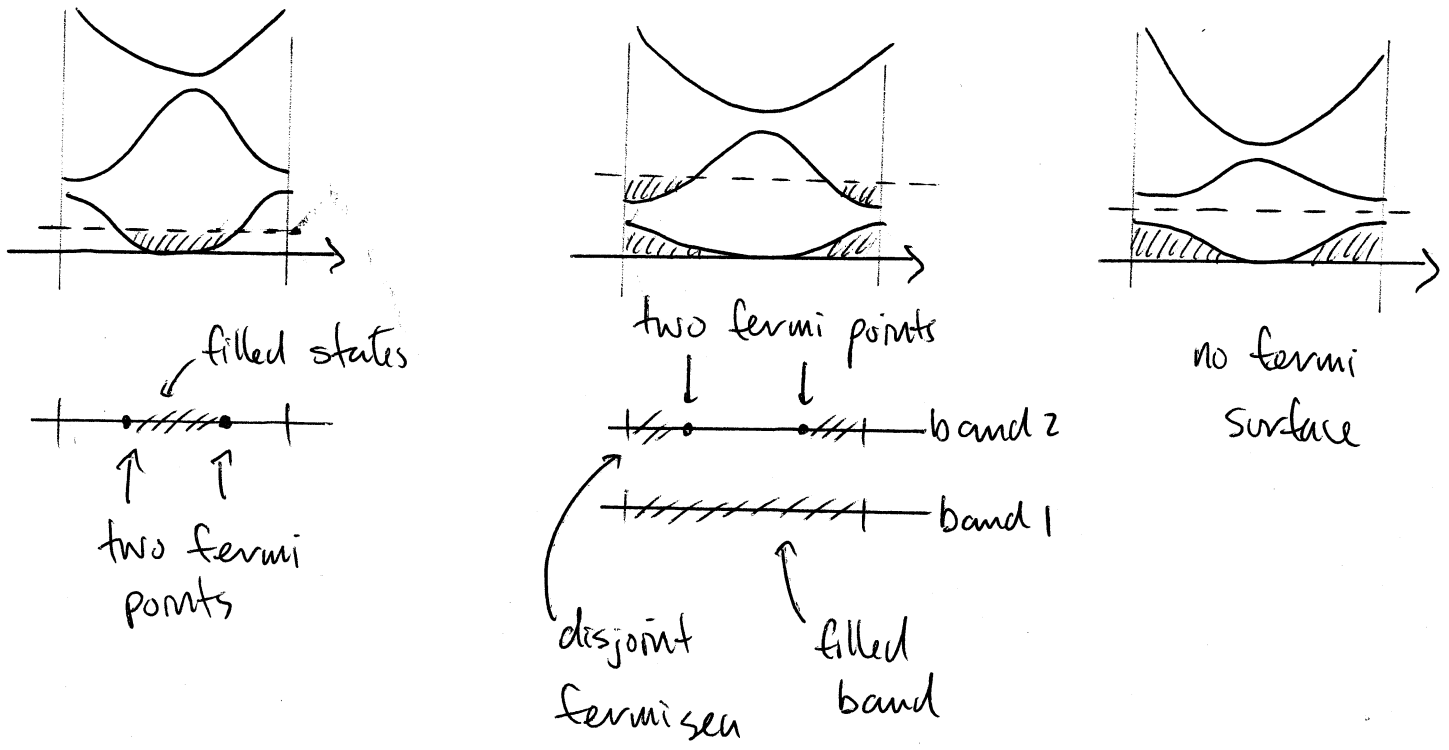
$$= \varepsilon\left(\frac{\pi}{a}\right) + \frac{\hbar^2}{2m_{\pm}^*} \delta k^2 \pm |U_{\frac{\pi}{a}}|$$



→ local curvature of the bands defines an effective mass

$$m_{\pm}^* = \frac{1}{\hbar^2} \left(\frac{\partial^2 E_{k,\pm}}{\partial k^2} \right)^{-1} = \frac{m}{1 \pm \frac{\hbar^2}{m} \cdot \frac{\pi^2}{|U_{\frac{\pi}{a}}| a^2}}$$

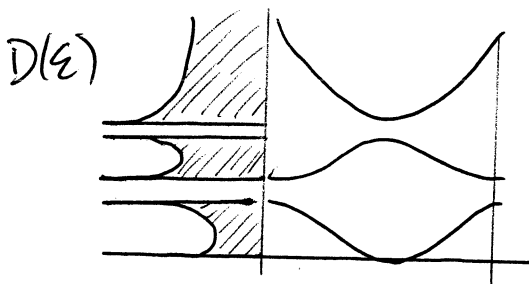
* Electronic behaviour depends largely on where the Fermi level sits within the band structure



* In the insulating case, carriers are only thermally activated

$$n_c = \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta(|U| + \hbar^2 k^2 / 2m^*)} + 1} \sim e^{-|U|/k_B T} \xrightarrow{\text{as } k_B T \rightarrow 0} 0$$

* DOS ~~is~~ is nontrivial = band gaps and van Hove singularities



Tight-binding bands

* there are other valid basis states besides plane waves!

→ each atomic location in the crystal has a set of atomic states associated with it

→ choose some subset that has good overlap with the valence and/or conduction bands

e.g. in Si, the 3s and 3p (usually in sp^3 combinations) offer a good description

* s-state band example

→ imagine a solid with one atom per unit cell

→ place an s-orbital $\phi(\vec{r}-\vec{R})$ at each lattice site \vec{R}

→ construct superpositions

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi(\vec{r}-\vec{R})$$

to get proper Bloch states

$$\begin{aligned} \text{NB } \psi_{\vec{k}}(\vec{r}+\vec{R}) &= \sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'} \phi(\vec{r}+\vec{R}-\vec{R}') = \sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}+\vec{R}')} \phi(\vec{r}-\vec{R}') \\ &= e^{i\vec{k}\cdot\vec{R}} \psi_{\vec{k}}(\vec{r}) \text{ etc.} \end{aligned}$$

* in real space

→ assume a general expansion $|\psi\rangle = \sum_{\vec{r}} \psi_{\vec{r}} |\phi_{\vec{r}}\rangle$

(in the nonorthogonal and not necessarily complete basis of states $\langle \vec{r}' | \phi_{\vec{r}} \rangle = \phi(\vec{r}' - \vec{r})$)

→ Schrödinger gives $\hat{H}|\psi\rangle = \sum_{\vec{r}} \psi_{\vec{r}} \hat{H}|\phi_{\vec{r}}\rangle = E \sum_{\vec{r}} \psi_{\vec{r}} |\phi_{\vec{r}}\rangle$

→ apply $\langle \phi_{\vec{r}'} |$ from the left to get

$$\sum_{\vec{r}} \langle \phi_{\vec{r}'} | \hat{H} | \phi_{\vec{r}} \rangle \psi_{\vec{r}} = E \sum_{\vec{r}} \langle \phi_{\vec{r}'} | \phi_{\vec{r}} \rangle \psi_{\vec{r}}$$

matrix form $H\psi = E S\psi$ of the generalized eigenvalue problem

* take advantage of translational symmetry

→ work in k -space with states

$$|\phi_{\vec{k}}\rangle = \sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}} |\phi_{\vec{r}}\rangle$$

$$\text{then } \langle \phi_{\vec{k}'} | \hat{H} | \phi_{\vec{k}} \rangle = \sum_{\vec{r}, \vec{r}'} e^{-i\vec{k}'\cdot\vec{r}'} e^{i\vec{k}\cdot\vec{r}} \langle \phi_{\vec{r}'} | \hat{H} | \phi_{\vec{r}} \rangle$$

$$= \sum_{\vec{r}} \sum_{\vec{r}' = \vec{r} + \delta\vec{r}} e^{-i(\vec{k}' - \vec{k})\cdot\vec{r}} e^{-i\vec{k}'\cdot\delta\vec{r}} \langle \phi_{\vec{r} + \delta\vec{r}} | \hat{H} | \phi_{\vec{r}} \rangle$$

$$= \sum_{\delta \vec{R}} \underbrace{\left(\sum_{\vec{R}} e^{-i(\vec{k}' - \vec{k}) \cdot \vec{R}} \right)}_{\delta_{\vec{k}, \vec{k}'}} e^{-i\vec{k}' \cdot \vec{R}} \underbrace{\langle \phi_{\vec{R} + \delta \vec{R}} | \hat{U} | \phi_{\vec{R}} \rangle}_{\equiv \langle \phi_{\delta \vec{R}} | \hat{U} | \phi_0 \rangle}$$

by transl. symmetry

$$= \sum_{\delta \vec{R}} e^{-i\vec{k} \cdot \delta \vec{R}} (-t(\delta \vec{R})) \delta_{\vec{k}, \vec{k}'}$$

↑ "hopping integral"

→ similarly,

$$\begin{aligned} \langle \phi_{\vec{k}'} | \phi_{\vec{k}} \rangle &= \sum_{\delta \vec{R}} e^{-i\vec{k} \cdot \delta \vec{R}} \langle \phi_{\delta \vec{R}} | \phi_0 \rangle \delta_{\vec{k}, \vec{k}'} \\ &= \sum_{\delta \vec{R}} e^{-i\vec{k} \cdot \delta \vec{R}} s(\delta \vec{R}) \delta_{\vec{k}, \vec{k}'} \end{aligned}$$

↑ overlap

→ ~~expanded~~ generalized eigenvalue problem collapses to the algebraic relation

$$- \sum_{\delta \vec{R}} e^{-i\vec{k} \cdot \delta \vec{R}} t(\delta \vec{R}) = \epsilon_{\vec{k}} \sum_{\delta \vec{R}} e^{-i\vec{k} \cdot \delta \vec{R}} s(\delta \vec{R})$$

→ both $-t$ and s decay rapidly with separation,
 so expand in nearest-neighbor shells

$$\begin{aligned}
 -t_0 + \sum_{\vec{r}_1} e^{-i\vec{k}\cdot\vec{r}_1} (-t_1) + \sum_{\vec{r}_2} e^{-i\vec{k}\cdot\vec{r}_2} (-t_2) + \dots \\
 = \epsilon_k \left(1 + \sum_{\vec{r}_1} e^{-i\vec{k}\cdot\vec{r}_1} s_1 + \sum_{\vec{r}_2} e^{-i\vec{k}\cdot\vec{r}_2} s_2 + \dots \right)
 \end{aligned}$$

eg. for the 1D chain

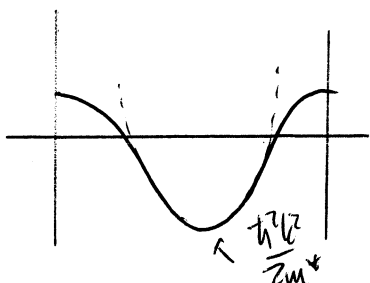
$$\epsilon_k = \frac{-t_0 - 2t_1 \cos ka - 2t_2 \cos 2ka - \dots}{1 + 2s_1 \cos ka + 2s_2 \cos 2ka + \dots}$$

$$\approx (-t_0 - 2t_1 \cos ka - \dots) (1 - 2s_1 \cos ka - \dots)$$

$$= -t_0 - 2(t_1 + t_0 s_1) \cos ka + \dots$$

$$= -t_0 - 2(t_1 + t_0 s_1) \left(1 - \frac{1}{2} k^2 a^2\right)$$

$$= -(t_0 + 2t_1 + 2t_0 s_1) + \underbrace{(t_1 + t_0 s_1) a^2 k^2}_{\approx \frac{\hbar^2}{2m^*}}$$



$\approx \frac{\hbar^2}{2m^*}$ at the bottom
 of the band