* 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

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

  - → Hamiltonian has only single-particle kinetic energy terms

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

eigenequation defines a dispersion $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ (parabolic) relating wavevector to energy

  - → Many-body wavefunction is the fully antisymmetrized Slater Determinant

$$\psi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_{k_1}(r_{P1}) \phi_{k_2}(r_{P2}) \cdots \phi_{k_N}(r_{PN})$$

$$= \frac{1}{\sqrt{N!}} \mathrm{Det} \begin{pmatrix} \phi_{k_1}(r\ ) & \phi_{k_2}(r\ ) & \cdots & \phi_{k_N}(r\ ) \\ \phi_{k_1}(r_1\ ) & \phi_{k_2}(r\ ) & \cdots & \phi_{k_N}(r_{P2}) \\ \vdots & & & \vdots \\ \phi_{k_1}(r\ ) & \phi_{k_2}(r\ ) & \cdots & \phi_{k_N}(r\ ) \end{pmatrix}$$

* Alternatively, describe system using <u>abstract state vectors</u> in the <u>Grand Canonical ensemble</u>

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

measures how many in mode k,σ

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

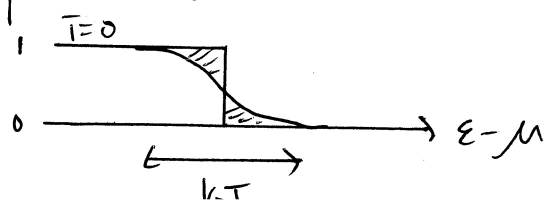
$$\{c_{k\sigma}, c^{+}_{k'\sigma'}\} = c_{k\sigma} c^{+}_{k'\sigma'} + c^{+}_{k'\sigma'} c_{k\sigma} = \delta_{kk'} \delta_{\sigma\sigma'}$$
)

→ 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

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

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

→ Can be reexpressed as

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

$$= \int d\varepsilon \underbrace{\int \frac{d^3k}{(2\pi)} \delta(\varepsilon-\varepsilon_k)} \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}$$

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

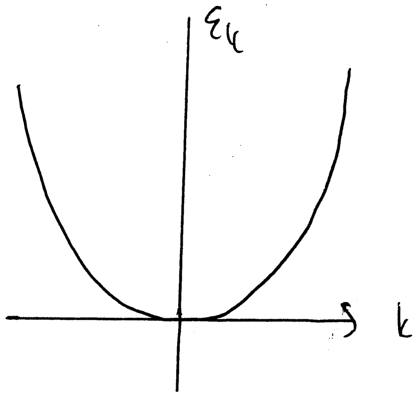
→ DOS turns out to be strongly dependent on spatial dimensionality:

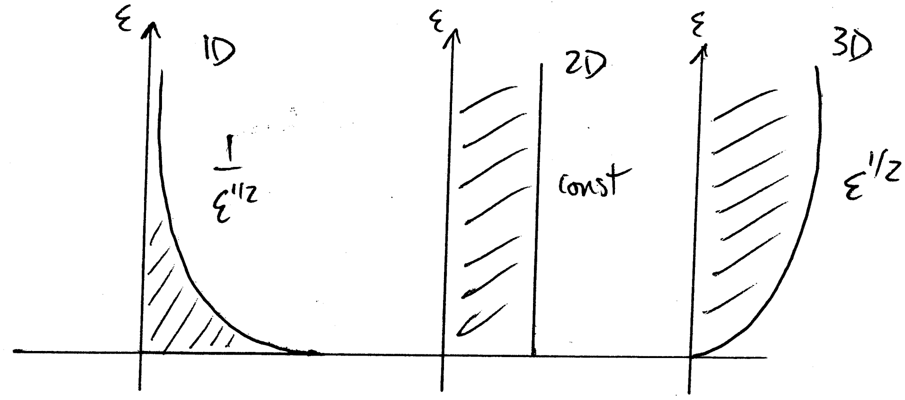
$$d^dk = \begin{cases} 2dk & d=1 \\ 2\pi k\,dk & d=2 \\ 4\pi k^2\,dk & d=3 \end{cases}$$

$\varepsilon = \varepsilon_k \sim k^2 \Rightarrow k \sim \sqrt{\varepsilon}$

$d\varepsilon = 2k\,dk \Rightarrow dk \sim \frac{d\varepsilon}{\sqrt{\varepsilon}}$

Hence $d^dk \sim k^{d-1}dk \sim \varepsilon^{\frac{d-1}{2}} \cdot \frac{d\varepsilon}{\varepsilon^{\frac{1}{2}}} \sim \varepsilon^{\left(\frac{d-2}{2}\right)}$





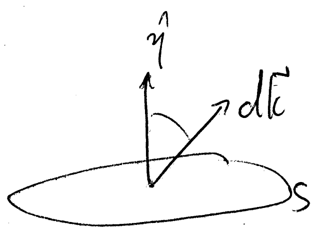
$D(\varepsilon)$

* More possibilities if the dispersion is not strictly parabolic

→ e.g. ε_k may not be isotropic in k-space

→ it may not be monotonically increasing in all directions

→ infinitesimal energy change $d\varepsilon_k = \vec{\nabla}\varepsilon_k \cdot d\vec{k}$



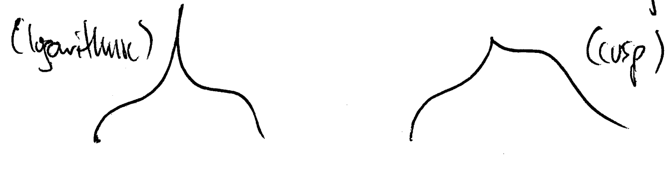
$$= |\vec{\nabla}\varepsilon_k|\, \hat{\eta} \cdot d\vec{k}$$

unit normal to level surface of the dispersion

$$\text{DOS} \sim \int \frac{dS}{|\nabla\varepsilon_k|}$$

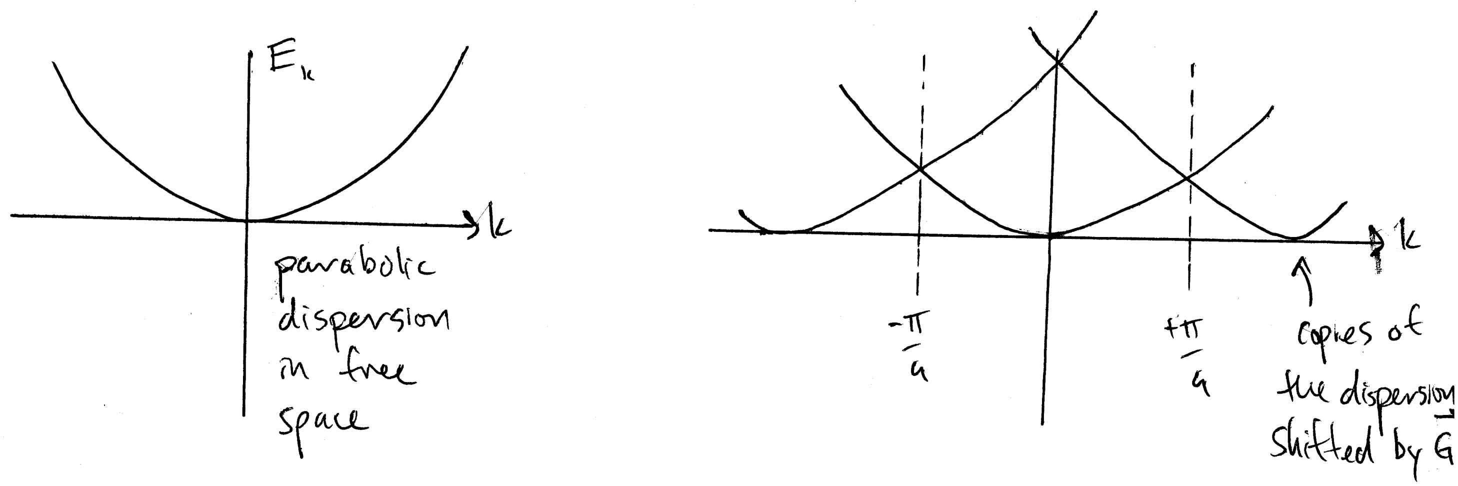
so there is a possibility of a divergent energy profile if the dispersion has regions that are flat (or nearly so) in k-space

→ 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:

$$\psi_k(\vec{r}) = \sum_{\vec{G}} C_{\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \quad \underset{\Longleftrightarrow}{\text{Bloch's Theorem}} \quad \begin{aligned} \psi_{\vec{k}}(\vec{r}+\vec{R}) &= \psi_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{R}} \\ \psi_{\vec{k}+\vec{k}'}(\vec{r}) &= \psi_{\vec{k}}(\vec{r}) e^{i\vec{k}'\cdot\vec{r}} \end{aligned}$$

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

↑ 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

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

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

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

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

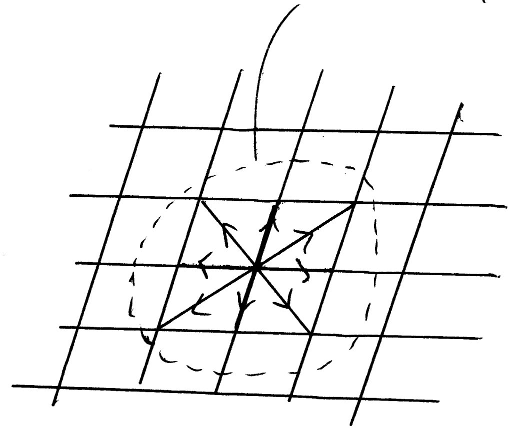
* Arrive at an infinite set ~~of~~ of coupled linear equations

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

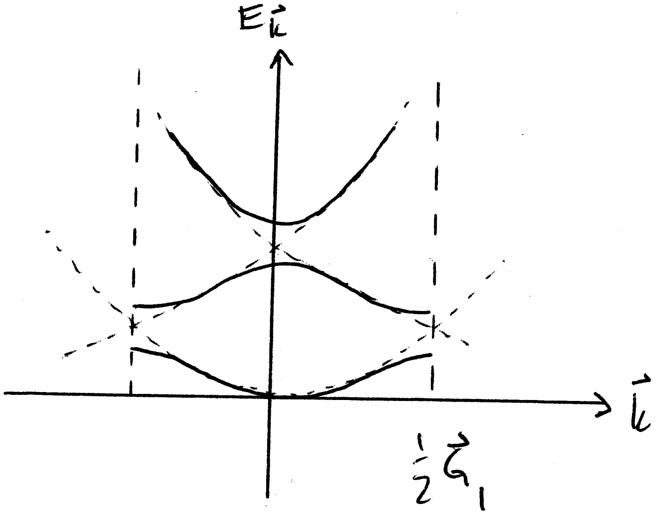
$\{\vec{G} : |\vec{G}| < G_{max}\}$

→ 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

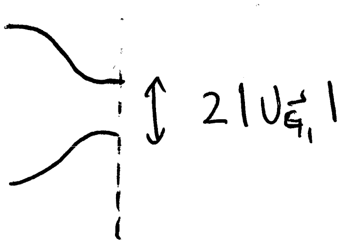


→ avoided level crossings open into band gaps

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

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

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 $k = \frac{\pi}{a} - \delta k$

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

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

→ take linear combinations

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

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

→ substitute

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

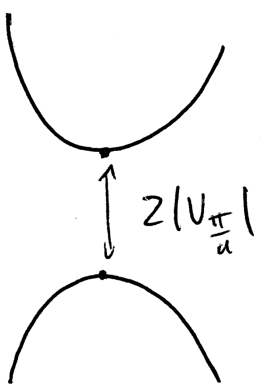
$$= \frac{1}{2}\left(\frac{\hbar^2}{2m}\left(\frac{2\pi^2}{a^2} + 2\delta k^2\right) \pm 2\left|U_{\frac{\pi}{a}}\right|\left(1 + \frac{1}{2}\frac{\left(\frac{\hbar^2}{2m}\right)^2\left(\frac{4\pi}{a}\delta k\right)^2}{4\left|U_{\frac{\pi}{a}}\right|^2}\right)\right)$$

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

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

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

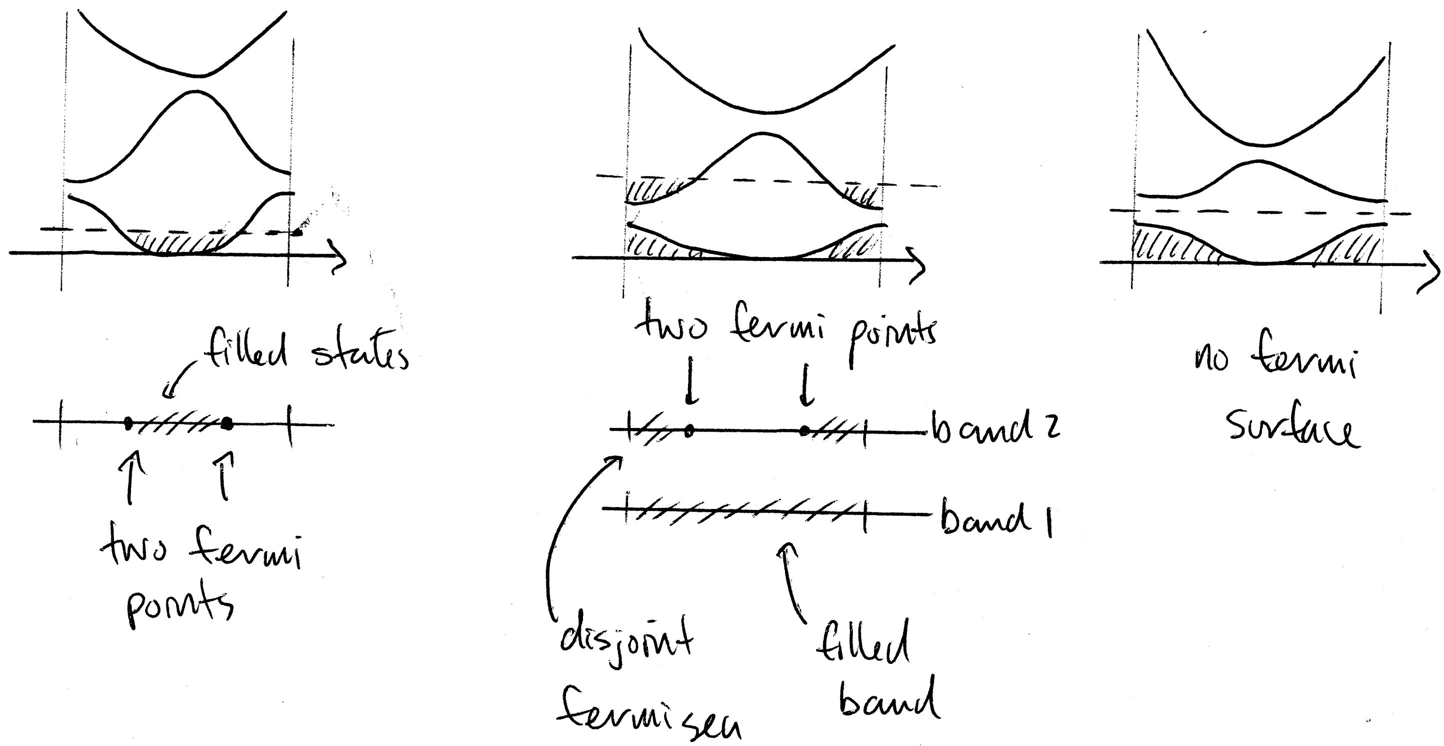
$$= \varepsilon\left(\frac{\pi}{a}\right) + \frac{\hbar^2}{2m^*_\pm} \delta k^2 \pm |U_{\frac{\pi}{a}}|$$



→ local curvature of the bands defines an effective mass

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

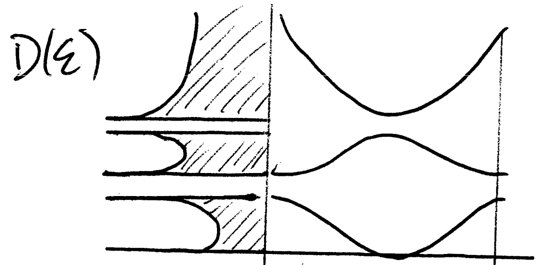
* Electronic behavior depends largely on where the Fermi level sits within the band structure



* In the insulating case, carriers are only thermally activated

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

* DOS 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 <u>one</u> 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

<u>NB</u> $$\psi_{\vec{k}}(\vec{r}+\vec{R}) = \sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'} \phi(\vec{r}+\vec{R}-\vec{R}') = \sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}+\vec{R}')} \phi(\vec{r}-\vec{R}')$$

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

* 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 $\hat{H}|\psi\rangle = \sum_{\vec{R}} \psi_{\vec{R}} \hat{H}|\phi_{R}\rangle = E \sum_{\vec{R}} \psi_{\vec{R}} |\phi_{\vec{R}}\rangle$

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

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

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

* take advantage of translational symmetry
  → work in k-space with states

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

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

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

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

by transl. symmetry

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

"hopping integral"

→ similarly,

$$\langle \phi_{\vec{k}'} | \phi_{\vec{k}} \rangle = \sum_{\delta\vec{R}} e^{-i\vec{k}\cdot\delta\vec{R}} \langle \phi_{\delta\vec{R}} | \phi_0 \rangle\, \delta_{\vec{k},\vec{k}'}$$

$$= \sum_{\delta\vec{R}} e^{-i\vec{k}\cdot\delta\vec{R}} s(\delta\vec{R})\, \delta_{\vec{k},\vec{k}'}$$

overlap

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

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

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

$$-t_0 + \sum_{\vec{\eta}_1} e^{-i\vec{k}\cdot\vec{\eta}_1}(-t_1) + \sum_{\vec{\eta}_2} e^{-i\vec{k}\cdot\vec{\eta}_2}(-t_2) + \cdots$$

$$= \varepsilon_k\left(1 + \sum_{\vec{\eta}_1} e^{-i\vec{k}\cdot\vec{\eta}_1} s_1 + \sum_{\vec{\eta}_2} e^{-i\vec{k}\cdot\vec{\eta}_2} s_2 + \cdots\right)$$

e.g. for the 1D chain

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

$$\simeq (-t_0 - 2t_1\cos ka - \cdots)(1 - 2s_1\cos ka - \cdots)$$

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

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

$$= -(t_0 + 2t_1 + 2t_0 s_1) + \underbrace{(t_1 + t_0 s_1)a^2}_{\equiv \frac{\hbar^2}{2m^*} \text{ at the bottom of the band}} k^2$$