What is Solid-State Physics?

Model physical parameters conferred by thermodynamically-large ensembles of microscopic systems forming a solid

- isotropic "gas" (continuous symmetry) / ordered lattices (periodic/discrete symmetry) / amorphous ("no" symmetry)
- interacting (additional terms in Hamiltonian) / noninteracting (statistics)

- what "physical parameters"?

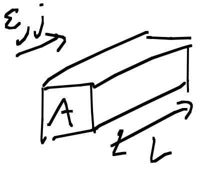
linear response static properties: change A, measure proportional change in B, where "property" is proportionality const.

spectroscopy: Absolute value of B not as important as (nonlinear) functional form + critical values of A.

Linear response

Example 1: Electric field $\vec{\mathcal{E}} \longrightarrow$ charge current density $\vec{j}$: electrical conductivity σ

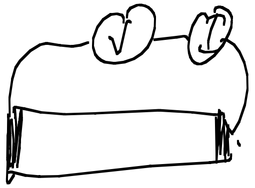
- $j = \sigma \mathcal{E}$ "Ohm's law"



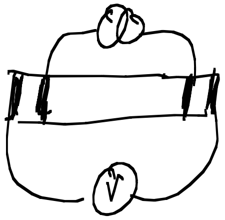
$$\frac{L}{\sigma A} jA = \mathcal{E}L \rightarrow V = IR$$

- measurement

two-wire



four-wire



- RT values $\left[\frac{S}{cm}\right]$: quartz $10^{-18} < \sigma < 10^{6}$ Ag
("insulator")

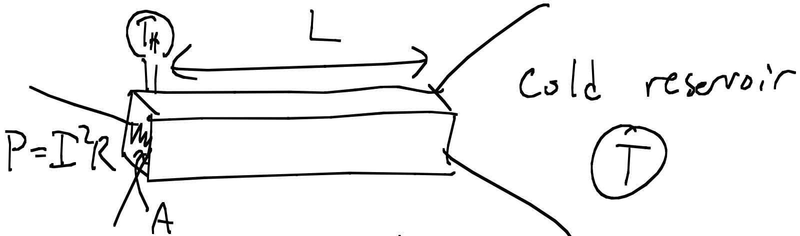
Example 2

Thermal gradient $\nabla T \longrightarrow$ heat flux j_Q : Thermal conductivity K

- $j_Q = -K \nabla T$ (equivalent to $j = \sigma \mathcal{E}$ for $\mathcal{E} = -\nabla \phi$)

  "Fourier's Law"

- measurement



$$K = \left(\frac{T_H - T}{L} \right) \frac{PL}{A}$$

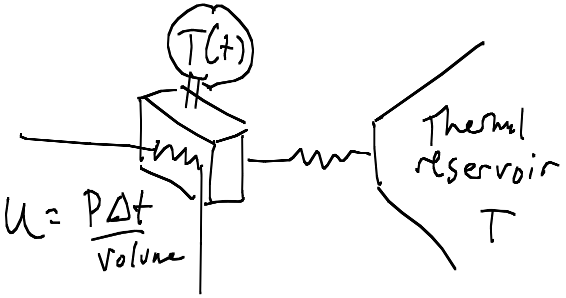
- RT values $\left[\frac{W}{K\,cm}\right]$: glass $1 < K <$ diamond 10^3

Example 3

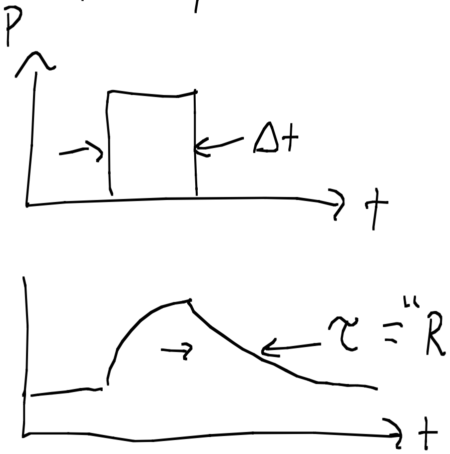
(work) energy density $U \longrightarrow$ change in Temperature ΔT: specific heat capacity C_v

- $U = C_v \Delta T$

- Measurement at "constant Temp": pulse method



$U = \frac{P\Delta t}{\text{volume}}$



$\tau = \text{"}RC\text{"} = \frac{C}{G}$

- RT values $\left[\frac{J}{K\,cm^3}\right]$: (almost everything) $C_v \sim 1$

Example 4

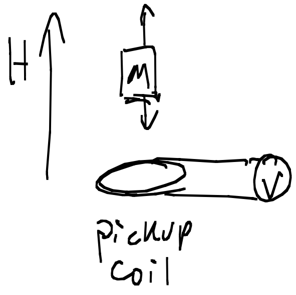
Magnetic field $\vec{H}$ ⟶ magnetization $\vec{M}$: magnetic susceptibility χ

- $M = \chi H \longrightarrow B = H + 4\pi M = (1 + 4\pi\chi) H = \mu H$

- Measurement

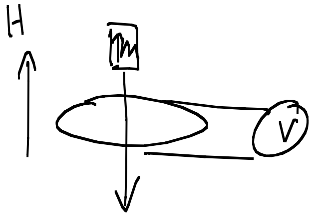
inductive

"Vibrating sample Magnetometer"



flux

SQUID



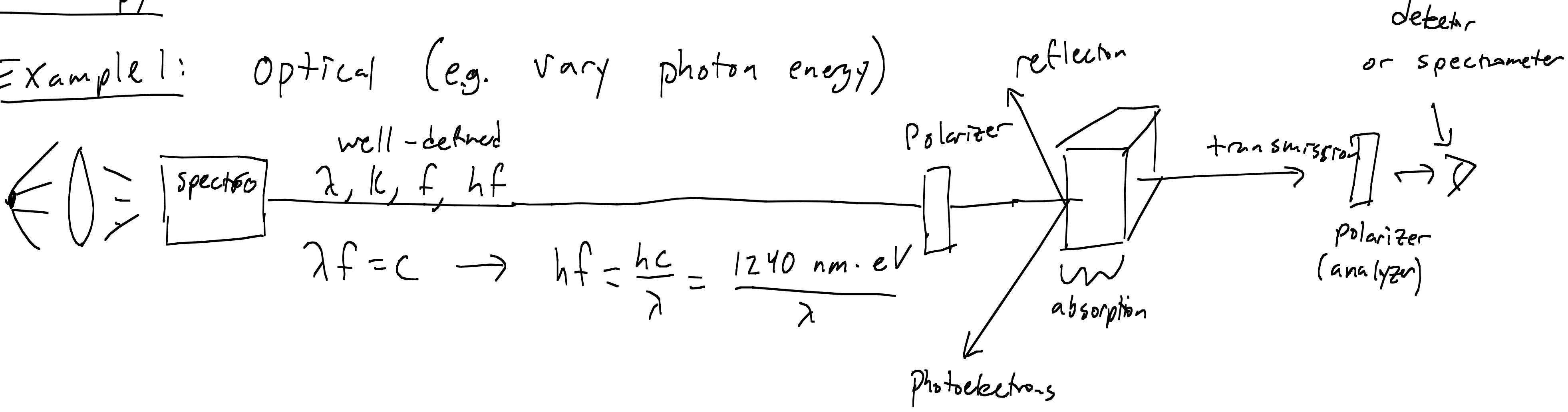
- RT values: $\chi > 0$ (paramagnetic)

  $\chi < 0$ (diamagnetic)

  $\chi \to \infty$ (ferromagnetic)

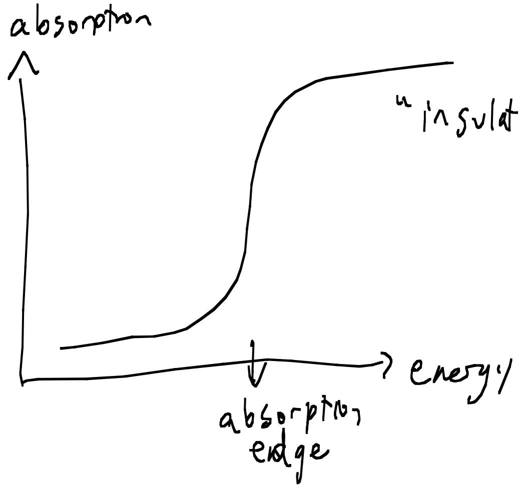
Spectroscopy

Example 1: optical (e.g. vary photon energy)

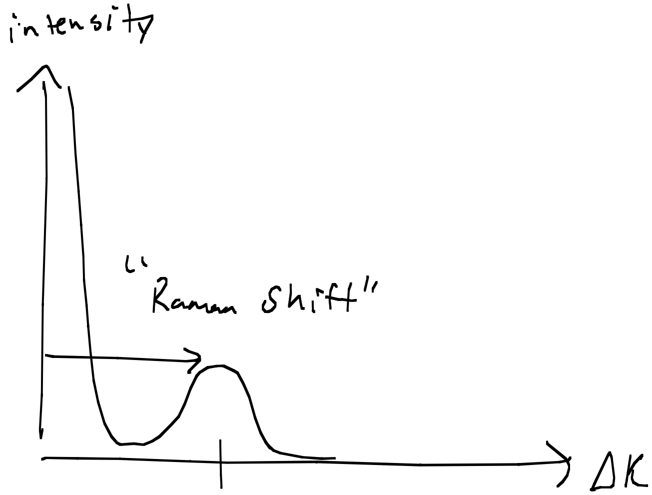


$$\lambda f = c \rightarrow hf = \frac{hc}{\lambda} = \frac{1240\ \text{nm}\cdot\text{eV}}{\lambda}$$

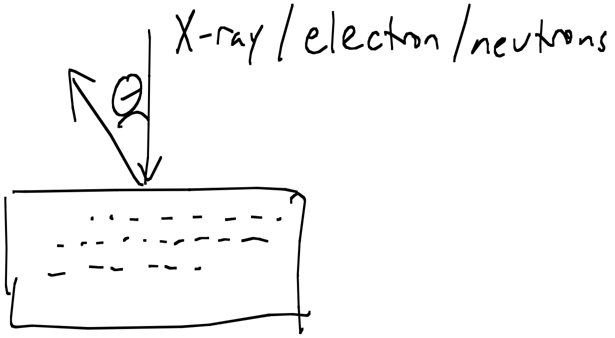
linear

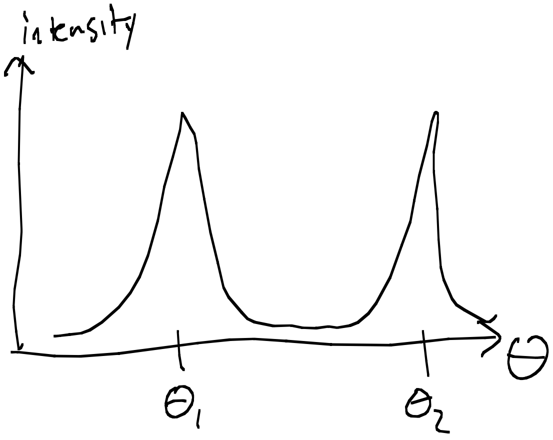


nonlinear



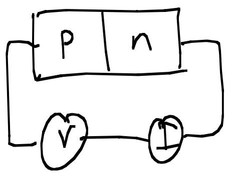
Example 2 : diffractive

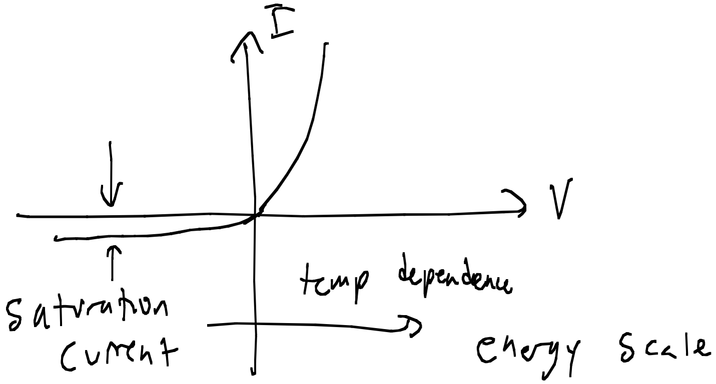




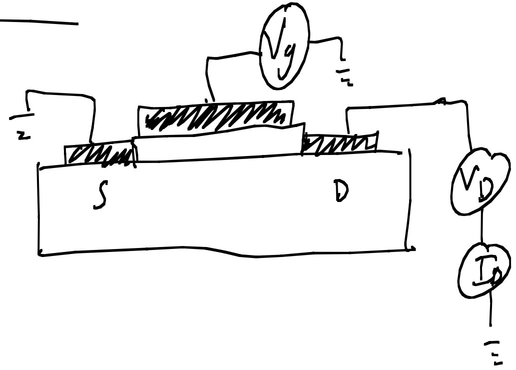
Example 3: electron transport ("device" physics)

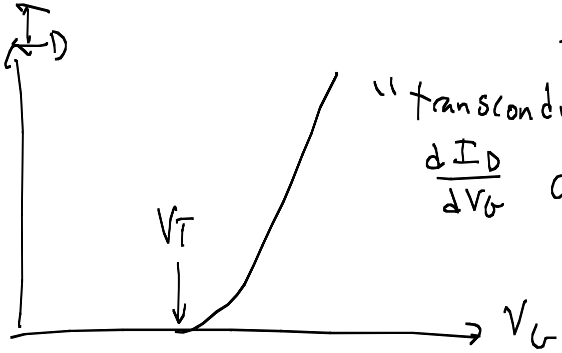
"local"





"nonlocal"



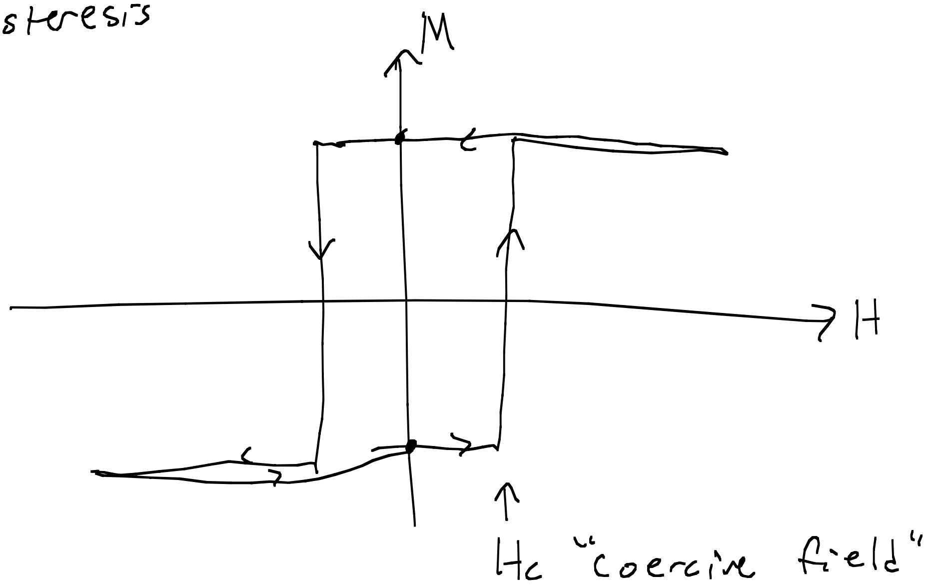


"transconductance"

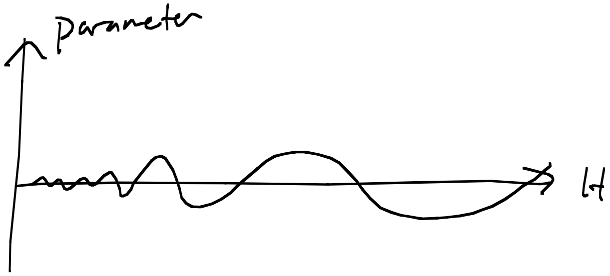
$$\frac{dI_D}{dV_G} \propto \text{mobility}$$

Example 4: Magnetic field

- ferromagnetic hysteresis



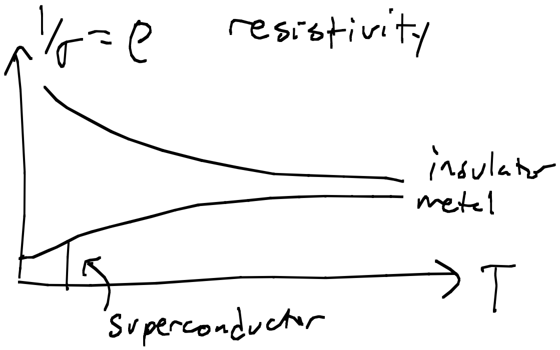
- oscillations w period $1/H$ for most physical parameters (de Haas - van Alphen)



As a function of temperature: Classification and physical regimes

- heat capacity regimes: ~const at high T, $\propto T^3$ low T, $\propto T$ very low T

- conductivity

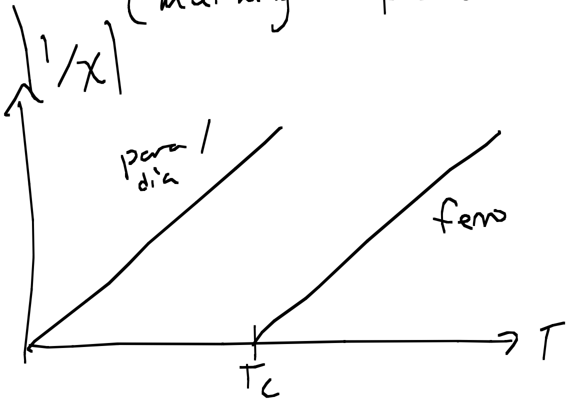


} clear qualitative difference!

- Susceptibility

  $|1/\chi|$ increases w/ T for (para/dia)magnet

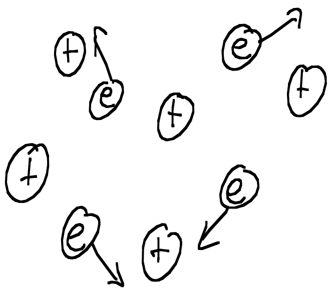
  zero below critical T_c for ferromagnet (marking phase transition)



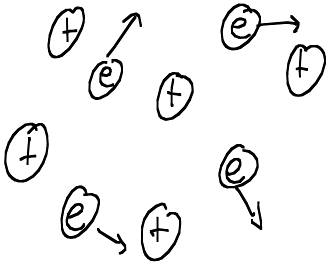
Classical Model of Metals (Drude, 1900)

ideal electron gas:

In equilibrium $\mathcal{E} = 0$ $\qquad\qquad$ $\mathcal{E} \neq 0$



$\langle v \rangle = 0$



$\langle v \rangle \neq 0$

equipartition: $\frac{1}{2} m v^2 = \frac{3}{2} k_B T \longrightarrow v = \sqrt{\frac{3 k_B T}{m}}$, $U = \frac{3}{2} n k_B T$

electron density

Eqn of motion $(\mathcal{E} \neq 0)$

$$ma = m\dot{v} = \dot{p} = F$$

$$\frac{dp}{dt} = -\underset{\substack{\uparrow \\ \text{Coulomb}}}{e\mathcal{E}} - \underbrace{\frac{p}{\tau}}_{\substack{\text{Collision} \\ \text{(relaxation)}}}$$

scattering time

Solution for const. $\mathcal{E}$

In steady state, $p = -e\mathcal{E}\tau$ so $\overset{\text{“drift velocity”}}{v_D} = \frac{p}{m} = -\frac{e\tau}{m}\mathcal{E} = \overset{\text{“mobility”}}{\mu}\mathcal{E}$

current density (charge flux) $j = -env_D = -ne\mu\mathcal{E} = \overset{\text{“conductivity”}}{\sigma}\mathcal{E}$

$$\underline{\sigma \equiv \frac{ne^2\tau}{m}}$$ Drude conductivity

- what are n and τ?

$$n \sim \frac{\overset{\frac{g}{cm^3}}{\text{mass density}}}{\underset{\frac{g}{mol}}{\text{atomic mass}}} \left(\overset{\frac{\text{atoms}}{\text{mol}}}{\text{Avogadro's const}}\right) \cdot Z \sim 10^{23}\ \text{cm}^{-3}$$

Volume per electron $\frac{1}{n} = \frac{4\pi}{3} r_s^3 \longrightarrow r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \sim 2\text{-}3\,a_0$

Scattering time τ

Empirical $\sigma \sim 10^6 \frac{S}{cm}$ for good metals @ RT

$$\sigma = \frac{ne^2\tau}{m} \longrightarrow \tau = \frac{m\sigma}{ne^2}$$

$$[\sigma] : \frac{S}{cm} = \frac{1}{\Omega\, cm} = \frac{C/s}{V cm} = \frac{e}{1.6\times10^{-19}\ V\, cm\, s} = \frac{e^2}{1.6\times10^{-19}\ eV\cdot cm\cdot s}$$

$$[m] : 5.11\times10^5\ eV/c^2$$ (electron mass)

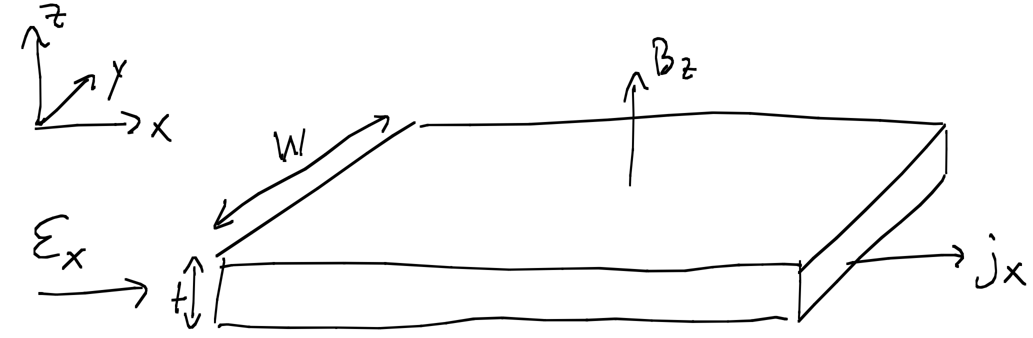
$$\tau = \frac{\dfrac{5\times10^5\ \cancel{eV}}{9\times10^{20}\ \cancel{cm^2}/\cancel{s^2}} \cdot 10^6 \dfrac{\cancel{e^2}}{1.6\times10^{-19}\ \cancel{eV}\ \cancel{cm}\ \cancel{s}}}{10^{23}\ \cancel{cm^{-3}}\ \ \cancel{e^2}} \sim 10^{-14}\ s$$

easier to compare to lengthscale $\lambda = v\tau$ "mean free path"

k_BT @ RT (300K) = 0.026 eV $\sim \frac{1}{40}$ eV $\quad v = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\cdot 0.026\ \cancel{eV}}{5\times10^5\ \cancel{eV}}}\cdot c \sim 10^7 \frac{cm}{s}$

$\lambda = v\tau \sim 10^{-7}$ cm (1nm, atomic lengthscale so model is self-consistent so far!)

τ – independent quantity : Hall effect



$$\frac{d\vec{p}}{dt} = -e\left(\vec{\mathcal{E}} + \frac{\vec{p}}{m} \times \vec{B}\right) - \frac{\vec{p}}{\tau}$$

Components:

$$x: \quad \dot{p}_x = -e\mathcal{E}_x - \frac{eB_z}{m}p_y - \frac{p_x}{\tau}$$

$$y: \quad \dot{p}_y = -e\mathcal{E}_y + \frac{eB_z}{m}p_x - \frac{p_y}{\tau}$$

Units : $\left[\frac{eB}{m}\right] = \frac{1}{\text{time}}$

define $\omega_c \equiv \frac{eB_z}{m}$

"cyclotron frequency"

In steady-state ($\dot{\vec{p}} = 0$, mult. by $\frac{ne\tau}{m}$)

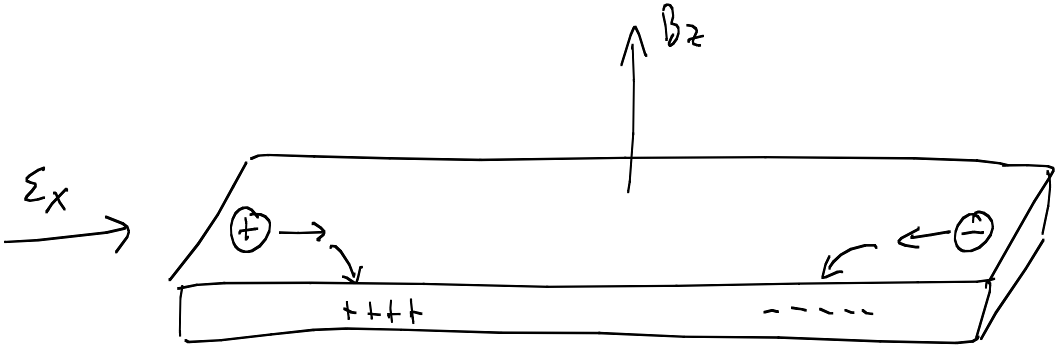
$$\sigma_0 \mathcal{E}_x = \omega_c \tau j_y + j_x$$

$$\sigma_0 \mathcal{E}_y = -\omega_c \tau j_x + j_y$$

$$\begin{bmatrix} \mathcal{E}_x \\ \mathcal{E}_y \end{bmatrix} = \frac{1}{\sigma_0} \begin{bmatrix} 1 & \omega_c \tau \\ -\omega_c \tau & 1 \end{bmatrix} \begin{bmatrix} j_x \\ j_y \end{bmatrix} \longrightarrow \vec{\mathcal{E}} = \overleftrightarrow{\rho} \, \vec{j}$$

$$\overleftrightarrow{\rho} = \begin{bmatrix} \rho_{xx} & \rho_{xy} \\ -\rho_{xy} & \rho_{yy} \end{bmatrix}$$

off-diagonal element : $\dfrac{\omega_c \tau}{\sigma_0} = \dfrac{\frac{\cancel{e}B}{\cancel{m}}\cancel{\tau}}{\frac{ne^{\cancel{2}}\cancel{\tau}}{\cancel{m}}} = \dfrac{B}{ne}$



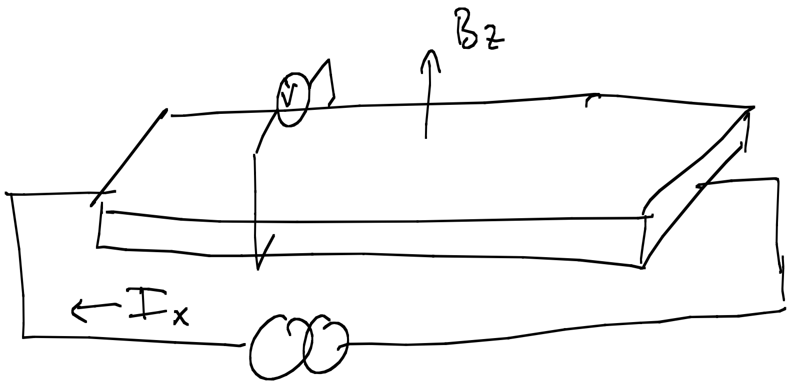
Charge accumulation will be determined by sign of charge carrier

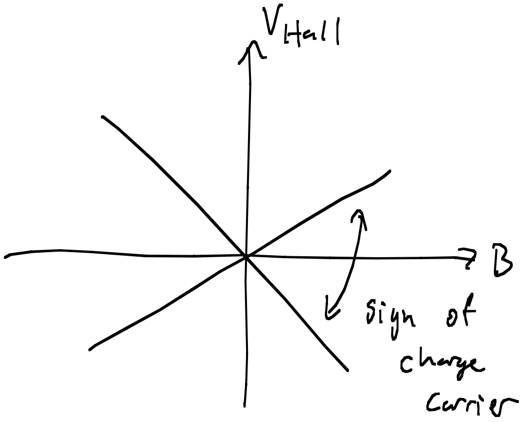
Open circuit measurement ($j_y = 0$)

$$\mathcal{E}_y = -\frac{B}{ne} j_x = \rho_{xy} j_x$$

measurement:

$$V_{Hall} = V_y = \mathcal{E}_y W = -\frac{B}{ne}\frac{I_x}{\cancel{W}t}\cancel{W} = -\frac{B}{net} I_x$$

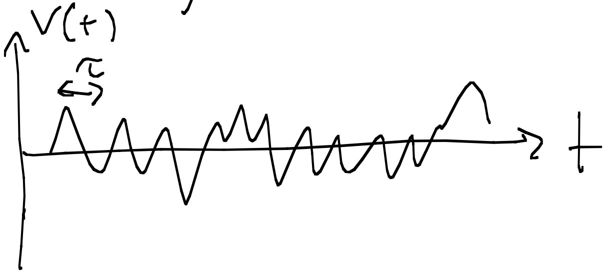




→ get sign of charge carrier, concentration from slope

→ w/ conductivity $\sigma = ne\mu$, get mobility

Noise : Scattering causes velocity fluctuation



correlation fn $C_V = \langle \delta v_i(t_0) \cdot \delta v_i(t_0+t) \rangle$

$= \langle \delta v_i^2 \rangle e^{-\frac{|t|}{\tau}}$

for N electrons w/ uncorrelated motion in one dimension,

Using equipartition gives $C_v = \frac{k_B T}{mN} e^{-\frac{|t|}{\tau}}$

From this, we calculate the "Power spectral density" (PSD)

$$\underbrace{S_v = 2\int_{-\infty}^{\infty} C_v e^{-i\omega t} dt}_{\text{"Wiener - Khinchin thm"}} = \frac{2k_B T}{mN}\left[\int_{-\infty}^{0} e^{-(i\omega - \frac{1}{\tau})t} dt + \int_{0}^{\infty} e^{-(i\omega + \frac{1}{\tau})t} dt\right]$$

$$= \frac{2k_B T}{mN}\left[\frac{1}{-(i\omega - \frac{1}{\tau})} + \frac{\cancel{-}1}{\cancel{-}(i\omega + \frac{1}{\tau})}\right]$$

$$= \frac{2k_B T}{mN}\left[\frac{-\tau}{i\omega\tau - 1} + \frac{\tau}{i\omega\tau + 1}\right] = \frac{2k_B T}{mN} \frac{2\tau}{1+\omega^2\tau^2}$$

Voltage PSD : we don't measure velocity fluctuations!

Units of $S_v \propto \frac{k_B T \tau}{m} \to \frac{eV}{eV/c^2} \cdot s \to \text{vel}^2/\text{Hz}$ ↙ Spectral density must be per bandwidth!

since

$$V = IR = Aj\,R = (RAne)\,v$$

dimensionally, The voltage PSD is Then

$$S_{Volt} = (RAne)^2 S_v = \frac{4k_BT}{\cancel{N}} \frac{\tau}{m} \frac{1}{1+\omega^2\tau^2} R^2 A^{\cancel{2}} n \frac{\cancel{N}}{AL} e^2$$

$$= 4k_BT \left(\overbrace{\frac{ne^2\tau}{m} \frac{A}{L}}^{1/R}\right) R^2 \frac{1}{1+\omega^2\tau^2}$$

$$= \frac{4k_BTR}{1+\omega^2\tau^2} \sim 4k_BTR \quad \left(\omega \ll \frac{1}{\tau}\right)$$

This frequency-independent "white" noise is same as Nyquist/Johnson PSD!

Voltage Noise

S_{volt} gives variance per bandwith so size of fluctuations "Noise" per bandwidth is

$$\sqrt{S_{volt}} = \sqrt{4k_B T R}$$

Example: for $R = 50\Omega$, $T = 300K$,

$$\sqrt{4k_B T R} \sim \sqrt{\frac{4}{40} eV \cdot 50\Omega} = \sqrt{10^{-1} eV \cdot 50 \frac{V}{Hz} \frac{1.6\times10^{-19}}{e}}$$

$$\cong 1\, nV/\sqrt{Hz}$$

noise from Thermal motion of charge carriers!

$$\boxed{\Omega = \frac{V}{A} = \frac{Vs}{C} = \frac{1.6\times10^{-19}\, V}{e \cdot Hz}}$$

Solution in time-varying $\mathcal{E}(t)$

$$\mathcal{E} \to \mathrm{Re}\left\{\mathcal{E}(\omega)\, e^{-i\omega t}\right\} \xrightarrow{\text{linear response}} p = \mathrm{Re}\left\{p(\omega)\, \bar{e}^{i\omega t}\right\}$$

NB: "e" not charge!

Eqn of motion: $\frac{dp}{dt} = -e\mathcal{E} - \frac{p}{\tau} \longrightarrow -i\omega p(\omega) = -e\mathcal{E}(\omega) - \frac{p(\omega)}{\tau}$

$$p\left(-i\omega + \frac{1}{\tau}\right) = -e\mathcal{E} \longrightarrow p = \frac{-e\tau}{1-i\omega\tau}\mathcal{E} \quad \text{so} \quad v = \underbrace{\frac{\overbrace{\left(-\frac{e\tau}{m}\right)}^{\mu_{DC}}}{1-i\omega\tau}}_{\mu_{AC}} \mathcal{E}$$

$$\sigma = ne\mu = \frac{ne\mu_{DC}}{1-i\omega\tau} = \frac{\sigma_{DC}}{1-i\omega\tau} \quad \text{so impedance} \quad Z = \frac{L}{\sigma A} = \frac{L}{\sigma_{DC}A}(1-i\omega\tau) = R - i\omega(\underset{\text{kinetic inductance}}{\tau R})$$

Regimes: $\omega \ll \frac{1}{\tau}$ (100s THz → IR), $\sigma \to \sigma_{DC}$

$\omega \gg \frac{1}{\tau}$ (optical, UV, etc), $\sigma \to \frac{i\sigma_{DC}}{\omega\tau}$

"collisionless plasma"

Wave propagation in metals

$$\vec{\nabla} \times \vec{\mathcal{E}} = -\frac{\partial \vec{B}}{\partial t} \longrightarrow \nabla \times \nabla \times \mathcal{E} = \nabla(\cancelto{0}{\nabla \cdot \mathcal{E}}) - \nabla^2 \mathcal{E} = -\frac{\partial}{\partial t}(\nabla \times B)$$

permittivity

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{j} + \frac{1}{c^2}\frac{\partial \vec{\mathcal{E}}}{\partial t} \qquad \frac{1}{c^2} \equiv \epsilon_0 \mu_0 \qquad = -\frac{\partial}{\partial t}\left(\mu\sigma\mathcal{E} + \frac{1}{c^2}\frac{\partial \mathcal{E}}{\partial t}\right)$$

permeability

permeability

plane wave solutions: $\mathcal{E} = \mathcal{E}(\omega) e^{-i\omega t}$

$$-\nabla^2 \mathcal{E} = \mu\sigma i\omega\mathcal{E} + \frac{\omega^2}{c^2}\mathcal{E} = \frac{\omega^2}{c^2}\left(1 + \frac{i\sigma\mu c^2}{\omega}\right)\mathcal{E} = \frac{\omega^2}{c^2}\left(1 + \frac{i\sigma}{\epsilon_0 \omega}\right)\mathcal{E}$$

Same as wave eqn in vacuum, except $\epsilon_0 \to \epsilon_0\left(1 + \frac{i\sigma}{\epsilon_0\omega}\right)$!

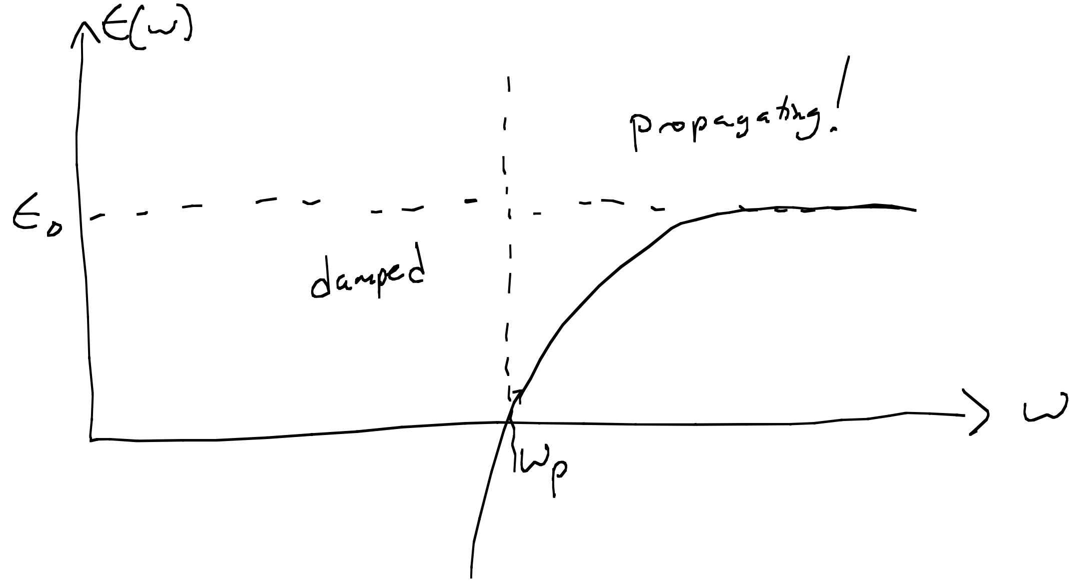
High frequency regime

$$\sigma \to \frac{i\sigma_{DC}}{\omega\tau} \quad \text{so} \quad \epsilon_0 \to \epsilon_0\left(1 - \frac{\sigma_{DC}}{\epsilon_0\tau\omega^2}\right) = \epsilon_0\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

(valid for $\omega_p \gg \frac{1}{\tau}$)

$$\omega_p = \sqrt{\frac{\sigma_{DC}}{\epsilon_0\tau}} = \sqrt{\frac{\frac{ne^2\cancel{\tau}}{m}}{\epsilon_0\cancel{\tau}}} = \sqrt{\frac{ne^2}{m\epsilon_0}}$$

independent of τ!



for real metals, $\omega_p \simeq \sqrt{\frac{10^{23}\,\text{cm}^{-3}}{5\times10^5\,\text{eV}/c^2}\frac{e^2}{\epsilon_0}}$

$$\frac{e^2}{4\pi\epsilon_0\hbar c} = \alpha \quad \text{so}$$

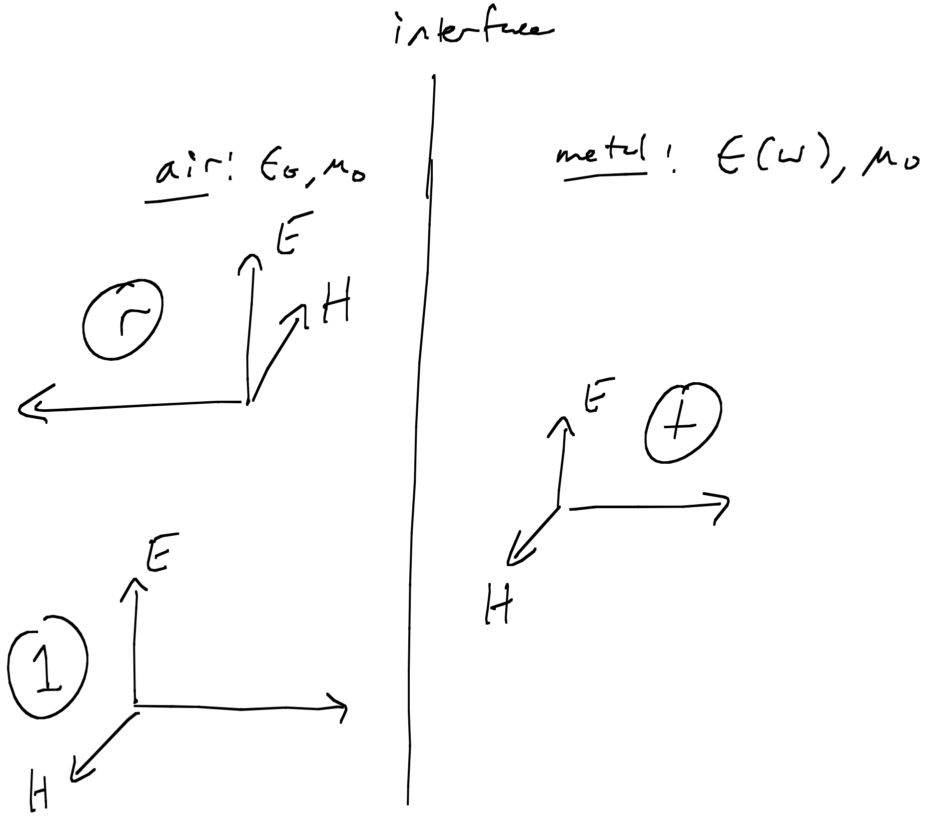
$$\frac{e^2}{\epsilon_0} = 2hc\alpha \simeq \frac{2480\ \text{nm}\cdot\text{eV}}{137} \simeq 18\ \text{nm eV}$$

so $\omega_p \sim 10^{16}\,\text{s}^{-1} \gg \frac{1}{\tau}$

Note! complex $\sqrt{\epsilon}$ → complex $\omega = kc$ → exponential damping (bulk)

Surface reflectivity of metal

(Normal incidence)



B.C.'s: $E_1'' = E_2''$ (Faraday's Law) , $H_1'' = H_2''$ (Ampere's law)

$$\left(H'' = \frac{n}{\mu_0 c} E'' = \sqrt{\frac{\epsilon}{\mu_0}}\, E'' \right)$$

$$1 + r = t$$

$$(1 - r)\sqrt{\epsilon_0} = \sqrt{\epsilon(\omega)}\; t$$

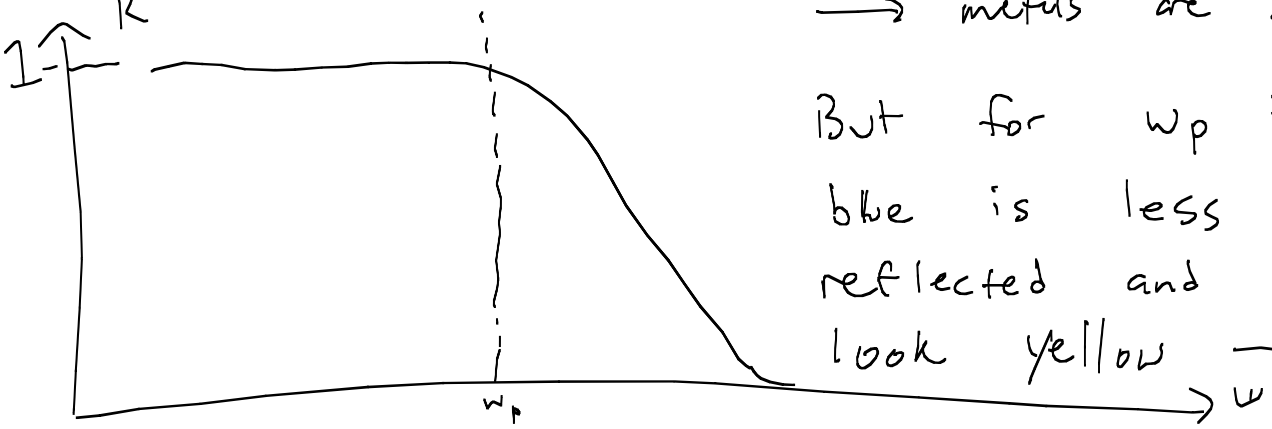
Solution

$$(1-r)\sqrt{\epsilon_0} = (1+r)\sqrt{\epsilon(\omega)}$$

$$r = \frac{\sqrt{\epsilon_0} - \sqrt{\epsilon(\omega)}}{\sqrt{\epsilon_0} + \sqrt{\epsilon(\omega)}} = \frac{1 - \sqrt{1-\frac{\omega_p^2}{\omega^2}}}{1 + \sqrt{1-\frac{\omega_p^2}{\omega^2}}}$$ (reflection amplitude)

Reflection coefficient $R = |r|^2$ $\sqrt{1-\frac{\omega_p^2}{\omega^2}} = A + iB$

$$R = \left| \frac{1-(A+iB)}{1+(A+iB)} \right|^2 = \frac{(1-A)^2 + B^2}{(1+A)^2 + B^2}$$



So purely imag. $\epsilon(\omega)$ for $\omega < \omega_p$ gives $R = 1$ → metals are shiny!

But for ω_p in visible, blue is less efficiently reflected and metal can look yellow → gold!

Charge density oscillation (plasmon, $k=0$ excitation) $\rho(t) = \mathrm{Re}\{\rho(\omega) e^{-i\omega t}\}$

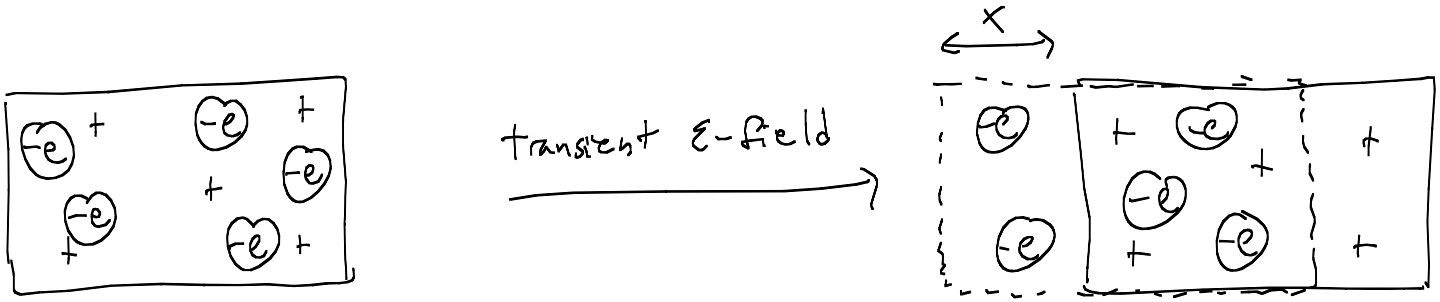
Continuity eqn.

$$\nabla\cdot j = -\frac{\partial \overset{\text{charge density}}{\rho}}{\partial t} = i\omega\rho(\omega)$$

By ohm's law, $\nabla\cdot j = \nabla\cdot\sigma\mathcal{E} = \sigma\nabla\cdot\mathcal{E} = \frac{\sigma\rho}{\epsilon_0}$ (last step by Gauss' law)

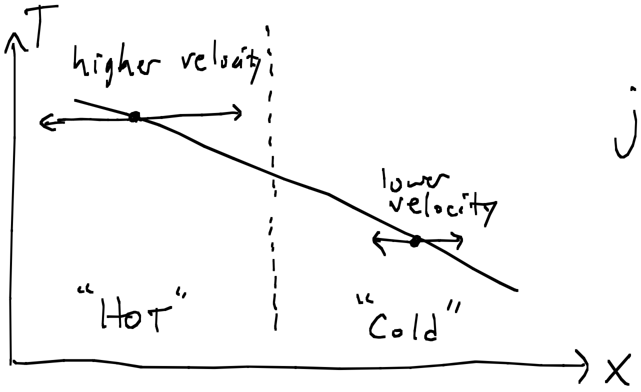
$$i\omega - \frac{\sigma}{\epsilon_0} = 0 \longrightarrow \omega = \frac{-i\sigma}{\epsilon_0} \sim \frac{-i\left(i\frac{\sigma_{DC}}{\omega\tau}\right)}{\epsilon_0} = \frac{ne^2\cancel{\tau}}{m\epsilon_0\omega\cancel{\tau}} \longrightarrow \omega^2 = \frac{ne^2}{m\epsilon_0} = \omega_p^2$$

So the "natural frequency" of excitations is the same plasma frequency that we found separated transmissive from reflective response!



$$m\ddot{x} = \left(\frac{nxe}{\epsilon_0}\right)e \longrightarrow x(t) \propto e^{i\sqrt{\frac{ne^2}{m\epsilon_0}}\,t} = e^{i\omega_p t} \quad (!)$$

Thermal conductivity: 1D heat transport



$$j_Q = -K\,\nabla T$$

what is K?

Heat flux:

$$j_Q^{H\to C} = \frac{1}{2} n v_x E\left(T(x - v_x\tau)\right)$$

$$j_Q^{C\to H} = -\frac{1}{2} n v_x E\left(T(x + v_x\tau)\right)$$

$$j_Q = j_Q^{H\to C} + j_Q^{C\to H} = \frac{1}{2} n v_x \frac{E\left(T(x - v_x\tau)\right) - E\left(T(x + v_x\tau)\right)}{\Delta T}\frac{dT}{dx}\Delta x$$

$$\xrightarrow{\text{continuum limit}} = \frac{1}{2} n v_x \left(-\frac{dE}{dT}\right)\frac{dT}{dx}\cdot 2 v_x \tau = -n v_x^2 \tau \frac{dE}{dT}\frac{dT}{dx} = -\left(v_x^2 \tau c_v\right)\nabla T$$

In 3-d, $v^2 = v_x^2 + v_y^2 + v_z^2$ so $j_Q = -\left(\frac{v^2}{3}\tau c_v\right)\nabla T \rightarrow K = \frac{v^2}{3}\tau c_v$

Wiedemann-Franz Law

$$\frac{K}{\sigma} = \frac{\frac{v^2}{3}\cancel{\tau} C_V}{\frac{ne^2\cancel{\tau}}{m}} = \frac{2\overset{\nearrow \frac{3}{2}k_BT}{\left(\frac{1}{2}mv^2\right)}\left(\frac{3}{2}\cancel{n}k_B\right)}{3\cancel{n}e^2} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T$$

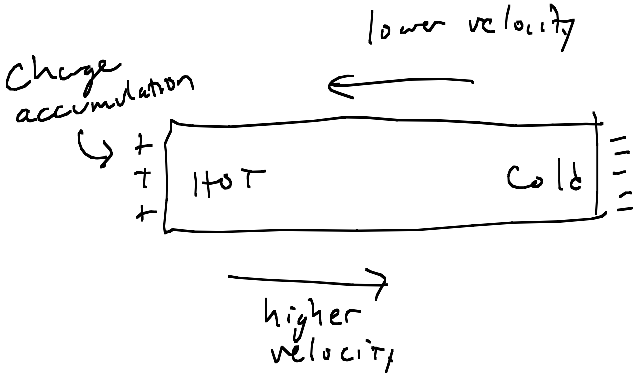
$$= \frac{3}{2}\left(\frac{\frac{0.026\,\cancel{e}V}{300\,K}}{\cancel{e}}\right)^2 T = \underset{\nwarrow}{L}\,T$$

"Lorenz number" ~ $7.5 \times 10^{-9}\,\frac{V^2}{K^2}$ $\left(\frac{W\Omega}{K^2}\right)$

Correct to within ~ factor of 2!

(only by miraculous cancellation of 2 huge errors! even insulators have $C_V \sim \frac{3}{2}nk_B$ @ RT (Dulong-Petit) So contribution from electrons must be negligible. It is actually ~100x smaller than this value. That error is counteracted by assuming kinetic energy 100 x too small ⟶ More later)

Seebeck effect



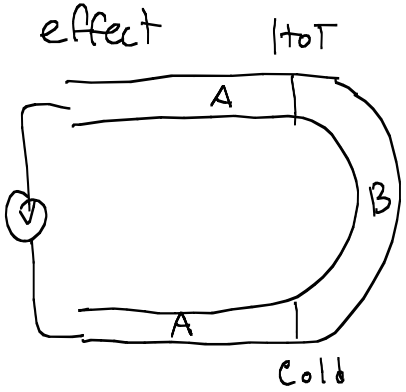
Charge accumulation sets up an $\mathcal{E}$-field

$$\mathcal{E} = Q \nabla T$$

"Thermopower"

What is Q?

Converse: Peltier effect



A, B different Thermopower

Heat-driven net velocity!

$$V_Q = \frac{1}{2}\underbrace{\left[V_x(x-v_x\tau) - V_x(x+v_x\tau)\right]}_{\Delta X} \overset{2v_x\tau}{\Delta X} = -\tau V_x \frac{dV_x}{dx} = -\tau \frac{d\left(V_x^2/2\right)}{dx} = -\tau \frac{d\, V_x^2/2}{dT}\frac{dT}{dx}$$

In steady-state, $j = 0$

heat-driven velocity must be counteracted by $\mathcal{E}$-field-driven velocity:

$$V_Q = -\frac{\tau}{3m}\frac{d}{dT}\left(\frac{1}{2}mv^2\right)\nabla T = -V_{\mathcal{E}}$$

$$-\frac{\tau}{3m}\frac{d}{dT}\overset{\nearrow\,\frac{3}{2}k_BT}{\left(\frac{1}{2}mv^2\right)}\nabla T = \frac{e\mathcal{E}\tau}{m}$$

$$\mathcal{E} = -\frac{k_B}{2e}\nabla T, \quad \text{so} \quad Q = -\frac{k_B}{2e} = -\frac{1}{2}\left(\frac{\frac{0.026\,eV}{300\,K}}{\cancel{e}}\right) \simeq -40\,\frac{\mu V}{K}$$

Too big!

QM: "non interacting" "free" electron gas

Single-particle Hamiltonian, no confining potential:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi = E\Psi$$

solution $\Psi \propto e^{i\vec{k}\cdot\vec{r}}$ where $|\vec{k}| = \sqrt{\frac{2mE}{\hbar^2}}$

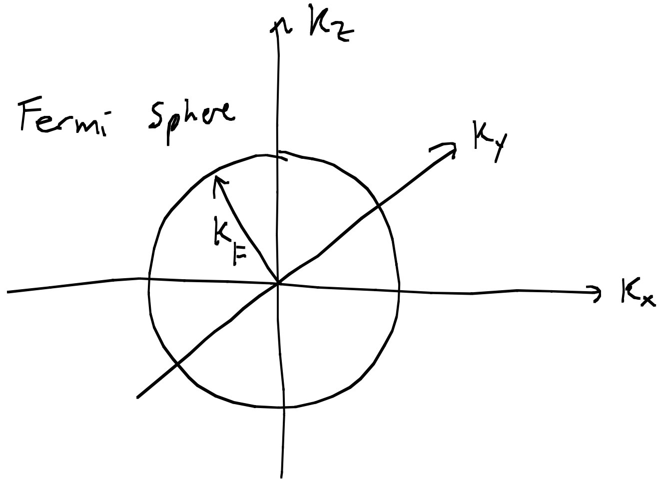
eigenstate of $p=\frac{\hbar}{i}\nabla$ so $\hbar k$ is momentum

How to fill N states in k-space?

@ T=0 (zero temperature)

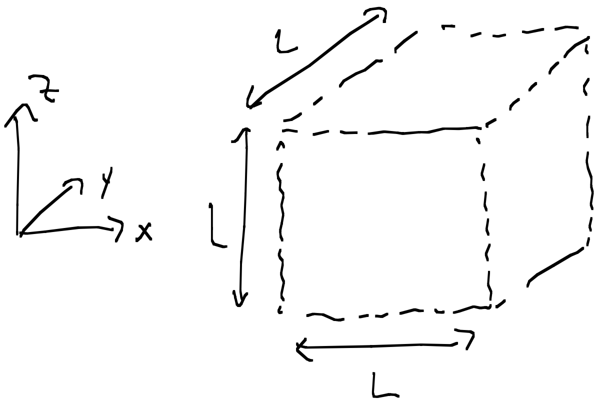
- Energy minimization
- Pauli Exclusion

Energy $\propto |\vec{k}|^2$



Fermi sphere has volume $\Omega = \frac{4}{3}\pi k_F^3$ How big is k_F?

Density of states in k-space



"free" → no confining potential
infinite volume

But, fixed electron density $n = \frac{N}{V}$

full translational symmetry
→ periodic boundary conditions

periodic B.C.'s: $\Psi(\vec{r}) = \Psi(\vec{r} + L\hat{x}) = \Psi(\vec{r} + L\hat{y}) = \Psi(\vec{r} + L\hat{z})$

$$e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot(\vec{r}+L\hat{x})} = e^{i\vec{k}\cdot\vec{r}}\, e^{ik_xL} \rightarrow k_xL = 2\pi\cdot\overset{\text{integer}}{\ell}$$

So spacing of states along k_x is $\Delta k_x = \frac{2\pi}{L}$

and in $\vec{k}$-space, $\Delta^3 k = \frac{(2\pi)^3}{Vol}$ per state

For k-space volume $\Omega = \frac{4}{3}\pi k_F^3$, $N = \underset{\text{spin degeneracy}}{2}\,\frac{\frac{4}{3}\pi k_F^3}{\frac{(2\pi)^3}{Vol}} \rightarrow n = \frac{k_F^3}{3\pi^2}$

Properties of Fermi Sphere

$k_F = (3\pi^2 n)^{1/3} \sim 10^8\ \text{cm}^{-1}$ for $n \sim 10^{23}\ \text{cm}^{-3}$

On Fermi surface

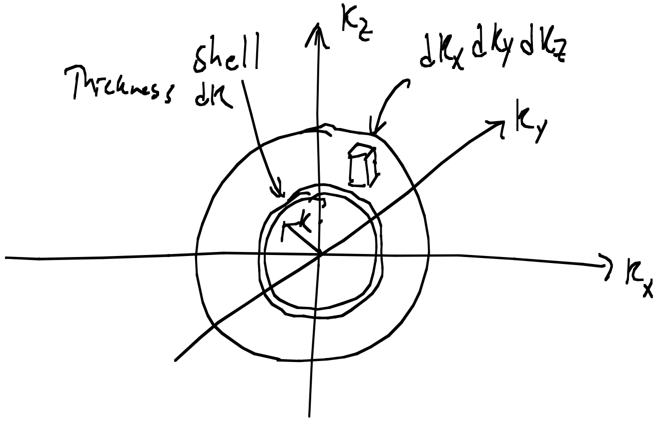
"Fermi velocity" $v_F = \frac{\hbar k_F}{m} = \frac{6.6\times10^{-16}\ \text{eV}\cdot\text{s} \cdot 9\times10^{20}\ \frac{\text{cm}^2}{\text{s}^2}}{5\times10^5\ \text{eV}} \cdot 10^8\ \text{cm}^{-1} \sim 10^8\ \frac{\text{cm}}{\text{s}} \sim \frac{c}{100}$

"Fermi Energy" $E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{(6.6\times10^{-16}\ \text{eV}\cdot\text{s})^2}{2\cdot5\times10^5}\ 9\times10^{20}\ \frac{\text{cm}^2}{\text{s}^2}\ (10^8\ \text{cm}^{-1})^2 \sim 10\ \text{eV}$

"Fermi Temperature" $T_F = \frac{E_F}{k_B} \sim \frac{10\ \text{eV}}{{}^{1}\!/_{40}\text{eV}/300\text{K}} \sim 10^5\ \text{K}$

so zero temperature
approximation is valid
even at RT!

Energy of FEG



$$E = \underset{\text{spin degeneracy}}{2} \sum_{|\vec{k}|<k_F} \frac{\hbar^2 k^2}{2m}$$

Since $\Delta^3 k = \frac{(2\pi)^3}{\text{Vol.}}$, $E = \frac{2\,\text{Vol.}}{(2\pi)^3} \sum_{|\vec{k}|<k_F} \frac{\hbar^2 k^2}{2m} \Delta^3 k$

$$\longrightarrow = \frac{2\,\text{Vol.}}{(2\pi)^3} \int_{\text{Fermi sphere}} \frac{\hbar^2 k^2}{2m} d^3k \longrightarrow \frac{2\,\text{Vol}}{(2\pi)^3} \int_0^{k_F} \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk$$

$$U = \frac{E}{\text{vol}} = \frac{\hbar^2}{2\pi^2} \frac{k^5}{5}\Big|_0^{k_F} = \frac{\hbar^2 k_F^5}{10\pi^2 m}$$

Avg. Energy per electron is $\frac{U}{n} = \frac{\frac{\hbar^2 k_F^5}{10\pi^2 m}}{\frac{k_F^3}{3\pi^2}} = \frac{3}{10}\frac{\hbar^2 k_F^2}{m} = \frac{3}{5} E_F \gg \frac{3}{2} k_B T$

Pressure of FEG

$$P = -\frac{\partial E}{\partial V}\bigg|_N = -\frac{\partial}{\partial V}\left[\frac{3}{5} N E_F\right]\bigg|_N = -\frac{3}{5} N \frac{\partial}{\partial V}\left[\frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}\right]\bigg|_N$$

$$= -\frac{3}{5} N \frac{\hbar^2}{2m} \frac{\left(3\pi \frac{N}{V}\right)^{2/3}}{V}\left(-\frac{2}{3}\right) = \frac{2}{5} E_F n$$

For real metals, $n \sim 10^{23}\ \text{cm}^{-3}$ so $P \sim 10^{24}\,\frac{\text{eV}}{\text{cm}^3}$

$$10^{24}\,\frac{\text{eV}}{\text{cm}^3}\;\frac{1.6\times10^{-19}\,\text{J}}{\text{eV}}\;\frac{10^{6}\,\text{cm}^3}{\text{m}^3} \approx 10^{11}\,\frac{\text{N}}{\text{m}^2} \rightarrow 10^{6}\ \text{atm} \qquad \text{huge!}$$

We can verify this by noting the negligible compressibility of metals:

$$\underset{\substack{\uparrow\\ \text{"compressivity"}}}{K} = -\frac{\frac{dV}{dP}}{V} \longrightarrow \underset{\substack{\uparrow\\ \text{"bulk modulus"}}}{B} = \frac{1}{K} = -V\frac{dP}{dV}$$

Since $P \propto V^{-5/3}$, $B = -V\left(-\frac{5}{3}\frac{P}{V}\right) = \frac{5}{3}P \sim \frac{2}{3}E_F n \sim 10^{6}\ \text{atm}$, K small.

When is $T=0$ approx. bad (@ RT)?

$$E_F \sim K_B T = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

$$n = \frac{\left(\frac{2 m k_B T}{\hbar^2}\right)^{3/2}}{3\pi^2} \sim 10^{19}\ \mathrm{cm}^{-3}$$

Below This, we have a classical Boltzmann gas ("nondegenerate")

$\longrightarrow$ "Semiconductors" can have such low carrier densities where $K_B T$ is The dominant energy scale

Electrical Conductivity

Each electron has different momentum so Eqn. motion not useful.

$f(\vec{K})$ occupation distribution of filled states ($f_0(\vec{K}) = 1$ for $|\vec{K}| < K_F$)

$$j = \frac{-2e \sum_{\text{filled}} v_K}{\text{Vol.}} \longrightarrow -2e \int f_0(\vec{K})\, V_z(\vec{K}) \frac{d^3k}{(2\pi)^3} = 0$$

in equilibrium

What is $f(\vec{k}) = f_0(\vec{K}) + g(\vec{K})$ out of equilibrium ($\mathcal{E} \neq 0$)?

"Boltzmann transport Equation": in steady-state, "excitation" = "relaxation"

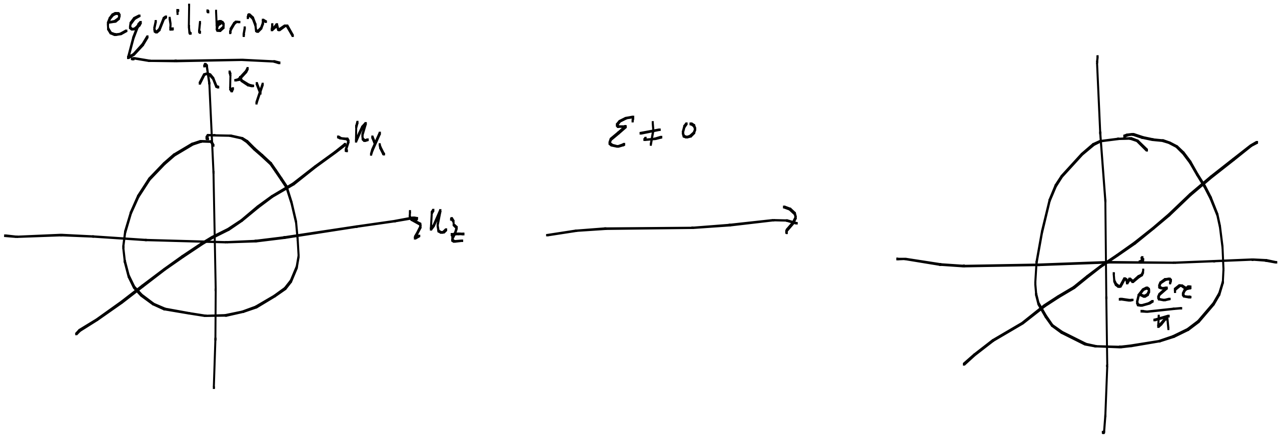
excitation: $$\frac{df}{dt} = \frac{df}{dp_z}\frac{dp_z}{dt} = \frac{df}{dk_z}\left(-\frac{e\mathcal{E}}{\hbar}\right)$$

relaxation: $$\frac{df}{dt} = -\left(\frac{f(\vec{K}) - f_0(\vec{K})}{\tau}\right) = -\frac{g(K)}{\tau}$$

$$\Longrightarrow \quad g(\vec{K}) = \frac{e\mathcal{E}\tau}{\hbar}\frac{df}{dk_z}$$

Interpretation

$$f(\vec{k}) = f_0(\vec{k}) + \frac{e\mathcal{E}\tau}{\hbar}\frac{df}{dk_z} \longrightarrow \sim f_0\left(\vec{k} + \frac{e\mathcal{E}\tau}{\hbar}\hat{k}_z\right)$$



asymmetry in $\vec{k}$ gives net flux and nonzero $\vec{j}$.

current density: $j = -2e\int g(\vec{k})\frac{\hbar k_z}{m}\frac{d^3k}{(2\pi)^3} = -2e\int \frac{e\mathcal{E}\tau}{\hbar}\frac{df}{dk_z}\frac{\hbar k_z}{m}\frac{d^3k}{(2\pi)^3}$

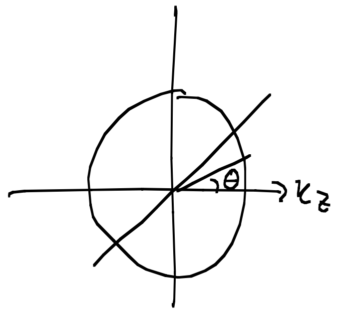
write $\frac{df}{dk_z} = \frac{df}{dk}\frac{dk}{dk_z}$ where $\frac{dk}{dk_z} = \frac{d}{dk_z}\sqrt{k_x^2+k_y^2+k_z^2} = \frac{\frac{1}{2}\cdot 2k_z}{\sqrt{k_x^2+k_y^2+k_z^2}} = \frac{k_z}{k}$

assumed const. here

$$j = \left[2\frac{e^2\tau}{m}\int\left(-\frac{df}{dk}\right)\frac{k_z^2}{k}\frac{d^3k}{(2\pi)^3}\right]\mathcal{E} = \sigma\mathcal{E}$$

Fermi - Surface integration

$$-\frac{df}{dk} = \delta\left(|\vec{k}| - k_F\right)$$ in $T=0$ limit. So



$$\sigma = \frac{1}{4\pi^3}\frac{e^2\tau}{m}\underset{\text{Fermi Surface}}{\int}\frac{k_z^2}{k}\,dS_k = \frac{1}{4\pi^3}\frac{e^2\tau}{m}\int\frac{(k_F\cos\theta)^2}{k_F}2\pi k_F^2\sin\theta\,d\theta$$

$$= \frac{k_F^3}{2\pi^2}\frac{e^2\tau}{m}\left[-\frac{\cos^3\theta}{3}\right]\Bigg|_0^\pi = \frac{k_F^3}{3\pi^2}\frac{e^2\tau}{m} = \frac{ne^2\tau}{m}$$ C.f. Drude result!

→ Fermi surface is fundamental in determining transport properties because only there can states make infinitesimal transitions

→ Fermi surface is not perfectly spherical in real metals due to lattice potential, etc.

"fluctuation - dissipation Thm"

Rewrite our integral as FS area times average value of integrand:

$$\sigma = \frac{1}{4\pi^3}\frac{e^2}{m}\frac{\langle k_z^2 \tau\rangle}{k_F}\cdot 4\pi k_F^2 = \frac{e^2\, k_F}{\pi^2 m}\frac{m^2}{\hbar^2}\left\langle \left(\frac{\hbar k_z}{m}\right)^2 \tau\right\rangle = \frac{e^2 k_F}{3\pi^2\hbar^2}\, m\, \langle v^2 \tau\rangle$$

But $\sigma = ne\mu = e\mu \frac{k_F^3}{3\pi^2}$ so

Diffusion coefficient "D" (also $\langle \frac{\lambda^2}{2\tau}\rangle$)

$$\frac{e^{\cancel{2}}\cancel{k_F}2m}{3\cancel{\pi^2}\hbar^2}\left\langle \frac{v^2\tau}{2}\right\rangle = \cancel{e}\mu\frac{k_F^{\cancel{3}\,2}}{3\cancel{\pi^2}} \longrightarrow \mu = \frac{2m}{\hbar^2 k_F^2}\left\langle \frac{v^2\tau}{2}\right\rangle e$$

Then we have $\frac{D}{\mu} = \frac{E_F}{e}$ (degenerate regime)

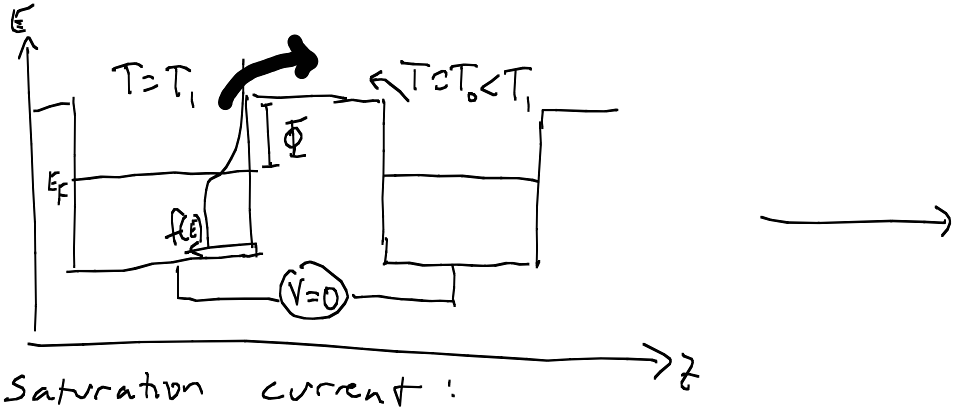
So mechanisms which cause a return to equilibrium are The same which cause fluctuations at equilibrium!

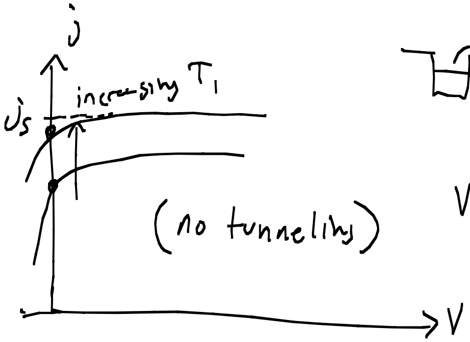
In non degenerate regime,

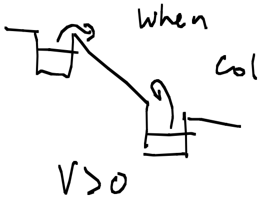
$$\langle \tfrac{1}{2}v^2\rangle \sim \frac{k_B T}{m}$$ so $$\frac{D}{\mu} = \frac{\langle \frac{v^2\tau}{2}\rangle}{\mu} \sim \frac{\frac{k_B T}{m}\tau}{\frac{e\tau}{m}} = \frac{k_B T}{e}$$

"Einstein relation" (derived for Brownian motion)

Beyond "Free" Approximation: Thermionic emission







Current density saturates when contribution from cold to hot is suppressed by electric field.

Saturation current:

$$j_s = 2e\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{k_{min}=\sqrt{\frac{2m(E_F+\Phi)}{\hbar^2}}}^{\infty}\frac{\hbar k_z}{m}\, e^{-(E-\mu)/k_BT}\,\frac{dk_x\, dk_y\, dz}{(2\pi)^3}$$

$$E = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)$$

$$= e^{\frac{E_F}{k_BT}}\frac{\hbar e}{4\pi^3 m}\int_{-\infty}^{\infty}e^{-\frac{\hbar^2}{2mk_BT}k_x^2}\,dk_x\int_{-\infty}^{\infty}e^{-\frac{\hbar^2}{2mk_BT}k_y^2}\,dk_y\int_{k_{min}}^{\infty}k_z\, e^{-\frac{\hbar^2}{2mk_BT}k_z^2}\,dk_z$$

$$\left(\text{Note: } \int_{-\infty}^{\infty}e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}\right)$$

$$= e^{\frac{E_F}{k_BT}}\frac{\hbar e}{4\pi^3 m}\left(\sqrt{\frac{2\pi m k_BT}{\hbar^2}}\right)^2\int_{k_{min}}^{\infty}e^{-\frac{\hbar^2}{2mk_BT}k_z^2}\,\frac{d(k_z^2)}{2} = e^{\frac{E_F}{k_BT}}\frac{\hbar e}{4\pi^3 m}\,\frac{2\pi m k_BT}{\hbar^2}\,\frac{1}{2}\left(-\frac{2mk_BT}{\hbar^2}e^{-\frac{\hbar^2}{2mk_BT}X}\right)\Bigg|_{X=k_{min}^2=\frac{2m}{\hbar}(E_F+\Phi)}^{\infty}$$

$$j_s = \frac{ek_BT}{2\pi^2\hbar}\,\frac{mk_BT}{\hbar^2}\,e^{-\Phi/k_BT} = \frac{4\pi m e}{h^3}(k_BT)^2e^{-\Phi/k_BT}$$

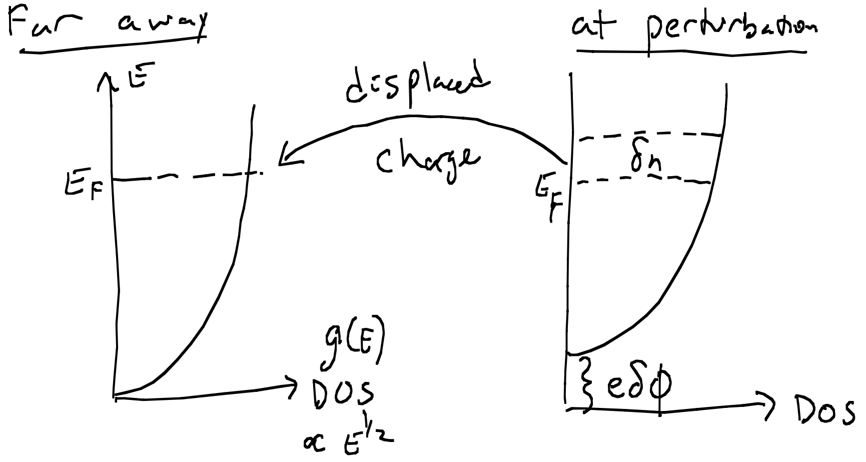
"Richardson - Dushman Eqn"

linearizing w/ ln gives measurement of Φ

→ valid even for internal barriers (schottky)

Beyond "Noninteracting" Approximation: Screening

Add perturbing potential to otherwise homogeneous electron gas:



$$\delta n \sim \overbrace{e\delta\phi}^{\text{energy interval}}\, \overset{\text{Density of states @ Fermi energy}}{g(E_F)}$$

At intermediate locations, solve Poisson eqn:

$$\nabla^2(\delta\phi) = \frac{\rho}{\epsilon_0} = \frac{e\,\delta n}{\epsilon_0} = \frac{e^2\,\delta\phi\, g(E_F)}{\epsilon_0} = \lambda^2 \delta\phi \qquad \left([\lambda] = \frac{1}{\text{length}} \right)$$

Similar to Poisson eqn in vacuum, where response to δ-function charge yields the Green's function $1/4\pi r$, we must here solve

$$\nabla^2(\delta\phi) - \lambda^2 \delta\phi = -\delta(\vec{r})$$

Green's function Solution

Use Fourier Transform, $\delta\phi = \frac{1}{(2\pi)^3}\int \tilde{\delta\phi}\, e^{i\vec{k}\cdot\vec{r}}\, d^3k$ so That $\nabla^2\delta\phi \rightarrow -k^2\delta\phi$ and $\delta(r) = \frac{1}{(2\pi)^3}\int e^{i\vec{k}\cdot\vec{r}}\, d^3k$

Then project onto orthonormal basis: $-k^2\tilde{\delta\phi} - \lambda^2\tilde{\delta\phi} = -1 \quad \longrightarrow \quad \tilde{\delta\phi} = \frac{1}{k^2+\lambda^2}$

So $$\delta\phi = \frac{1}{(2\pi)^3}\int_{\substack{\text{all } k\\ \text{space}}} \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2+\lambda^2}\, d^3k$$

In spherical coordinates, $d^3k = k^2\sin\theta\, d\theta\, d\varphi\, dk$ and $\vec{k}\cdot\vec{r} = kr\cos\theta$

$$\delta\phi = \frac{2\pi}{(2\pi)^3}\int_0^\infty\int_0^\pi \frac{k^2 e^{ikr\cos\theta}}{k^2+\lambda^2}\sin\theta\, d\theta\, dk$$

$$= \frac{1}{(2\pi)^2}\int_0^\infty \frac{k^2}{k^2+\lambda^2}\left(-\frac{e^{ikr\cos\theta}}{ikr}\Bigg|_0^\pi\right)dk = \frac{1}{(2\pi)^2}\int_0^\infty \frac{k^2}{k^2+\lambda^2}\left(\frac{e^{ikr}-e^{-ikr}}{ikr}\right)dk$$

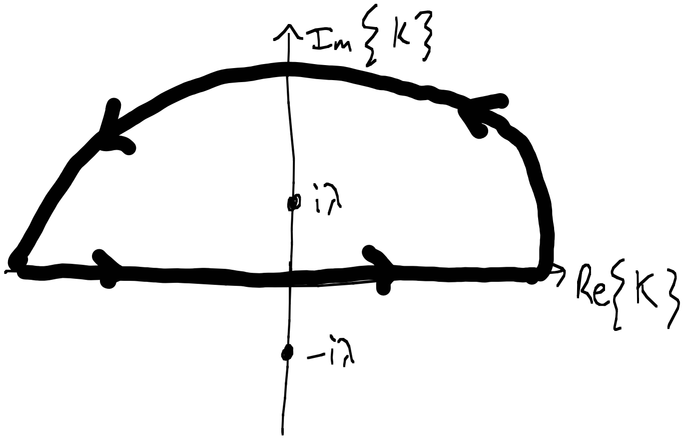
Split integral and change variables on second from $k \rightarrow -k$, Then invert bounds to get

$$= \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} \frac{k^2}{k^2+\lambda^2}\frac{e^{ikr}}{ikr}\, dk$$

How to evaluate this?

Contour Integration

$$\delta\phi = \frac{1}{(2\pi)^2 r}\int_{-\infty}^{\infty} \frac{k}{(k+i\lambda)(k-i\lambda)}\frac{e^{ikr}}{i}\,dk \xrightarrow[\text{at } |k|=\infty]{\text{Close the loop in complex plane}}$$



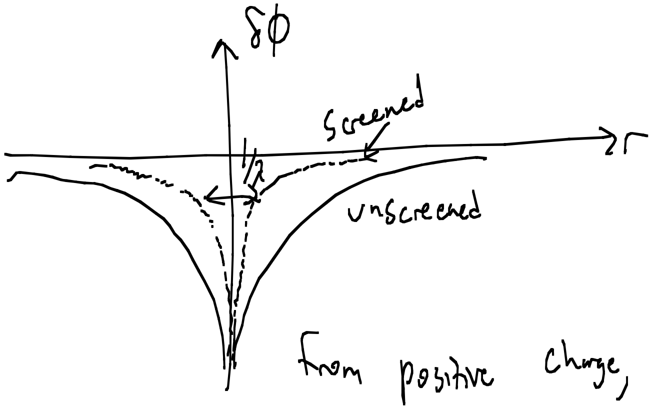
so $$\delta\phi = \frac{1}{(2\pi)^2 r}\left(2\pi i \,\mathrm{Res}\left\{\frac{k e^{ikr}}{(k+i\lambda)(k-i\lambda)\,i},\ i\lambda\right\}\right)$$

$$= \frac{1}{(2\pi)^2 r}\left(\cancel{2}\pi\cancel{i}\ \frac{\cancel{i\lambda}\, e^{-\lambda r}}{\cancel{2i\lambda}\ \cancel{i}}\right) = \frac{1}{4\pi r}e^{-\lambda r}$$

"Screened Coulomb potential"

or "Yukawa potential"

Note "Thomas-Fermi Screening length" $\lambda^{-1} = \sqrt{\frac{\epsilon_0}{e^2 g(E_F)}}$ gets smaller w/ increasing density (larger $g(E_F)$)

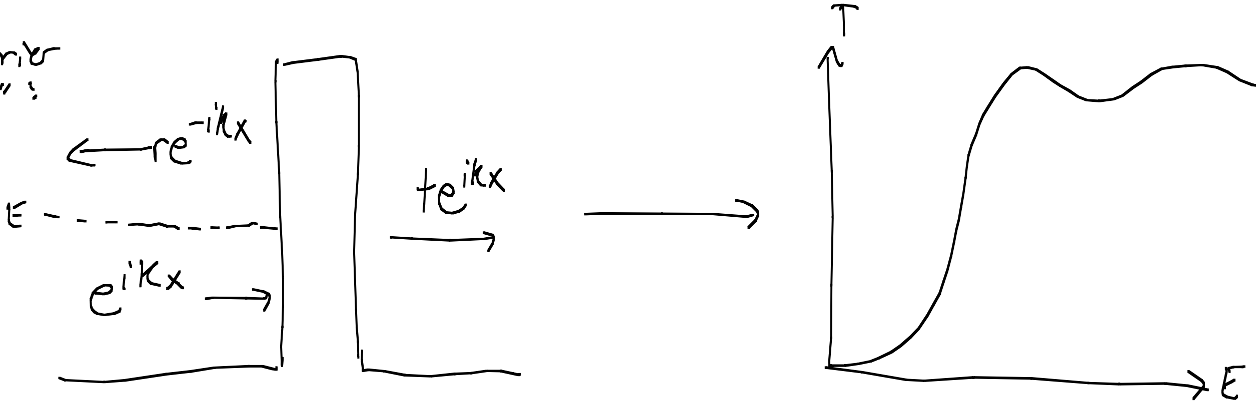


Physically, this suppression of 1/r coulomb potentials is due to the polarizability of the electron gas, An attractive potential i.e. from positive charge, will be surrounded by a cloud of negative electrons, partly cancelling the attractive force.

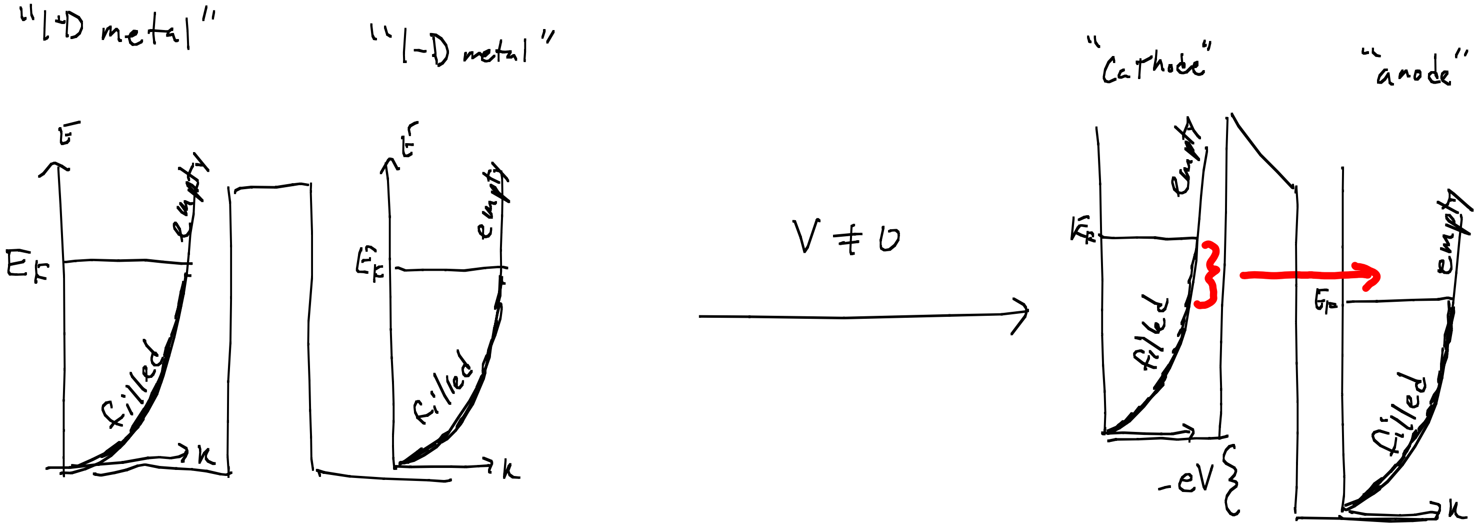
Current-Voltage relations: QM scattering in ballistic regime

What if scattering is elastic and localized? Then bulk conductivity not dominant.

"Single barrier tunneling":



How can we recover an experimentally relevant quantity from this dimensionless transmission coef?

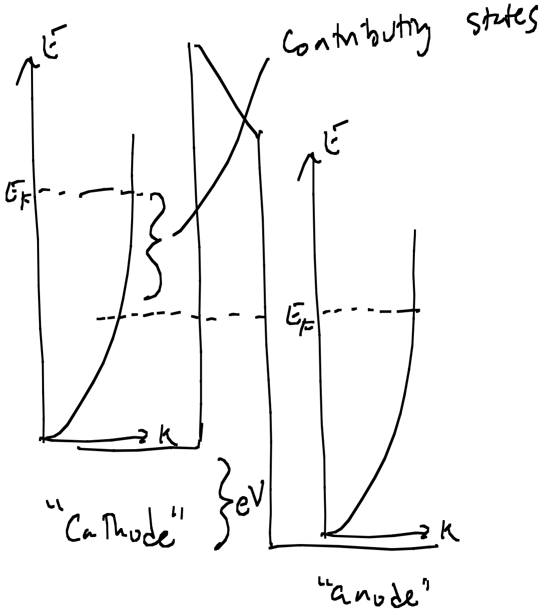


$j = 0$

(no asymmetry)

$j \neq 0$

1-D transport: Summation over states



Elastic Tunneling: Energy conserved, so

$$E + eV > E_F \longrightarrow \frac{\hbar^2 k^2}{2m} + eV > \frac{\hbar^2 k_F^2}{2m}$$

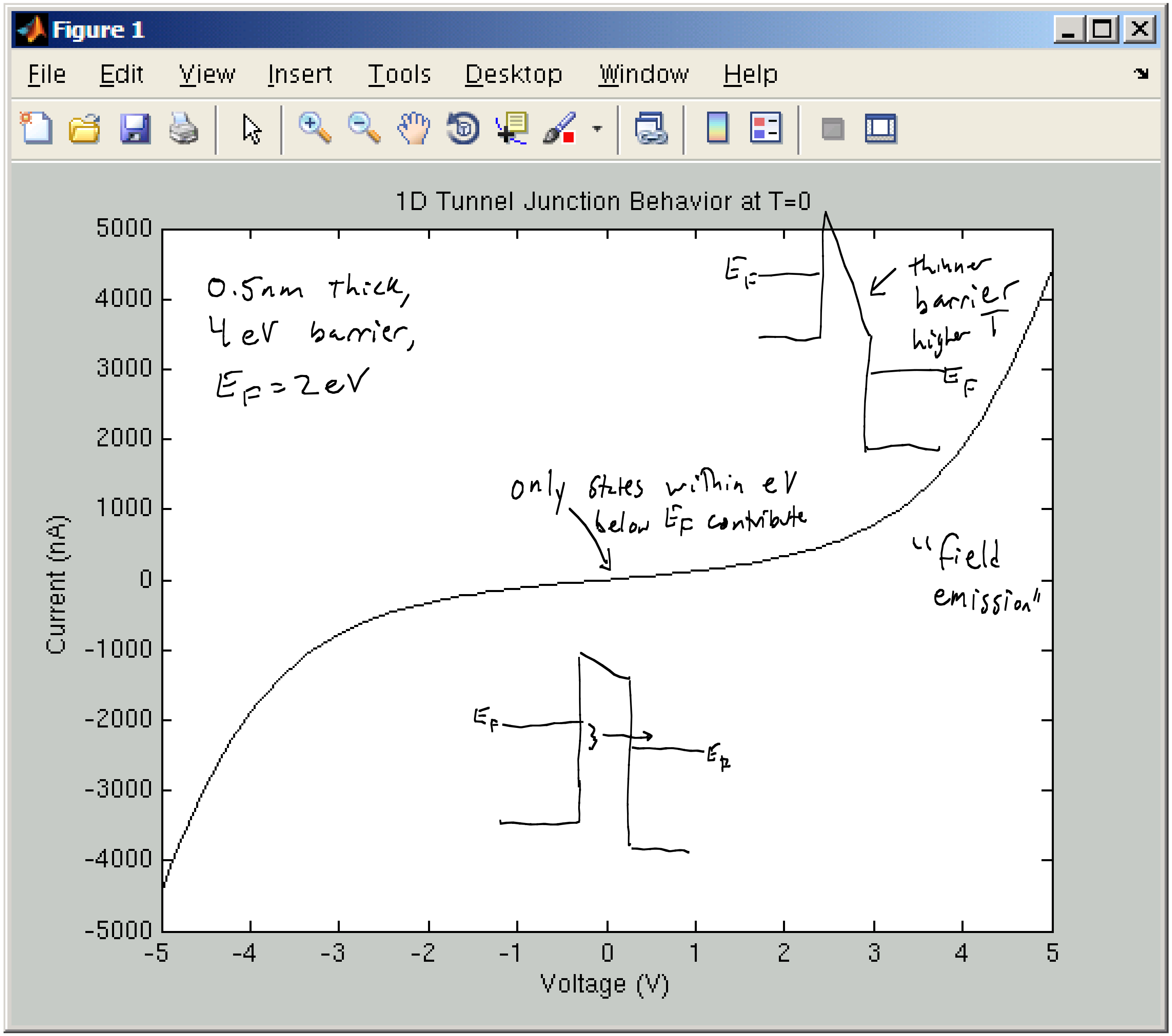
$$k > k_{min} = \sqrt{\frac{2m(E_F - eV)}{\hbar^2}} = \sqrt{k_F^2 - \frac{2meV}{\hbar^2}}$$

1-D current:

$$I(V) = 2e \int_{k_{min}(V)}^{k_F} \frac{\hbar k}{m} T(E(k), V) \frac{dk}{2\pi}$$

Numerical Integration Result

See, e.g. STM, M-I-M junctions, etc!

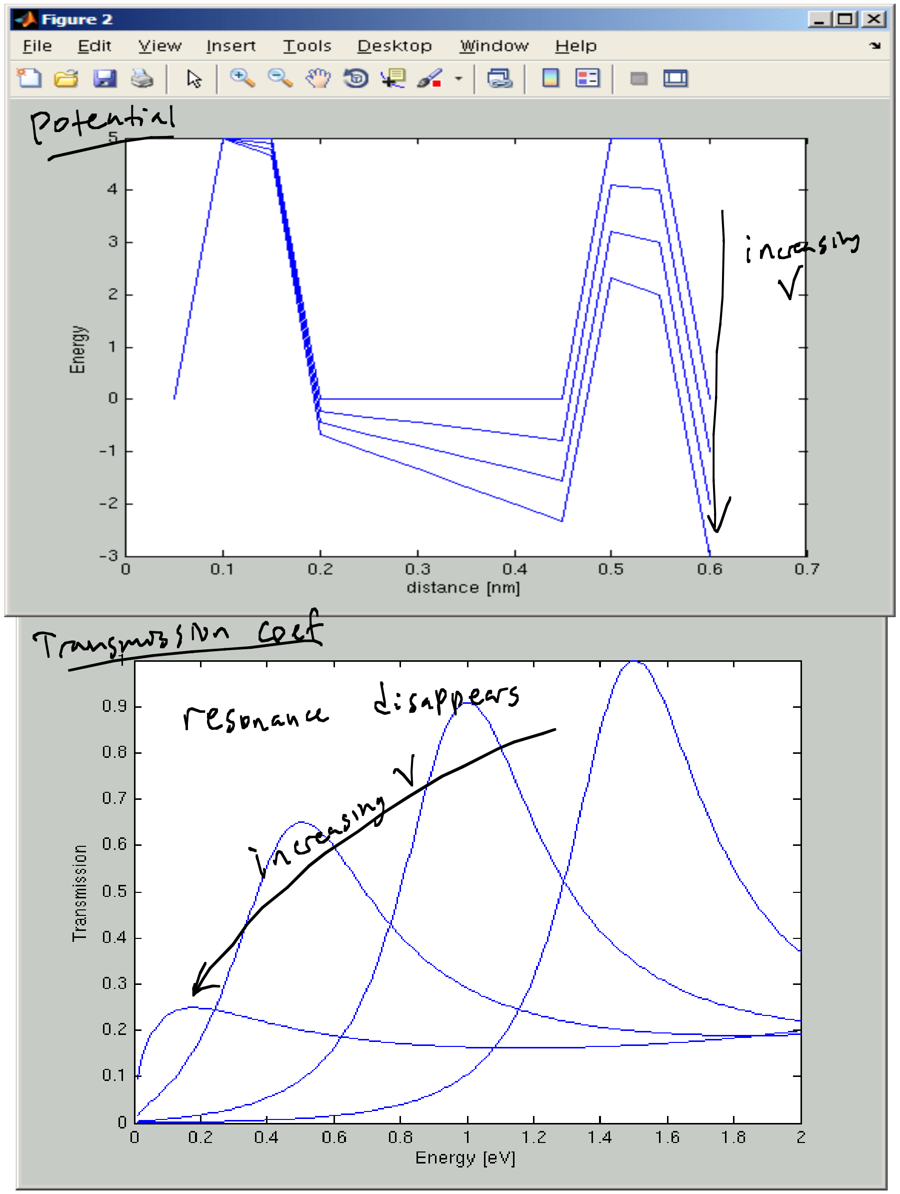


0.5nm thick, 4eV barrier, $E_F = 2$eV

only states within eV below E_F contribute

"field emission"

Double-barrier resonant Scatterer



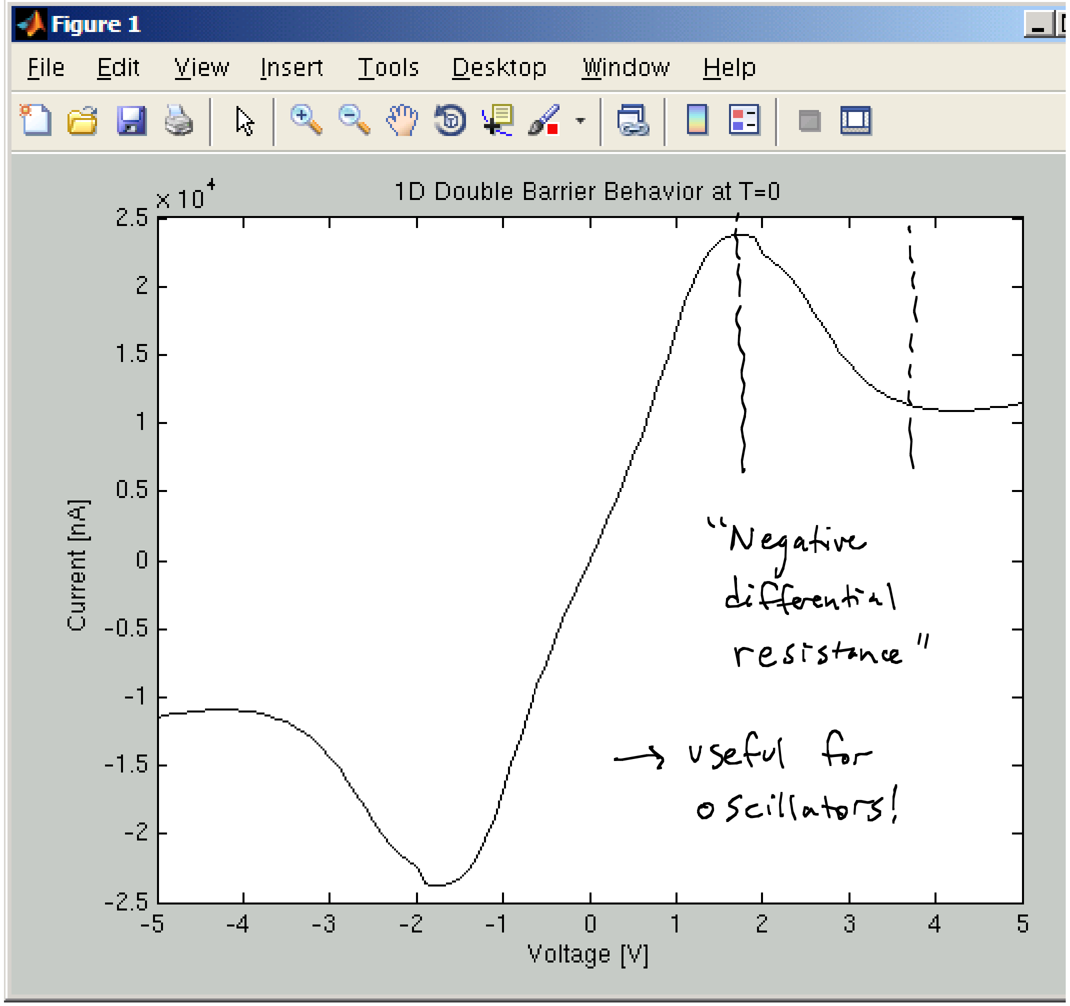
Potential

increasing V

Transmission coef

resonance disappears

increasing V



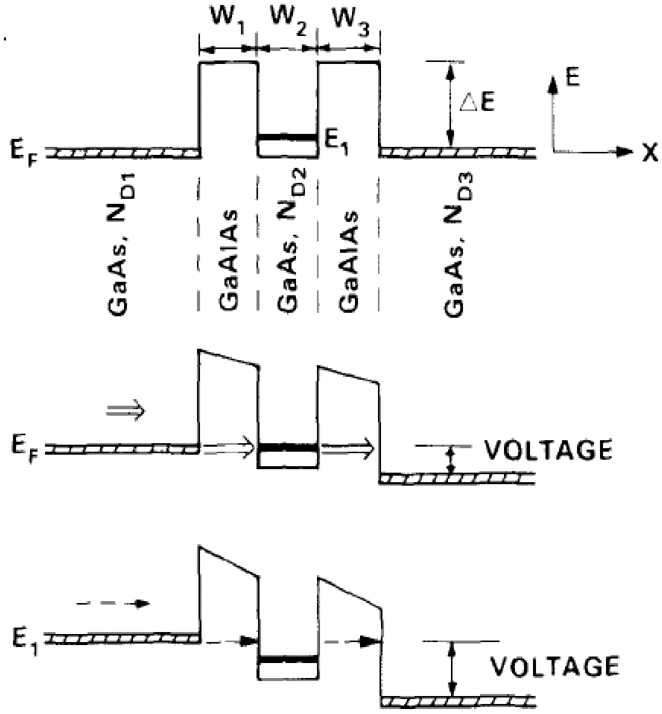
"Negative differential resistance"

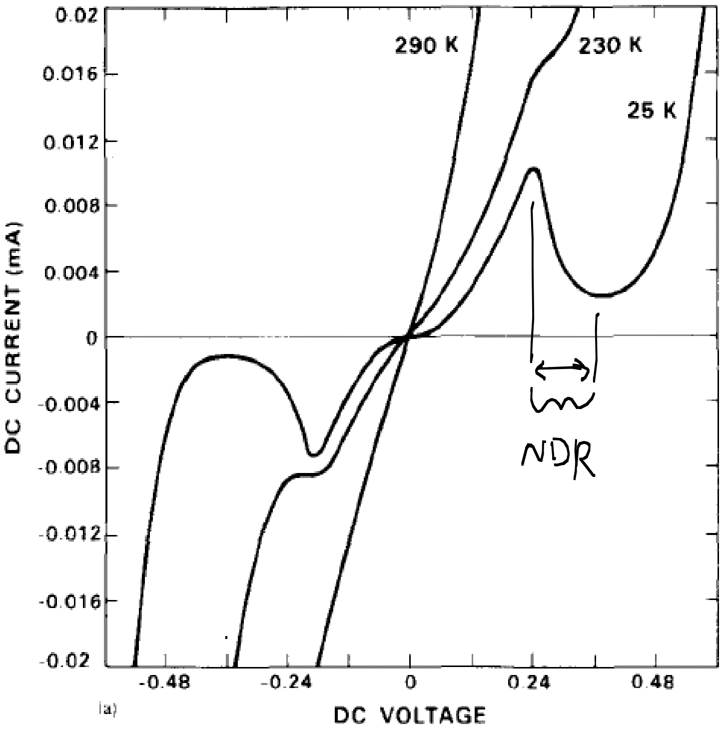
→ useful for oscillators!

Resonant tunneling through quantum wells at frequencies up to 2.5 THz

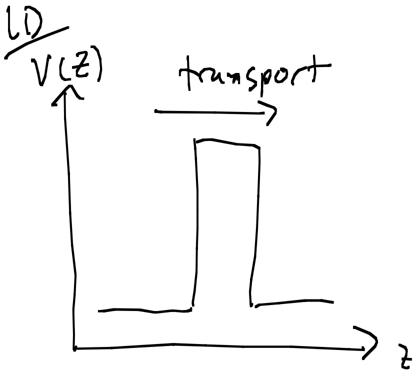
T. C. L. G. Sollner, W. D. Goodhue, P. E. Tannenwald, C. D. Parker, and D. D. Peck
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

588 Appl. Phys. Lett. **43** (6), 15 September 1983

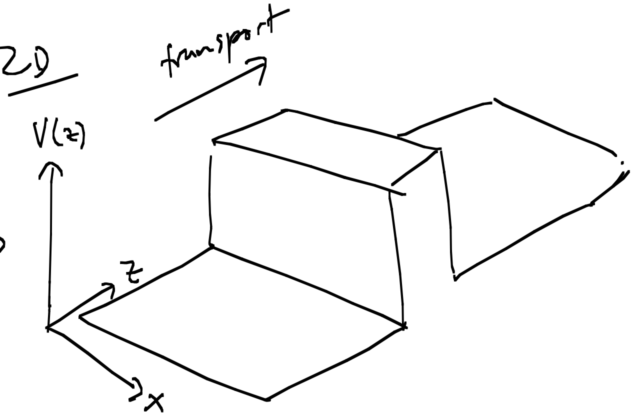




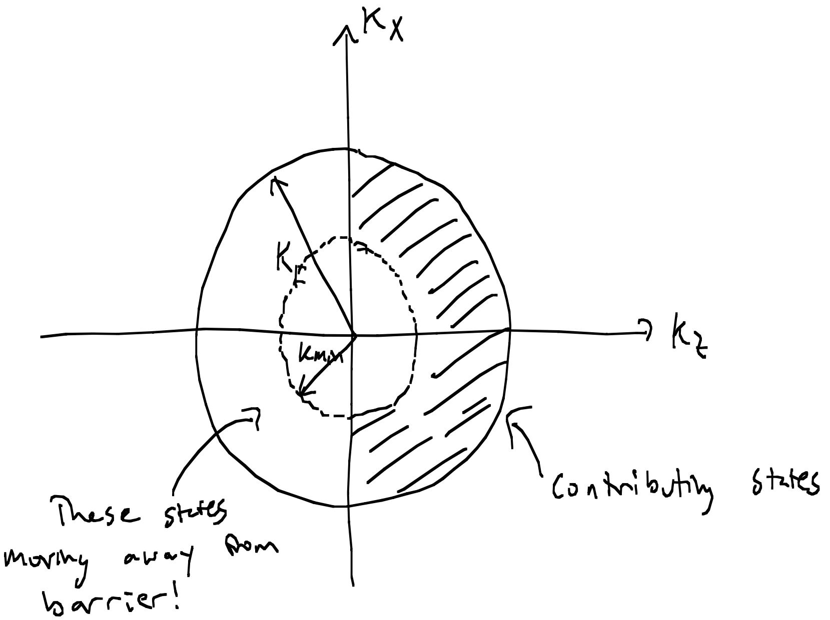
Transport Calculation in 2D



$$\xrightarrow[\text{coordinate}]{\text{add transverse}}$$



Application of Energy minimization and pauli exclusion in 2D gives a "Fermi disk":



$$E + eV > E_F$$

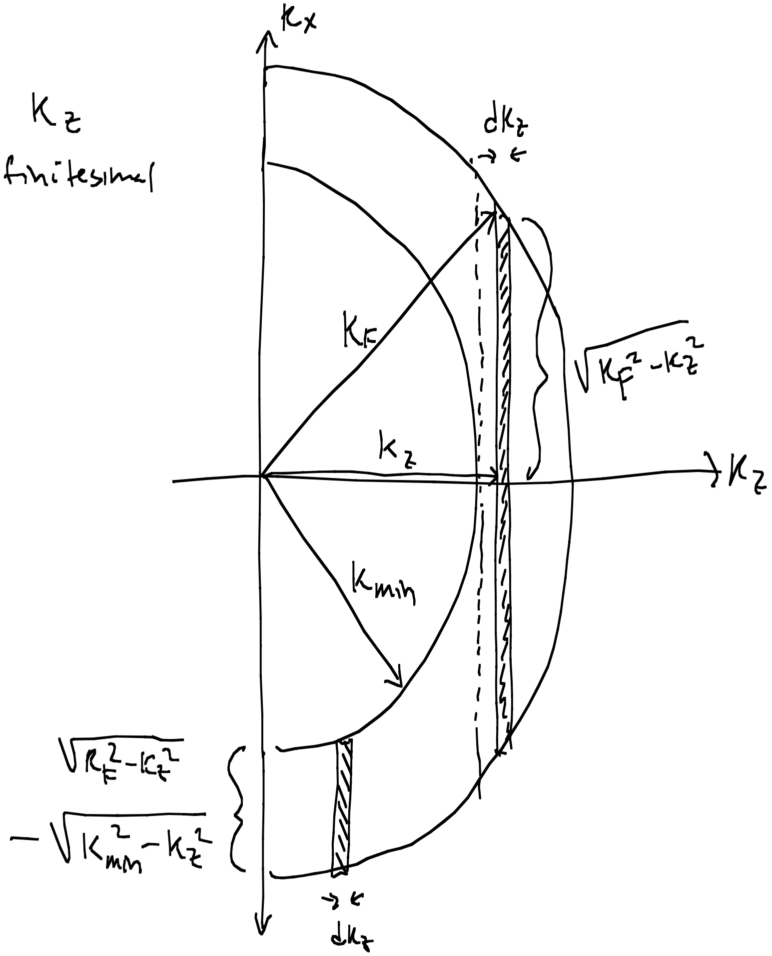
$$\frac{\hbar^2}{2m}\left(k_x^2 + k_z^2\right) > \frac{\hbar^2 k_F^2}{2m} - eV$$

$$k_x^2 + k_z^2 > k_{min}^2 = \left(\sqrt{\frac{2m(E_F - eV)}{\hbar^2}}\right)^2$$

$$J = 2e \iint_{k_{min} < |\vec{k}| < k_F} \frac{\hbar k_z}{m} T(k_z, V) \frac{dk_x}{2\pi} \frac{dk_z}{2\pi}$$

Evaluating the integral

Integrand only depends on k_z so choose appropriate infinitesimal to simplify integral:

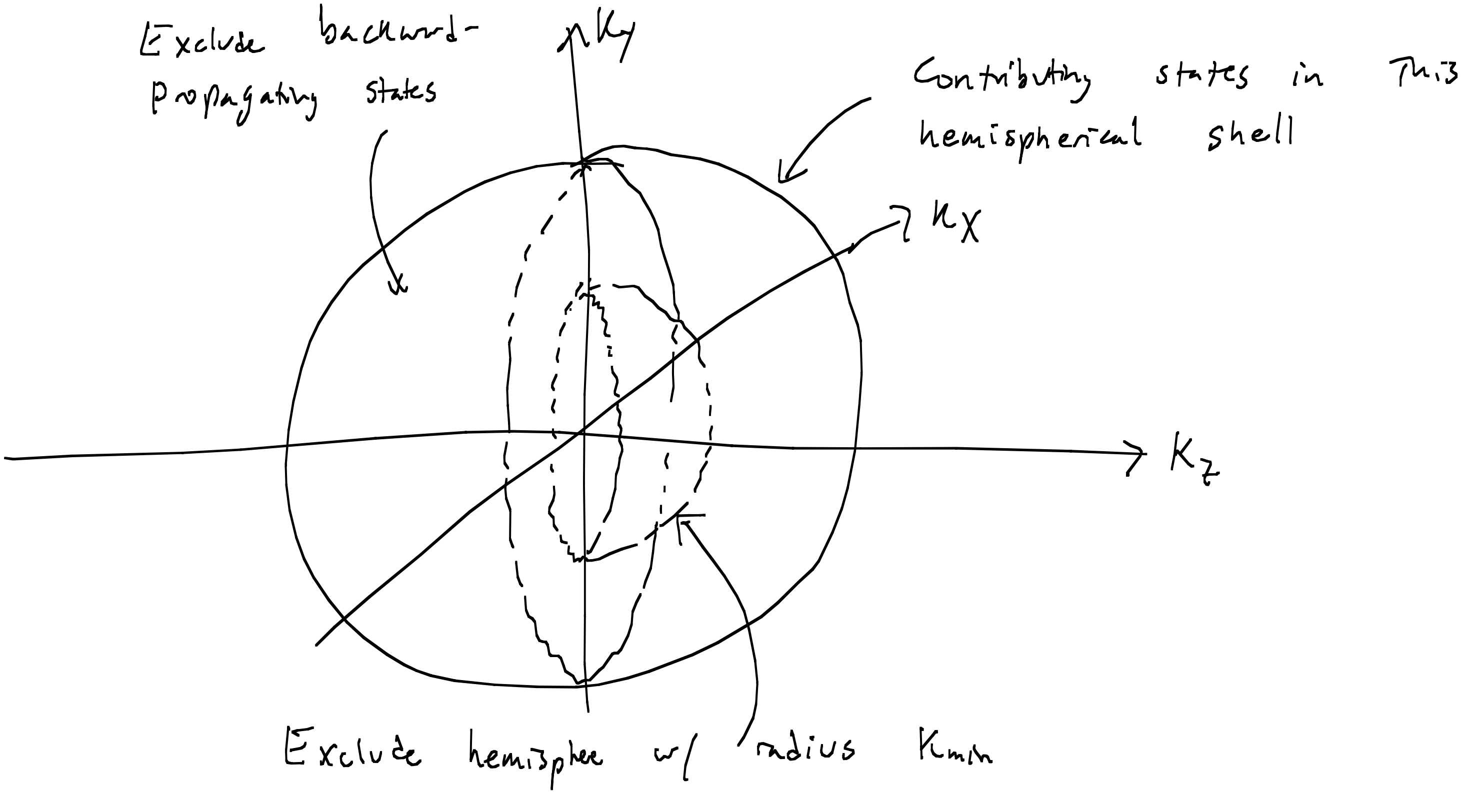


Now just two 1D integrals:

$$J_{2D} = 2e\left[\int_0^{k_{min}} \frac{\hbar k_z}{m} T(k_z,V)\, 2\left(\sqrt{k_F^2-k_z^2}-\sqrt{k_{min}^2-k_z^2}\right)\frac{dk_z}{2\pi} + \int_{k_{min}}^{k_F} \frac{\hbar k_z}{m} T(k_z V)\, 2\sqrt{k_F^2-k_z^2}\,\frac{dk_z}{2\pi}\right]$$

In 3-D

Now we go back to The Fermi sphere. The same considerations identify The states which contribute to transport:



By a suitable choice of volume infinitesimal, we can reduce this calculation to two 1D integrals (over k_z) as well.

Linear response in 1D

for small V $\quad T(E(k),V) \sim T(E_F,V)$

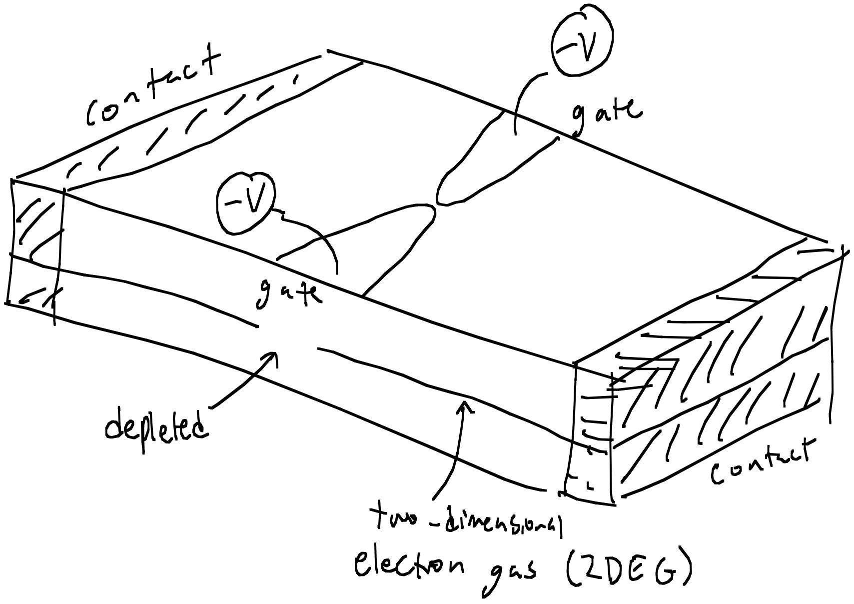
$$I = 2e\int_{k_{min}}^{k_F} \frac{\hbar k}{m}\, T(E(k),V)\, \frac{dk}{2\pi} \sim 2e\frac{\hbar}{2\pi m} T \int_{k_{min}}^{k_F} k\, dk = \frac{e\hbar}{\pi m} T \left. \frac{k^2}{2} \right|_{k_{min}=\sqrt{k_F^2 - \frac{2meV}{\hbar^2}}}^{k_F}$$

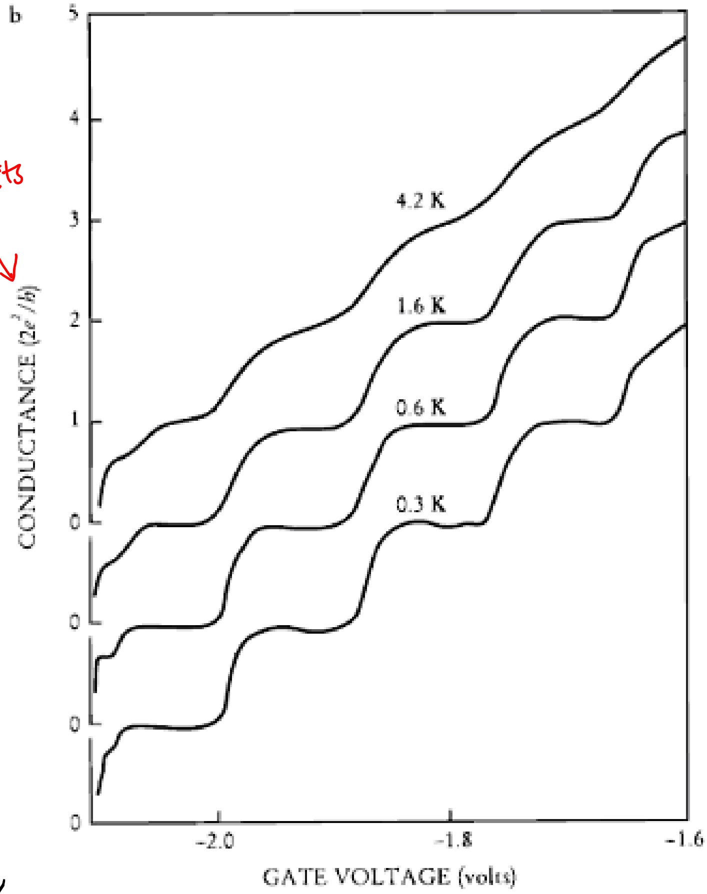
$$\sim \frac{e\hbar}{2\pi m} T \left(k_F^2 - \left(k_F^2 - \frac{2meV}{\hbar^2}\right)\right) = \frac{e^2}{\pi\hbar} T V = \underbrace{\left(2\frac{e^2}{h} T\right)}_{\text{Conductance}} V \qquad \text{"ohmic"} \ (\propto V)$$

Note $T \leq 1$ so even for perfect transmission, current in 1-D channel is bounded by "quantum of conductance" $\frac{2e^2}{h}$!

$$\frac{2e^2}{h} = \frac{e^2}{\pi\hbar} = \frac{e^{\cancel{2}}}{\pi\ 6.6\times10^{-16}\ \cancel{e}V\cdot s} = \frac{1.6\times10^{-19}\ A}{\pi\cdot 6.6\times10^{-16}\ V} \sim \frac{1}{13\ k\Omega}$$

Experiment : Quantum Point Contact (QPC)





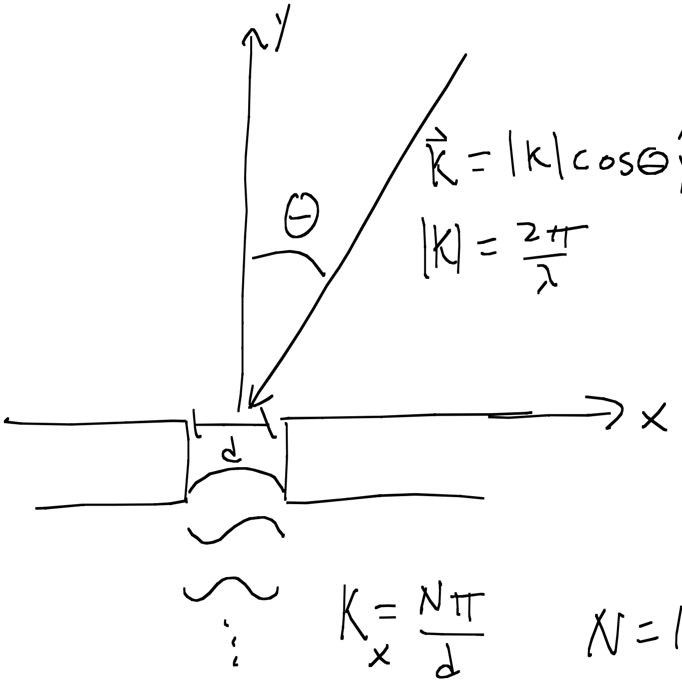
Units

Each 1-D channel contributes $\frac{2e^2}{h}$ so as the constriction gets wider with increasing gate voltage, more channels can fit and we see a conductance staircase

→ width of 1-D conductor set by Fermi wavelength $\left(\begin{array}{c} \lambda_F \sim 50\,\text{nm} \\ \text{for } n \sim 10^{11}\,\text{cm}^{-2} \end{array} \right)$

Optical "Quantized Conduction"

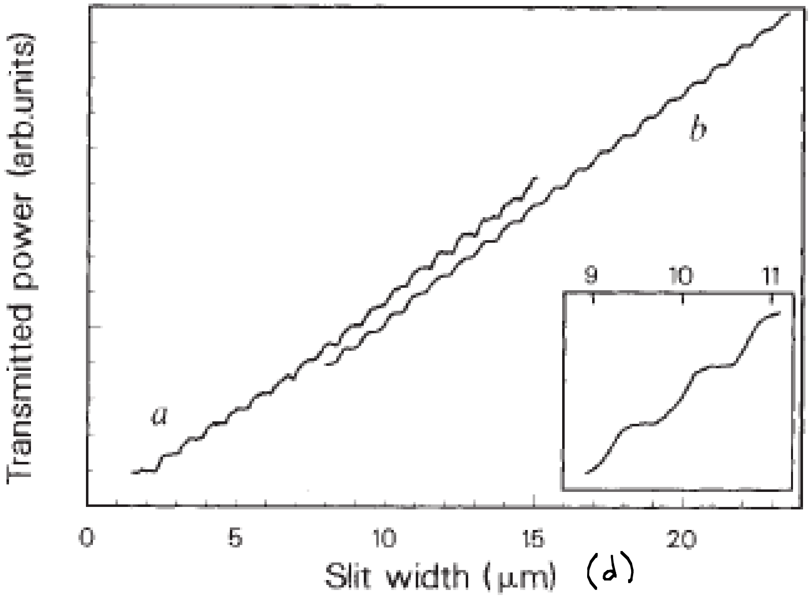
This phenomenon can also be seen in optical transmission of diffuse monochromatic photons thru a slit (where $\lambda_F \to \lambda$)



$$\vec{K} = |K|\cos\Theta\,\hat{y} + |K|\sin\Theta\,\hat{x}$$

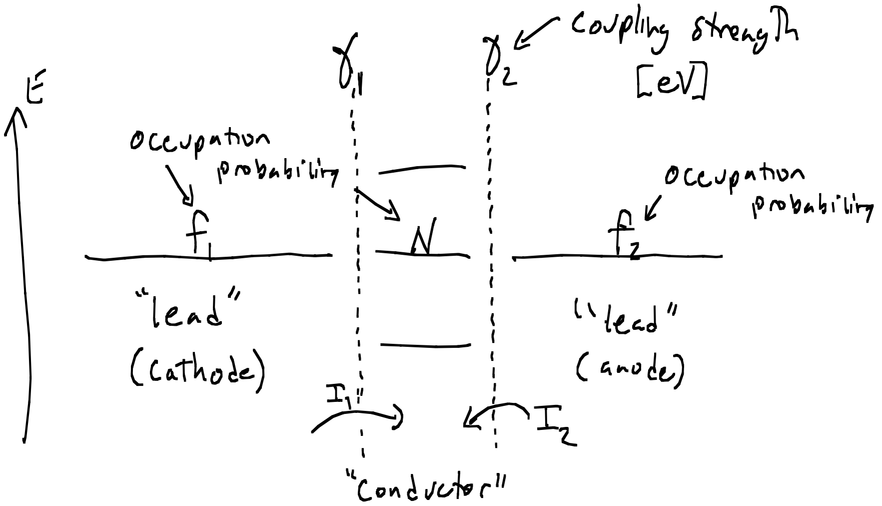
$$|K| = \frac{2\pi}{\lambda}$$

$$K_x = \frac{N\pi}{d} \qquad N = 1, 2, 3 \ldots$$



Nature $\underline{350}$ 594 (1991)

A microscopic view of 1-D transport



In steady state, $I_1 = -I_2$

$$e\underbrace{\frac{\gamma_1}{\hbar}}_{\substack{\text{rate}\\ 1/\text{time}}}\left[f_1(1-N) - N(1-f_1)\right] = -e\frac{\gamma_2}{\hbar}\left[f_2(1-N) - N(1-f_2)\right]$$

$$\gamma_1\left[f_1 - N\right] = -\gamma_2\left[f_2 - N\right]$$

$$N(\gamma_1+\gamma_2) = \gamma_1 f_1 + \gamma_2 f_2$$

$$N = \frac{\gamma_1 f_1 + \gamma_2 f_2}{\gamma_1+\gamma_2}$$

Makes sense: If $\gamma_1 = \gamma_2$, then occupation is average value of leads. If $f_1 = f_2$, then N has same occupancy as leads.

A contradiction?

Current flowing from left lead to right:

$$I = I_1 = e\frac{\gamma_1}{\hbar}(f_1 - N) = e\frac{\gamma_1}{\hbar}\left(f_1 - \frac{\gamma_1 f_1 + \gamma_2 f_2}{\gamma_1+\gamma_2}\right) = e\frac{\gamma_1}{\hbar}\left(\frac{f_1(\gamma_1+\gamma_2) - (\gamma_1 f_1 + \gamma_2 f_2)}{\gamma_1+\gamma_2}\right)$$

$$= \frac{e}{\hbar}\gamma_1 \frac{f_1\gamma_2 - \gamma_2 f_2}{\gamma_1+\gamma_2} = \frac{e}{\hbar}\frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}(f_1 - f_2)$$

This predicts infinite conductance as $\gamma_1, \gamma_2 \to \infty$

But what about limiting quantum of conductance $\frac{e^2}{h}$?!

Solution: Uncertainty principle

$\Delta E \Delta t \sim \hbar$ tells us that Energy and time are Fourier transform pairs

Example: "Bound"/"stationary" state wavefunction has time dependence $\varphi(t) = e^{-i\frac{E_0}{\hbar}t}$

Amplitude $= 1$ for all time t, so uncertainty $\Delta t \to \infty$. Fourier transform of $\varphi(t)$ is $\varphi(E) = \delta(E - E_0)$, reflecting the discrete quantized nature of bound states. Clearly, $\Delta E \to 0$ such that $\Delta E \Delta t \sim \hbar$.

For a "conductor" state coupled to "leads", time dependence is $\varphi(t) = e^{-i\frac{E_0}{\hbar}t} e^{-\frac{|t|}{\tau}}$, where the state acquires a "lifetime" τ due to tunneling from/to leads w/ coupling $\frac{\gamma_1 + \gamma_2}{\hbar} \sim \frac{1}{\tau}$.

Fourier Transform $$\int_{-\infty}^{\infty} e^{-i\frac{E_0}{\hbar}t} e^{-\frac{|t|}{\tau}} e^{i\omega t}\, dt = \int_{-\infty}^{0} e^{i\left(\omega - \frac{E_0}{\hbar} - \frac{i}{\tau}\right)t} dt + \int_{0}^{\infty} e^{i\left(\omega - \frac{E_0}{\hbar} + \frac{i}{\tau}\right)t} dt$$

$$= \left.\frac{e^{i\left(\omega - \frac{E_0}{\hbar} - \frac{i}{\tau}\right)t}}{i\left(\omega - \frac{E_0}{\hbar} - \frac{i}{\tau}\right)}\right|_{-\infty}^{0} + \left.\frac{e^{i\left(\omega - \frac{E_0}{\hbar} + \frac{i}{\tau}\right)t}}{i\left(\omega - \frac{E_0}{\hbar} + \frac{i}{\tau}\right)}\right|_{0}^{\infty} = \frac{1}{i\left(\omega - \frac{E_0}{\hbar} - \frac{i}{\tau}\right)} - \frac{1}{i\left(\omega - \frac{E_0}{\hbar} + \frac{i}{\tau}\right)} = \frac{1}{i} 2i \,\mathrm{Im}\left\{\frac{1}{\left(\omega - \frac{E_0}{\hbar} - \frac{i}{\tau}\right)}\right\}$$

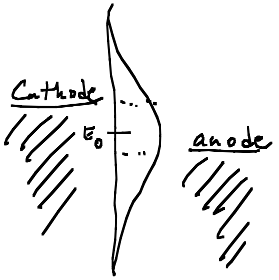
$$= 2\,\mathrm{Im}\left\{\frac{1}{\left(\omega - \frac{E_0}{\hbar} - \frac{i}{\tau}\right)} \frac{\omega - \frac{E_0}{\hbar} + \frac{i}{\tau}}{\omega - \frac{E_0}{\hbar} + \frac{i}{\tau}}\right\} = 2\frac{\frac{1}{\tau}}{\left(\omega - \frac{E_0}{\hbar}\right)^2 + \left(\frac{1}{\tau}\right)^2} \xrightarrow{\text{Normalize}} \frac{\hbar^2}{\hbar^2}\frac{\frac{2}{\pi}\frac{1}{\tau}\,d\omega}{\left(\omega - \frac{E_0}{\hbar}\right)^2 + \left(\frac{1}{\tau}\right)^2} \Longrightarrow \frac{\frac{2}{\pi}(\gamma_1 + \gamma_2)\, dE}{(E - E_0)^2 + (\gamma_1 + \gamma_2)^2}$$

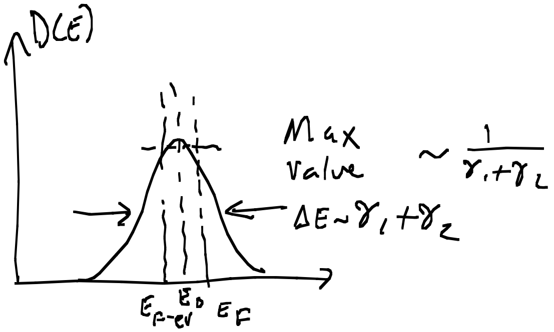
Broadened state!

Re-Calculate current

broadened state

$$I = \frac{e}{\hbar}\int_{-\infty}^{\infty}\frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}\left(f_1-f_2\right)D(E)\,dE$$





@ T=0 and no energy dependence of coupling γ_1,γ_2 $\Bigg\}$

$$\Rightarrow \quad I = \frac{e}{\hbar}\frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}\int_{E_F-eV}^{E_F} D(E)\,dE = \frac{e}{\hbar}\frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}\int_{E_F-eV}^{E_F}\frac{\frac{2}{\pi}(\gamma_1+\gamma_2)\,dE}{(E-E_0)^2+(\gamma_1+\gamma_2)^2}$$

Further, assume E_0 lies midway between L and R Fermi levels and broadening $\gamma_1+\gamma_2 > eV$

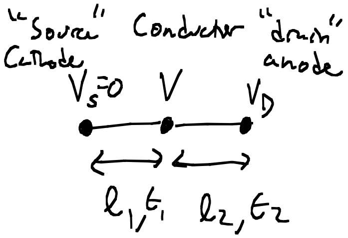
$$\Rightarrow \quad I = \frac{e}{\hbar}\frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}\frac{2}{\pi}\frac{eV}{(\gamma_1+\gamma_2)}$$

If $\gamma_1=\gamma_2$, $\quad I = \frac{e^2}{\hbar\cdot 2\pi}V = \frac{e^2}{h}V$

This recovers the familiar "quantum of conductance": State lifetime and broadening resolves the inconsistency with our previous continuous transport theory.

Where does the conductor state lie?

We assumed the state lies in-between the cathode and anode Fermi levels, but this is properly determined by Electrostatics: we need to solve



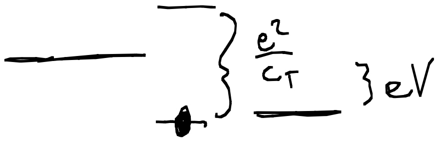
poisson's eq $\nabla \epsilon \nabla V = \rho$ for discrete model

$$\frac{\frac{\epsilon_1 V}{l_1} - \frac{\epsilon_2 (V_D - V)}{l_2}}{l_1 + l_2} = \frac{\Delta N e}{l_1 + l_2} \longrightarrow \quad C_S V - C_D (V_D - V) = \Delta N e$$

$$(C_S + C_D) V = C_D V_D + \Delta N e$$

potential energy $eV = \underbrace{\frac{C_D}{C_S + C_D}}_{\text{leads}} eV_D + \underbrace{\frac{e^2}{C_S + C_D}}_{\text{single-electron charging energy}} \Delta N$

This charging energy pushes all unfilled states to higher energy and leads to "Coulomb blockade": splitting of otherwise degenerate states by $\Delta E = \frac{e^2}{C_S + C_D} = \frac{e^2}{C_T}$ which eliminates transport at small bias $eV < \Delta E$.



But, only if thermal energy $k_B T$ and broadening $\gamma_1 + \gamma_2 << \Delta E$.

Calculation of lengthscale for "Coulomb blockade"

Approx w/ Sphere: $C = \frac{q}{V} \Longrightarrow \frac{q}{\frac{q}{4\pi\varepsilon_0\varepsilon_r R}} = 4\pi\varepsilon_0\varepsilon_r R$ ← radius

single-electron charging energy $\frac{e^2}{C} = \frac{\left(\frac{e^2}{4\pi\varepsilon_0}\right)}{\varepsilon_r R}$

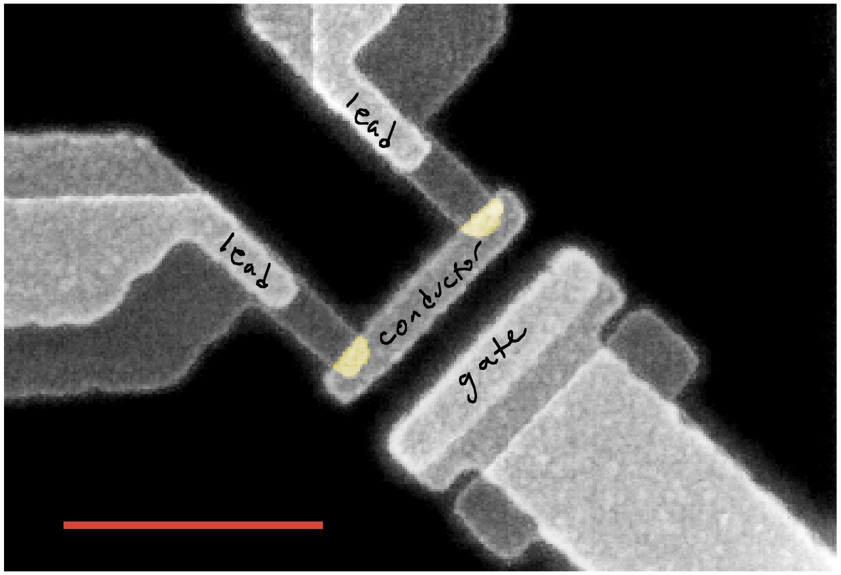
$\frac{e^2}{4\pi\varepsilon_0\hbar c} = \alpha$ so $\frac{e^2}{4\pi\varepsilon_0} = \alpha\hbar c = \frac{1}{137}\cdot 6.6\times10^{-16}\,\text{eVs}\cdot 3\times10^{10}\,\frac{\text{cm}}{\text{s}} \sim 1.4\times10^{-7}\,\text{cm}\cdot\text{eV}$

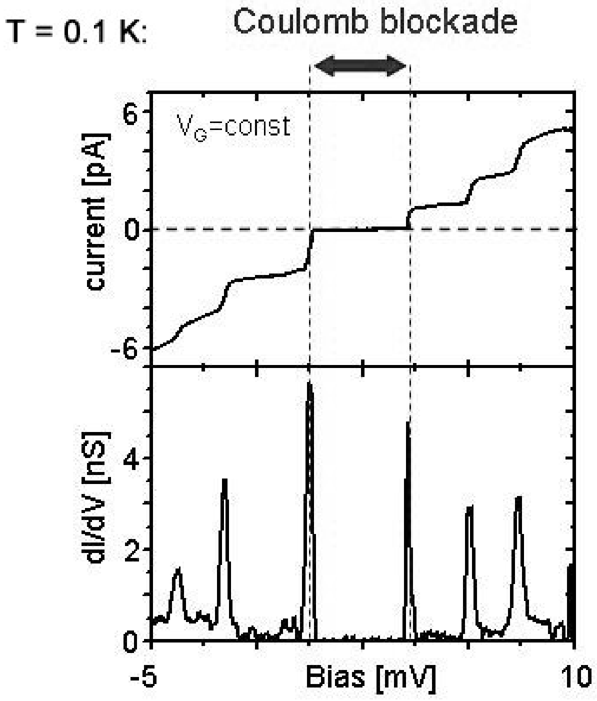
Then if $\frac{e^2}{4\pi\varepsilon_0\varepsilon_r R} > k_B T = 0.026\,\text{eV}$ @ RT we have Coulomb blockade.

$R < \frac{1.4\times10^{-7}\,\text{eV cm}}{10\cdot 0.026\,\text{eV}} \cong 5\times10^{-7}\,\text{cm} \rightarrow 5\,\text{nm}$

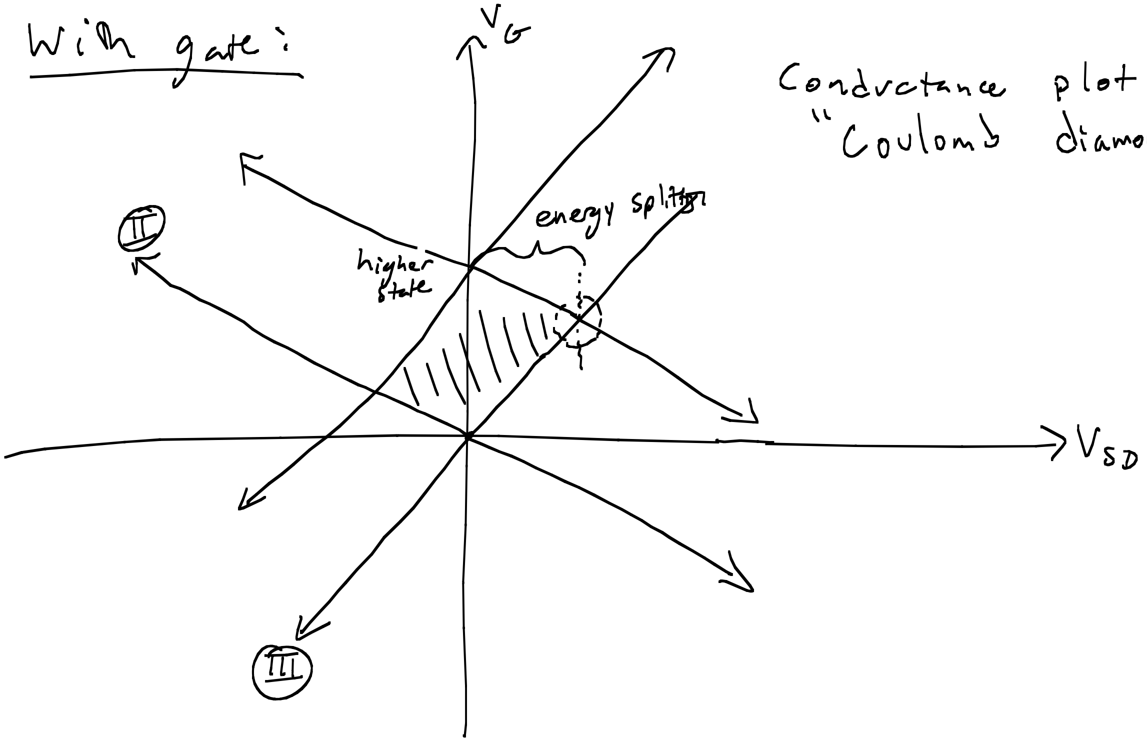
This sets the lengthscale for conductors where we may expect to see Coulomb blockade @ RT. Lower temps allow larger lengthscales.

Experiment

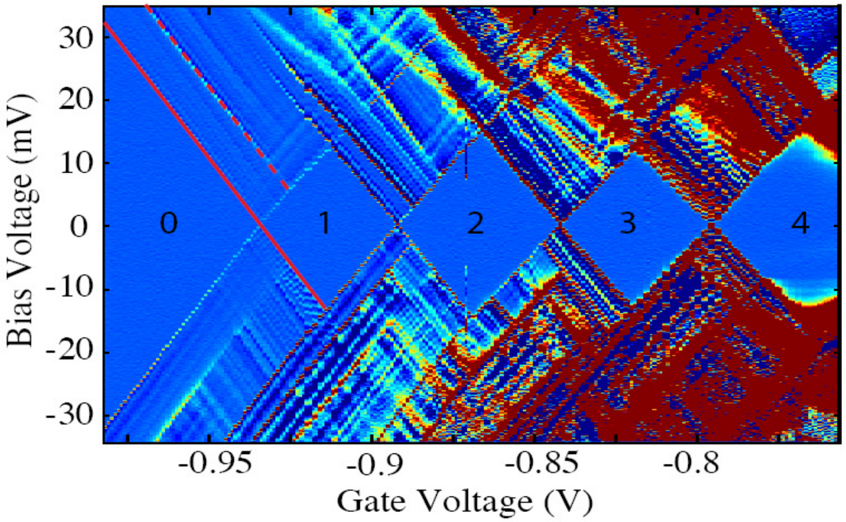




With gate:



Conductance plot: "Coulomb diamond"



Quantum Hall Effect (Integer / 2DEG)

Magnetic field enters Hamiltonian thru kinetic energy term $\frac{\vec{p}^2}{2m} \longrightarrow \frac{(\vec{p}-e\vec{A})^2}{2m}$

For $\vec{B} = B\hat{z}$, choose symmetric gauge $\vec{A} = \frac{B}{2}(x\hat{y} - y\hat{x})$

$$\vec{B} = \vec{\nabla}\times\vec{A} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \partial_x & \partial_y & \partial_z \\ -\frac{By}{2} & \frac{Bx}{2} & 0 \end{vmatrix} = B\hat{z} \quad ✓$$

Then,

$$H = \frac{\left(p_x + \frac{eBy}{2}\right)^2 + \left(p_y - \frac{eBx}{2}\right)^2 + p_z^2}{2m} = \frac{p_x^2+p_y^2+p_z^2}{2m} + \frac{1}{2}m\frac{e^2B^2}{4m^2}(x^2+y^2) - \frac{eB}{2m}(p_y x - p_x y)$$

$$= \underbrace{\frac{p^2}{2m} + \frac{1}{2}m\left(\frac{\omega_c}{2}\right)^2(x^2+y^2)}_{\text{Harmonic oscillator in 2D}} - \frac{\omega_c}{2}L_z$$

→ States equally separated by $\overset{\text{x and y dir}}{2\times}\frac{\hbar\omega_c}{2} = \hbar\omega_c$: "Landau levels"

→ wavefunction $\propto \exp\left(-\frac{x^2+y^2}{2\ell_0^2}\right)$ where $\ell_0 = \sqrt{\frac{2\hbar}{m\omega_c}}$

Filling fraction

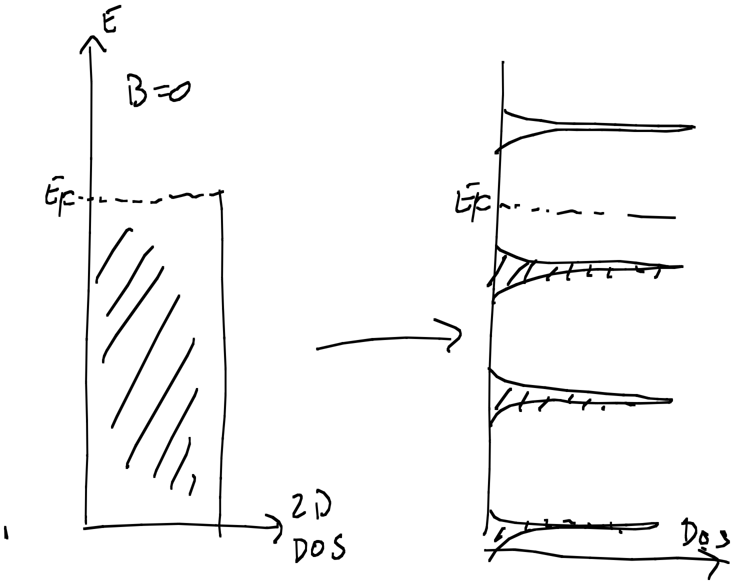
In 2-D, density of states $\frac{d^2k}{(2\pi)^2} \rightarrow \frac{2\pi k\,dk}{(2\pi)^2} = \frac{1}{2\pi}\sqrt{\frac{2m\cancel{E}}{\hbar^2}}\,\frac{\sqrt{\frac{2m}{\hbar^2 \cancel{E}}}}{2}\,dE = \frac{m}{2\pi\hbar}\,dE$

(Spin degeneracy is lifted by magnetic field)

States within $\Delta E = \hbar\omega_c$ condense to density

$$n_{2d} = \hbar\omega_c \frac{m}{2\pi\hbar^2} = \cancel{\hbar}\frac{eB}{\cancel{m}}\frac{\cancel{m}}{2\pi\hbar^{\cancel{2}}} = \frac{eB}{h}$$

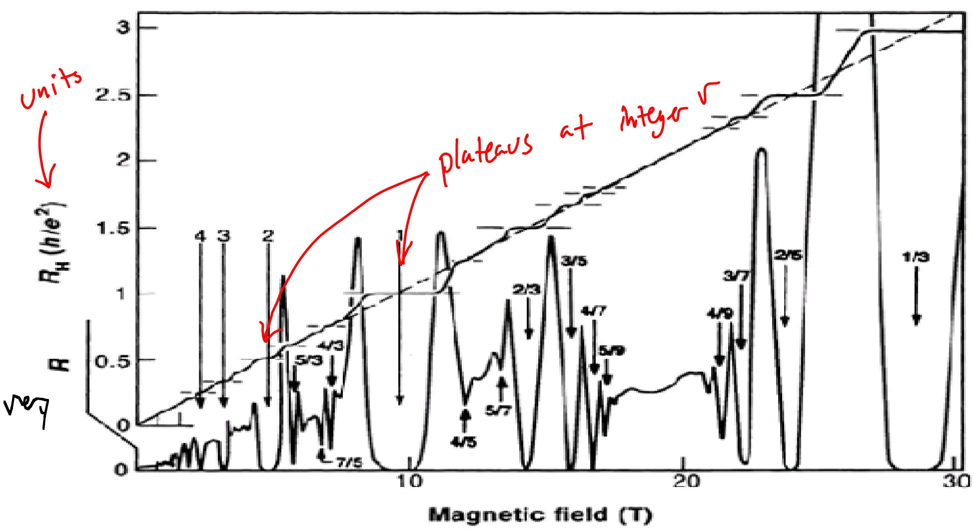
fill each of ν Landau levels.
"filling fraction"



So Hall resistance

resistance quantum
~26kΩ

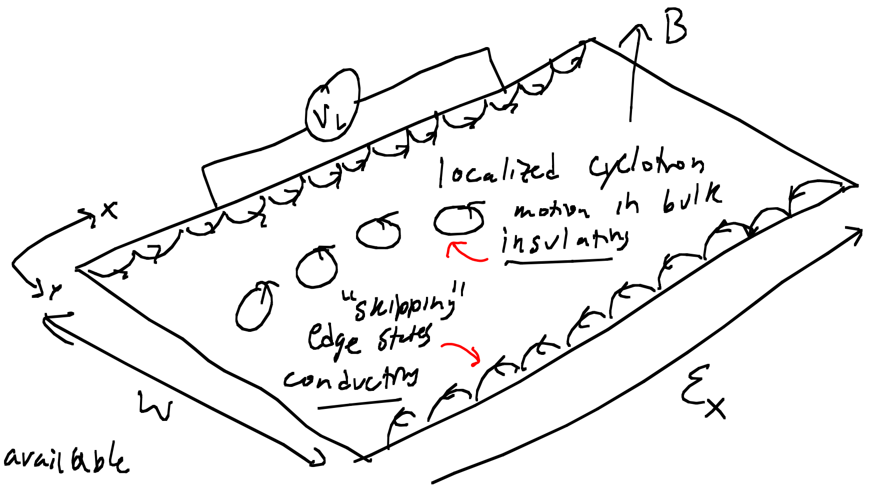
$$R_{Hall} = \frac{V_{Hall}}{I} = -\frac{B}{e(nt)} = -\frac{\cancel{B}}{e\left(\frac{e\cancel{B}}{h}\right)\nu} = \frac{h}{e^2}\frac{1}{\nu}$$

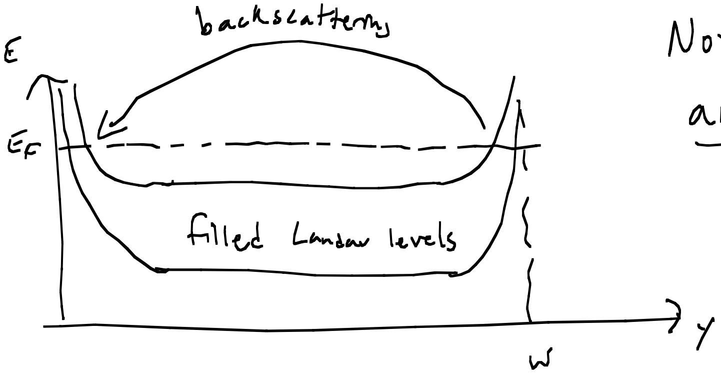


Von Klitzing won 1985 Nobel prize for discovery of exact quantization of Hall resistance

Edge states and ρ_{xx} in QHE

Note ρ_{xx} is zero at ρ_{xy} plateaus when integer # of Landau levels are filled. This is because the current is carried by "chiral" edge states that cannot be backscattered unless empty states at E_F are available to carry them across the bulk. Then, the longitudinal resistance rises.





Notably, because ρ is a tensor, we can have $\rho_{xx}=0$ and $\sigma_{xx}=0$ simultaneously!

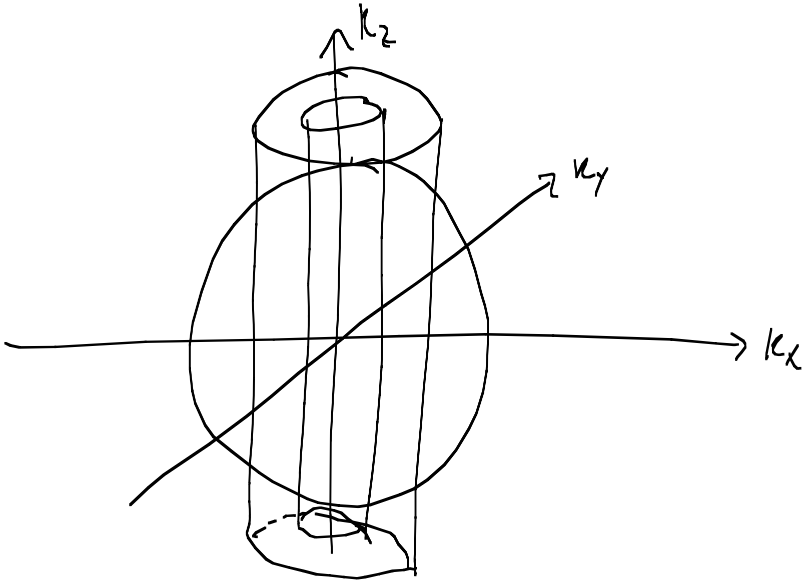
$$\overleftrightarrow{\sigma} = \overleftrightarrow{\rho}^{-1} = \begin{bmatrix} 0 & \rho_{xy} \\ -\rho_{xy} & 0 \end{bmatrix}^{-1} = \begin{bmatrix} 0 & -\frac{1}{\rho_{xy}} \\ \frac{1}{\rho_{xy}} & 0 \end{bmatrix}$$

Also Note: cyclotron orbits have area $A = \pi \ell_0^2 = \pi\left(\sqrt{\frac{2\hbar}{m\omega_c}}\right)^2$

So the flux per orbit $\Phi = B\cdot A = \cancel{B}\frac{2\pi\hbar}{\cancel{m}\frac{e\cancel{B}}{\cancel{m}}} = \frac{h}{e}$ is also quantized!

$\uparrow$ magnetic flux quantum

Landau levels in 3D



Applying $\vec{B} = B\hat{z}$ quantizes energy associated with motion in the x-y plane (cyclotron orbits). States inside Fermi sphere must collapse onto "Landau tubes" where $k_x^2 + k_y^2$ is constant.

As B increases, these tubes leave the Fermi sphere and the occupation at the Fermi surface changes, This causes essentially all the physical thermodynamic properties to oscillate w/ $1/B$.

→ How many "Landau tubes" in typical 3D metal @ typical fields?

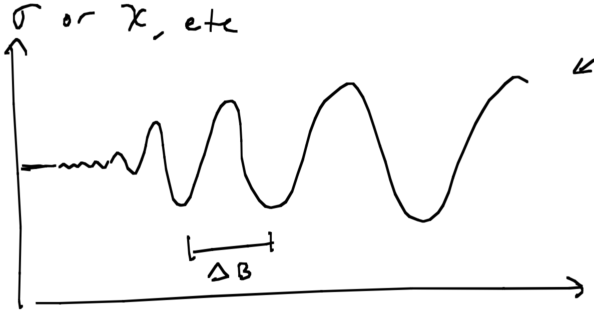
$$\nu = \frac{E_F}{\hbar\omega_c} = \frac{E_F}{\hbar \frac{eB}{m}} = \frac{E_F}{2 \cdot \mu_B B} \sim \frac{10\,\text{eV}}{2 \cdot 5.8\times10^{-5}\,\text{eV}/T \cdot B} \sim 10^5 \text{ in } 1T \text{ field}$$

This is a huge number, far exceeding $\nu \sim 1$ in 2DEG Quantum Hall regime

Shubnikov-de Haas / de Haas-van Alphen effect: (oscillations in σ or χ)

As we change B, filling fraction changes in proportion to the cross-sectional area of the Fermi surface perpendicular to B:

$$\nu = \frac{E_F}{\hbar\omega_c} = \frac{\frac{\hbar^{\cancel{2}} k_F^2}{2\cancel{m}}}{\cancel{\hbar}\frac{e}{\cancel{m}}B} = \frac{\hbar}{2\pi e}\underbrace{\left(\pi k_F^2\right)}_{\substack{\text{cross-sectional area} \\ \text{of Fermi surface}}}\frac{1}{B} = \left(\frac{S_F}{2\pi}\frac{\hbar}{e}\right)\frac{1}{B}$$



magnitude of oscillation becomes larger as filling fraction decreases and losing each LL makes a larger relative change.

We can find the period of oscillation in B:

$$\frac{1}{B} = \frac{2\pi e}{S_F\hbar}\nu \rightarrow \Delta\frac{1}{B} = \frac{2\pi e}{S_F\hbar}\Delta\nu \rightarrow -\frac{\Delta B}{B^2} = \frac{2\pi e}{S_F\hbar} \rightarrow |\Delta B| = \frac{2\pi e}{S_F\hbar}B^2$$

This relationship is true even when the Fermi surface is not a sphere!

By changing orientation of $\vec{B}$, anisotropy of S_F can be measured and Fermi surface reconstructed!

Thermodynamic properties in 3D

integral over 3D k-space ⟶ integral over (1D) Energy

infinitesimal $$2\frac{d^3k}{(2\pi)^3} \rightarrow 2\frac{4\pi k^2 dk}{(2\pi)^3} \rightarrow \frac{1}{\pi^2}\left(\sqrt{\frac{2mE}{\hbar^2}}\right)^2 \sqrt{\frac{2m}{\hbar^2 E}}\,\frac{dE}{2} = g(E)\,dE$$

density of states $$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Since $$E_F = \frac{\hbar^2 k_F^2}{2m}$$

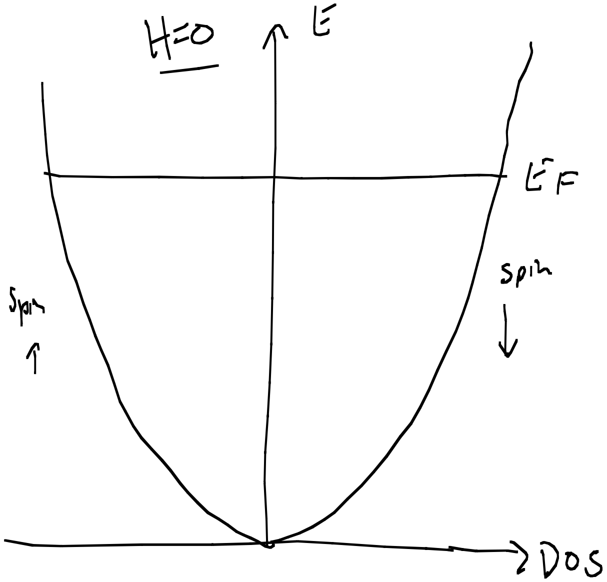
$$g(E) = \frac{1}{2\pi}\frac{1}{E_F}\left(\frac{E}{E_F}\right)^{1/2}\left(k_F^2\right)^{3/2} = \frac{1}{2\pi^2}\frac{1}{E_F}\left(\frac{E}{E_F}\right)^{1/2}\left(3\pi^2 n\right) = \frac{3}{2}\frac{n}{E_F}\left(\frac{E}{E_F}\right)^{1/2}$$

we can then recover a nicely compact expression for DOS @ E_F:

$$g(E_F) = \frac{3}{2}\frac{n}{E_F}$$

This is very valuable in approximating thermodynamic values of the 3DEG

Application of 3D DOS @ E_F: magnetic susceptibility $\chi = M/H$ @ $T=0$

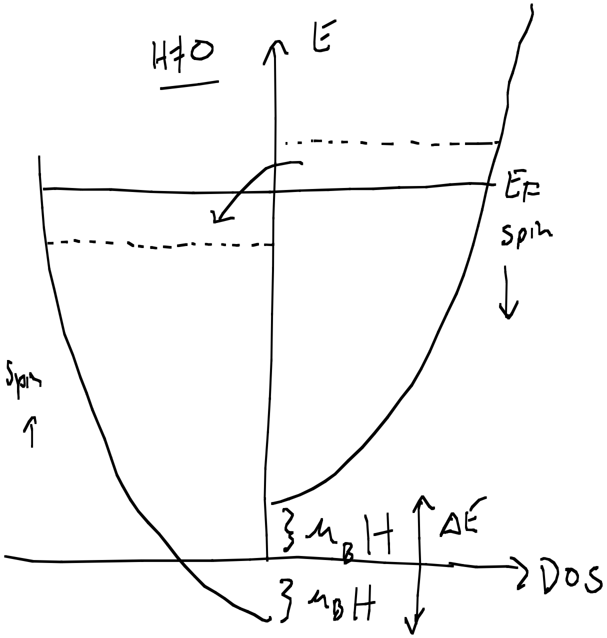


$$E_{Zeeman} = -\vec{\mu}\cdot\vec{H}$$

$$= -g\mu_B \vec{S}\cdot\vec{H}$$

$$= \pm \mu_B H$$

for spin 1/2: $g=2$ and $|\mu| = \mu_B$



Magnetization: $M = (n_\uparrow - n_\downarrow)\mu_B = \left[\frac{1}{2}\int_{-\mu_B H}^{E_F} g(E+\mu_B H)\,dE - \frac{1}{2}\int_{\mu_B H}^{E_F} g(E-\mu_B H)\,dE\right]\mu_B \neq 0$

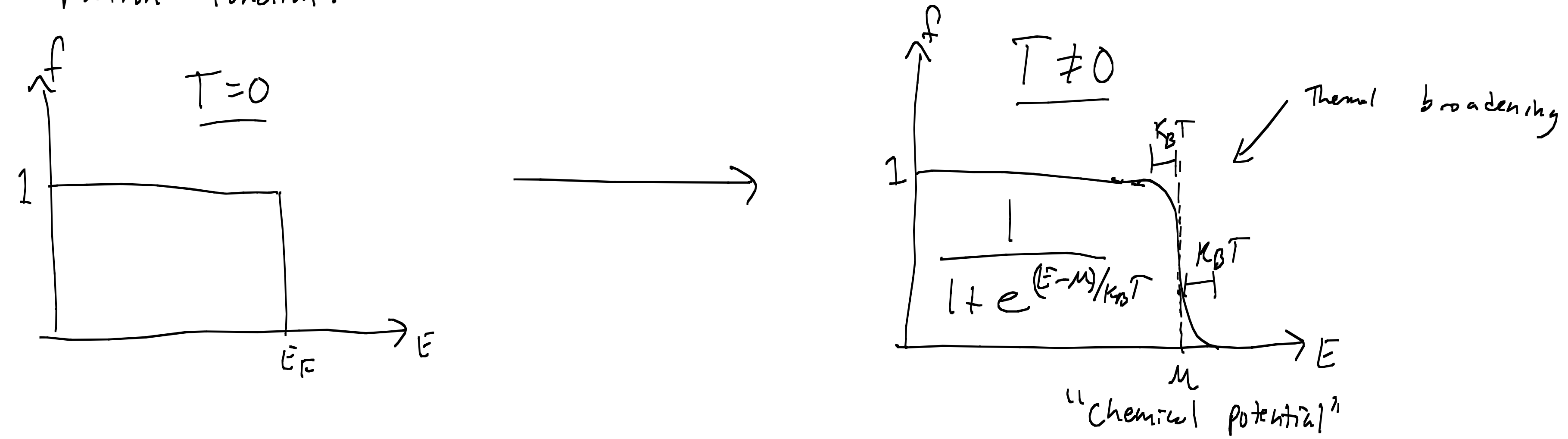
We can approximate the difference by accounting only for asymmetry at Fermi Energy

$$M \sim \overbrace{\Delta E \cdot \frac{g(E_F)}{2}}^{\#\text{ of states per volume}} \cdot \overset{\text{magnetic moment per state}}{\mu_B} = \frac{1}{2}\left(2\mu_B H \cdot \frac{3}{2}\frac{n}{E_F}\right)\mu_B = \left(\frac{3}{2}\frac{n\mu_B^2}{E_F}\right)H \quad \text{so} \quad \chi = \frac{3}{2}\,n\,\frac{\mu_B^2}{E_F}$$

Equivalently, we can Taylor expand $g(E \pm \mu_B H)$ and arrive at the same answer.

Application #2: Approximation of specific heat

occupation function:



Due to Pauli exclusion, thermal energy can only be absorbed within ~k_BT of E_F

$$\text{Energy density } u \sim \overbrace{k_BT \cdot g(E_F)}^{\#\text{ of states per volume}} \cdot \overbrace{k_BT}^{\text{energy per state}} = \frac{3}{2}\frac{n}{E_F}(k_BT)^2$$

So heat capacity $$C_v = \left.\frac{du}{dT}\right|_V = 3nk_B\left(\frac{k_BT}{E_F}\right) = 3nk_B\left(\frac{T}{T_F}\right)$$

Small at RT!

This is *much* smaller than the classical value $\frac{3}{2}nk_B$!

"Exact" Thermodynamic Calculation for 3DEG

T=0 energy density

$$u = \int_0^{E_F} E\, g(E)\, dE \quad \text{(easy!)} \longrightarrow \overset{T \neq 0}{u} = \int_0^{\infty} E\, g(E) f(E)\, dE = \int_0^{\infty} \frac{E\, g(E)}{1 + e^{(E-\mu)/k_BT}}\, dE \quad \text{(hard!)}$$

"Sommerfeld expansion":

For $\int_{-\infty}^{\infty} H(E) f(E)\, dE$, define $K(E) \equiv \int_{-\infty}^{E} H(E')\, dE'$ so that $H(E) = \frac{dK(E)}{dE}$

Then $$\int_{-\infty}^{\infty} H(E) f(E)\, dE = \int_{-\infty}^{\infty} f(E)\, dK \xrightarrow{\text{integration by parts}} \cancelto{0}{K(E) f(E) \Big|_{-\infty}^{\infty}} - \int_{-\infty}^{\infty} K \frac{df}{dE}\, dE$$

Since $\frac{df}{dE}$ is non-negligible only near $E=\mu$, Taylor expand $K(E)$:

$$K(E) = K(\mu) + (E-\mu) \frac{dK}{dE}\Big|_{E=\mu} + \frac{(E-\mu)^2}{2} \frac{d^2K}{dE^2}\Big|_{E=\mu} + \cdots$$

Then we have

$$K(\mu) \int_{-\infty}^{\infty} \cancelto{1}{\left(-\frac{df}{dE}\right)} dE + \frac{dK}{dE}\Big|_{E=\mu} \int_{-\infty}^{\infty} \cancelto{0 \text{ by symmetry}}{\overset{\text{odd}}{(E-\mu)} \overset{\text{even}}{\left(-\frac{df}{dE}\right)}} dE + \sum_{n=1}^{\infty} \frac{d^{2n}K}{dE^{2n}} \int \frac{(E-\mu)^{2n}}{(2n)!} \left(-\frac{df}{dE}\right) dE$$

all odd powers vanish by symmetry

To second order:

$$\int_{-\infty}^{\infty} H(E)\, f(E)\, dE = \int_{-\infty}^{\mu} H(E)\, dE + \frac{dH}{dE}\Big|_{E=\mu} \int_{-\infty}^{\infty} \frac{(E-\mu)^2}{2}\left(-\frac{df}{dE}\right) dE + \ldots$$

define $X \equiv \frac{E-\mu}{k_B T}$ Then

$$= \int_{-\infty}^{\mu} H(E)\, dE + a_1 (k_B T)^2 \frac{dH}{dE}\Big|_{E=\mu} + \ldots$$

where $a_1 = \int_{-\infty}^{\infty} \frac{X^2}{2}\left(-\frac{d}{dX}\frac{1}{1+e^X}\right) dX = \frac{\pi^2}{6}$

So $$\int_{-\infty}^{\infty} H(E)\, f(E)\, dE = \int_{-\infty}^{\mu} H(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \frac{dH}{dE}\Big|_{E=\mu} + \text{(higher order terms)}$$

Examples at finite temperature

electron density:

$$n = \int_{-\infty}^{\infty} g(E)\, f(E)\, dE \qquad \left(\text{since } f(E) = \frac{1}{e^{(E-\mu)/k_B T}+1}, \text{ this sets } \mu \right)$$

$$= \int_{-\infty}^{\mu} g(E)\, dE + \frac{\pi^2}{6} (k_B T)^2 \left.\frac{dg}{dE}\right|_{E=\mu} + \ldots$$

$$= \int_{0}^{E_F} g(E)\, dE + \int_{E_F}^{\mu} g(E)\, dE + \frac{\pi^2}{6} (k_B T)^2 \left.\frac{dg}{dE}\right|_{E=\mu} + \ldots$$

$$\downarrow$$

$$= n + \left\{ (\mu - E_F)\, g(E_F) + \frac{\pi^2}{6} (k_B T)^2 \left.\frac{dg}{dE}\right|_{E=\mu} + \ldots \right\} = 0$$

so

$$\Rightarrow \mu \approx E_F - \frac{\pi^2}{6} (k_B T)^2 \left.\frac{dg(E)/dE}{g(E)}\right|_{\overset{\downarrow}{E=E_F}} \xrightarrow{g \propto E^{1/2}} \mu \approx E_F - \frac{\pi^2}{6} (k_B T)^2 \left(\frac{1}{2E_F}\right) = E_F \left(1 - \frac{1}{3} \left(\frac{\pi k_B T}{2E_F} \right)^2 \right)$$

$\mu = E_F$ @ $T=0$ as expected, and $\mu \sim E_F$ is a good approx @ RT!

Energy density and heat capacity

$$u = \int_{-\infty}^{\infty} E\, g(E)\, f(E)\, dE$$

$$= \int_{-\infty}^{\mu} E\, g(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \frac{d}{dE}\left(E\, g(E)\right)\Big|_{E=\mu} + \; \ldots$$

$$= \int_{-\infty}^{E_F} E\, g(E)\, dE + \int_{E_F}^{\mu} E\, g(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \left(g + E\frac{dg}{dE}\right)\Big|_{E=\mu} + \ldots$$

$$\sim \underbrace{\int_{0}^{E_F} E\, g(E)\, dE}_{u(T=0)=u_0!} + E_F \left\{(\mu - E_F)\, g(E_F) + \frac{\pi^2}{6}(k_B T)^2 \frac{dg}{dE}\Big|_{E=\mu}\right\}^{=0\ \text{(see last page!)}} + \frac{\pi^2}{6}(k_B T)^2\, g(E)\Big|_{E=E_F}$$

So

$$u \sim u_0 + \frac{\pi^2}{6}(k_B T)^2\, g(E_F)$$

And

$$C_V = \frac{du}{dT}\Big|_V = \frac{\pi^2}{3} k_B^2\, T\, g(E_F) = \frac{\pi^2}{2}\frac{k_B T}{E_F}\, n k_B = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right) n k_B$$

C.f. $3\left(\frac{T}{T_F}\right) n k_B$ from heuristic approx!

Thermal properties Redux

Weidemann-Franz Law

$$\frac{\kappa}{\sigma} = \frac{\frac{1}{3} v^2 \cancel{\tau} c_v}{\frac{ne^2 \cancel{\tau}}{m}} = \frac{\frac{1}{3}\left(\frac{\cancel{2}\cancel{E_F}}{\cancel{m}}\right)\frac{\pi^2}{\cancel{2}}\frac{k_B T}{\cancel{E_F}} n k_B}{\frac{\cancel{n}e^2}{\cancel{m}}} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T \qquad \text{C.f. Drude } \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T$$

$$= LT \sim \left(2.4 \times 10^{-8} \frac{W\Omega}{K^2}\right) T$$

Thermopower

We previously found $\mathcal{E} = -\frac{1}{3e}\frac{dE}{dT}\nabla T = -\frac{1}{3en}\frac{d(nE)}{dT}\nabla T = -\frac{c_v}{3en}\nabla T = Q\nabla T$

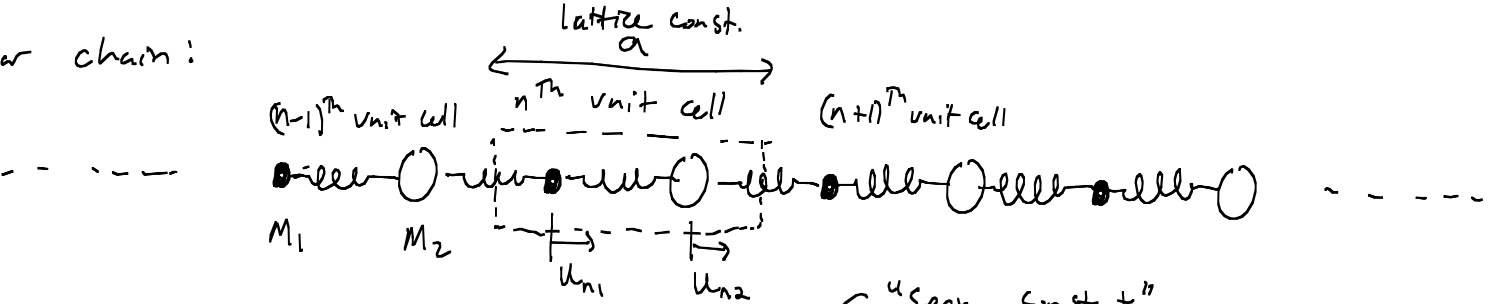
so $$Q = -\frac{c_v}{3en} = -\frac{\frac{\pi^2}{2}\frac{k_B T}{E_F}\cancel{n} k_B}{3e\cancel{n}} = -\frac{\pi^2}{6}\frac{k_B}{e}\left(\frac{T}{T_F}\right) \qquad \text{C.f. Drude } -\frac{k_B}{2e}$$

Small @ RT!

This smaller value is consistent with experiment and resolves the discrepancy calculated w/ the Drude model.

Atom dynamics: model 1D "crystal"

diatomic linear chain:



Newton's 2nd Law: $F = ma$, $F = -\overset{\text{"spring constant"}}{f}\,\Delta u$ ← distance between nearest neighbors relative to equilibrium

atom 1 (●): $-f(u_{n1}-u_{n-1,2}) - f(u_{n1}-u_{n2}) = M_1\ddot{u}_{n1}$

atom 2 (○): $-f(u_{n2}-u_{n+1,1}) - f(u_{n2}-u_{n1}) = M_2\ddot{u}_{n2}$

Ansatz: plane wave solution $u_{n\alpha} = \frac{1}{\sqrt{M_\alpha}}u_\alpha(q)e^{i(qr_n-\omega t)}$ where $\alpha = 1,2$ labels atom type

Substitution:

$$-\frac{2f}{\sqrt{M_1}}u_1(q)e^{i(qna-\omega t)} + \frac{f}{\sqrt{M_2}}u_2(q)\left(e^{i(q(n-1)a-\omega t}+e^{i(qna-\omega t)}\right) = -\sqrt{M_1}\,\omega^2 u_1(q)e^{i(qna-\omega t)}$$

$$-\frac{2f}{\sqrt{M_2}}u_2(q)e^{i(qna-\omega t)} + \frac{f}{\sqrt{M_1}}u_1(q)\left(e^{i(q(n+1)a-\omega t}+e^{i(qna-\omega t)}\right) = -\sqrt{M_2}\,\omega^2 u_2(q)e^{i(qna-\omega t)}$$

Hermitian matrix eigenvalue equation

Equivalent to:

$$\begin{bmatrix} \frac{2f}{m_1} & -\frac{f}{\sqrt{m_1 m_2}}\left(1+e^{-iqa}\right) \\ -\frac{f}{\sqrt{m_1 m_2}}\left(1+e^{+iqa}\right) & \frac{2f}{m_2} \end{bmatrix} \begin{bmatrix} u_1(q) \\ u_2(q) \end{bmatrix} = w^2 \begin{bmatrix} u_1(q) \\ u_2(q) \end{bmatrix}$$

which has analytic eigenvalues:

$$w^2 = f\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm f\left[\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}\sin^2\frac{qa}{2}\right]^{1/2}$$

(Note $\frac{2\pi}{a}$ periodicity in q!)

For $qa \ll 1$

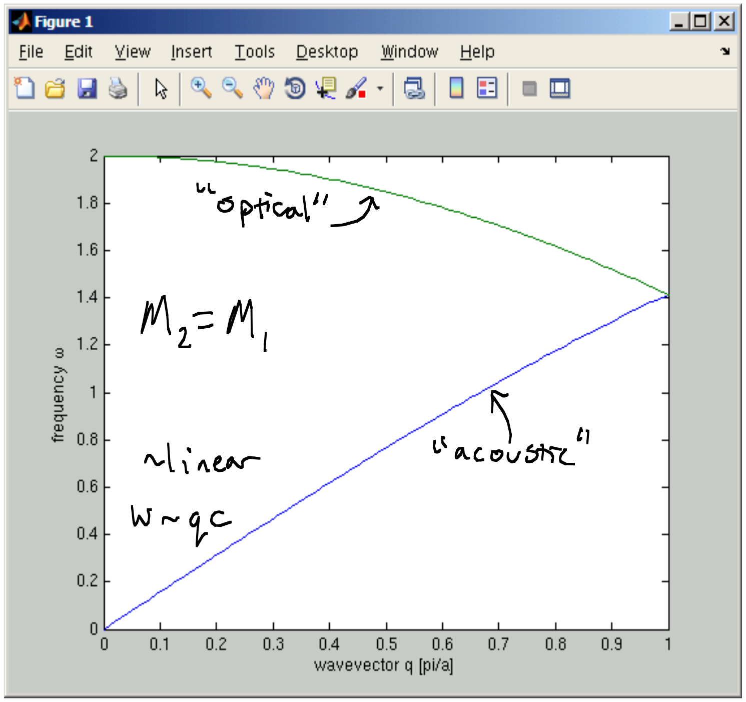
$$w^2 \sim f\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\left(1 \pm \left(1 - \frac{1}{2}\frac{\cancel{4}}{\cancel{m_1}m_2}\frac{(m_1 m_2)^{\cancel{2}}}{(m_1+m_2)^2}\frac{(qa)^2}{\cancel{4}}\right)\right) \sim \begin{cases} 2f\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \\ \text{and} \\ \frac{f}{m_1+m_2}\frac{(qa)^2}{2} \end{cases}$$

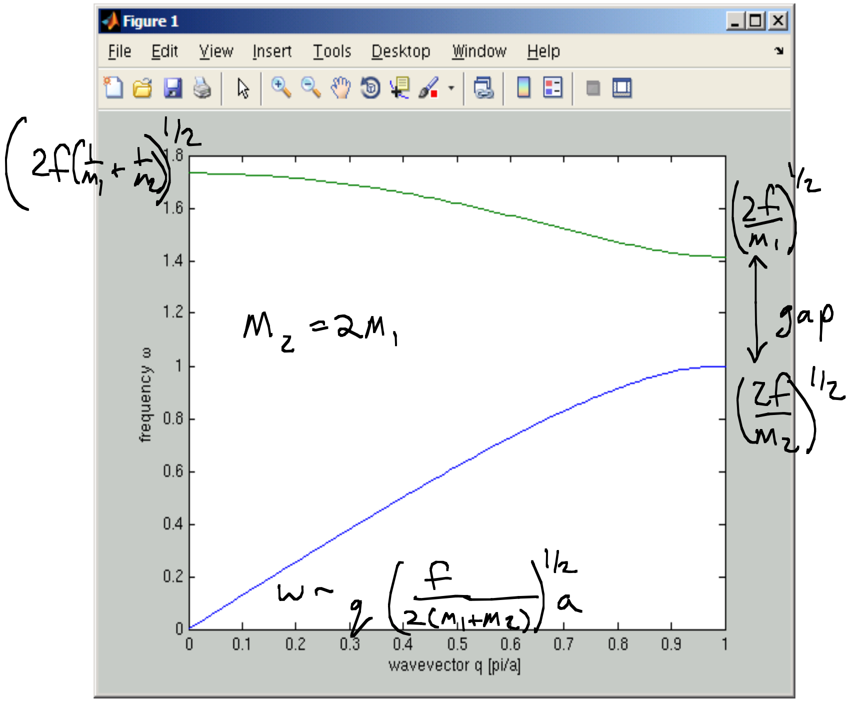
For $q = \frac{\pi}{a}$,

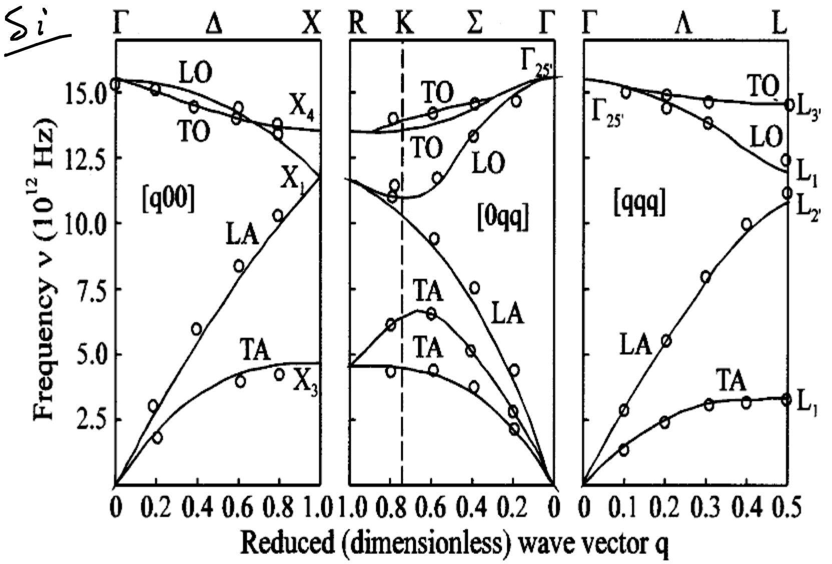
$$w^2 = f\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm f\left[\frac{(m_1+m_2)^2 - 4m_1 m_2}{(m_1 m_2)^2}\right]^{1/2} = f\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm f\left(\frac{1}{m_1}-\frac{1}{m_2}\right)$$

(So degeneracy when $m_1 = m_2$)

Dispersion relation







In 3 dimensions, we still have "acoustic" and "optical" phonons, but now displacement $\vec{u}$ can be both longitudinal $(\vec{u}\parallel\vec{q})$ or transverse $(\vec{u}\perp\vec{q})$.

This gives 1 and 2 "branches" for each type of mode ⟶

Thermodynamics of Coupled Harmonic Oscillators

We previously used classical mechanics theory to derive a linear atom displacement wave dispersion. For thermodynamic properties, we must consider QM spectrum of harmonic oscillator which gives $E_n = \hbar\omega(n+\frac{1}{2})$ $(n=0,1,2,\ldots)$.

Relative occupation determined by Maxwell factor: $P_n \propto e^{-E_n/kT}$

where the total occupation probability is unity: $\sum_{n=0}^{\infty} P_n = 1$

This gives $\sum_n C e^{-\hbar\omega(n+\frac{1}{2})/kT} = C e^{-\frac{\hbar\omega}{2kT}} \sum_{n=0}^{\infty} e^{-\hbar\omega n/kT}$ (a geometric series)

$$\left[1+x+x^2+\ldots = 1+x(1+x+x^2+\ldots) \rightarrow \sum_n x^n = 1+x\sum_n x^n \quad \text{so} \quad \sum_n x^n = \frac{1}{1-x} \right]$$

Then, $C e^{-\frac{\hbar\omega}{2kT}} \frac{1}{1-e^{-\hbar\omega/kT}} = 1$ so $C = \frac{1-e^{-\frac{\hbar\omega}{kT}}}{e^{-\hbar\omega/2kT}} = e^{\frac{\hbar\omega}{2kT}}\left(1-e^{-\hbar\omega/kT}\right)$

and $P_n = e^{\frac{\hbar\omega}{2kT}}\left(1-e^{-\hbar\omega/kT}\right) e^{-\frac{\hbar\omega}{kT}(n+\frac{1}{2})} = e^{-\frac{\hbar\omega n}{kT}}\left(1-e^{-\frac{\hbar\omega}{kT}}\right)$

Energy of Ensemble of Harmonic Oscillators

we use this discrete distribution to evaluate expectation value of energy:

$$\langle E\rangle = \sum_{n=0}^{\infty} E_n P_n = \sum_n e^{-\frac{\hbar\omega n}{kT}}\left(1-e^{-\frac{\hbar\omega}{kT}}\right)\hbar\omega\left(n+\tfrac{1}{2}\right) = \hbar\omega\left(1-e^{-\hbar\omega/kT}\right)\sum_n \left(n+\tfrac{1}{2}\right)e^{-\frac{\hbar\omega n}{kT}}$$

Since geometric sum $\sum_n x^n = \frac{1}{1-x}$, we have $\frac{d}{dx}\sum_n x^n = \sum_n n x^{n-1} = \frac{1}{(1-x)^2}$

So $\sum_n n x^n = \frac{x}{(1-x)^2}$ and we have

$$\langle E\rangle = \hbar\omega\left(1-e^{-\hbar\omega/kT}\right)\left[\frac{e^{-\hbar\omega/kT}}{\left(1-e^{-\hbar\omega/kT}\right)^2} + \frac{1}{2}\,\frac{1}{\left(1-e^{-\hbar\omega/kT}\right)}\right] = \hbar\omega\left[\frac{e^{-\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}} + \frac{1}{2}\right]$$

$$= \hbar\omega\left(\frac{1}{e^{\hbar\omega/kT}-1} + \frac{1}{2}\right) = \hbar\omega\left(\langle n\rangle + \frac{1}{2}\right)$$

In comparison to the spectrum $E_n = \hbar\omega(n+\frac{1}{2})$, identify $\langle n\rangle \equiv$ number of "phonons" in oscillator w/ freq. ω at temperature T

From this form, we see "phonon" quanta follow "Bose-Einstein" statistics!

Specific heat Capacity

Sum over states: In analogy to electron ensemble, energy of system w/ oscillators labeled by q is

$$U = V\iiint \langle E\rangle \frac{d^3q}{(2\pi)^3}$$

But we saw that $\langle E\rangle$ is function of of (scalar) freq. ω, not (vector) $\vec{q}$!

We can convert this integral over $\vec{q}$ into integral over frequency ω by noting that in small q limit, we found $\omega = qc$ for low-energy acoustic branch. Bounds of integration determined by total number of modes:

$$\underset{\text{dimension}}{3}\,\underset{\text{\# atoms per unit cell}}{r}\,\overset{\text{\# of unit cells}}{N} = V\underset{\text{filled states}}{\iiint}\frac{d^3q}{(2\pi)^3} \longrightarrow V\int_0^{q_{max}}\frac{4\pi q^2\,dq}{(2\pi)^3} \longrightarrow \frac{V}{2\pi^2}\int_0^{\overset{\text{“Debye frequency”}}{\omega_D}}\frac{\omega^2\,d\omega}{c^3} = \frac{V}{2\pi^2}\frac{\omega_D^3}{3c^3}$$

(for each branch!
1x for longitudinal
2x for transverse)

So acoustic phonon DOS is $\frac{V}{2\pi^2}\frac{\omega^2}{c^3}$ giving

$$U = \frac{\hbar}{2\pi^2}\left(\frac{1}{c_L^3}+\frac{2}{c_T^3}\right)\int_0^{\omega_D}\left(\frac{1}{e^{\hbar\omega/kT}-1}+\frac{1}{2}\right)\omega^3\,d\omega$$

Specific heat capacity

$$C_V = \frac{dU}{dT} = \frac{\hbar}{2\pi^2}\left(\frac{1}{C_L^3}+\frac{2}{C_T^3}\right)\int_0^{\omega_D}\frac{e^{\hbar\omega/kT}\,\frac{\hbar\omega}{kT^2}}{\left(e^{\hbar\omega/kT}-1\right)^2}\,\omega^3\,d\omega$$

From normalization condition, $\frac{3rN}{V} = \frac{1}{2\pi^2}\left(\frac{1}{C_L^3}+\frac{2}{C_T^3}\right)\frac{\omega_D^3}{3}$

By substitution $y \equiv \frac{\hbar\omega}{kT}$, $\omega = \frac{ykT}{\hbar}$ $d\omega = \frac{kT}{\hbar}dy$ so that

$y_{max} = \frac{\hbar\omega_D}{kT} = \frac{\Theta}{T}$ ← Debye temperature

$$C_V = \hbar\,\frac{3rN}{V}\,\frac{3}{\omega_D^3}\int_0\frac{e^y\,\frac{y}{T}}{(e^y-1)^2}\,y^3\left(\frac{kT}{\hbar}\right)^4dy = \frac{3rNk}{V}\cdot 3\overbrace{\left(\frac{kT}{\hbar\omega_D}\right)^3}^{\left(\frac{T}{\Theta}\right)^3}\int_0^{\Theta/T}\frac{e^y\,y^4\,dy}{(e^y-1)^2}$$

For $kT \gg \hbar\omega_D$ $(T \gg \Theta)$ expand $e^y \sim 1+y$. Then

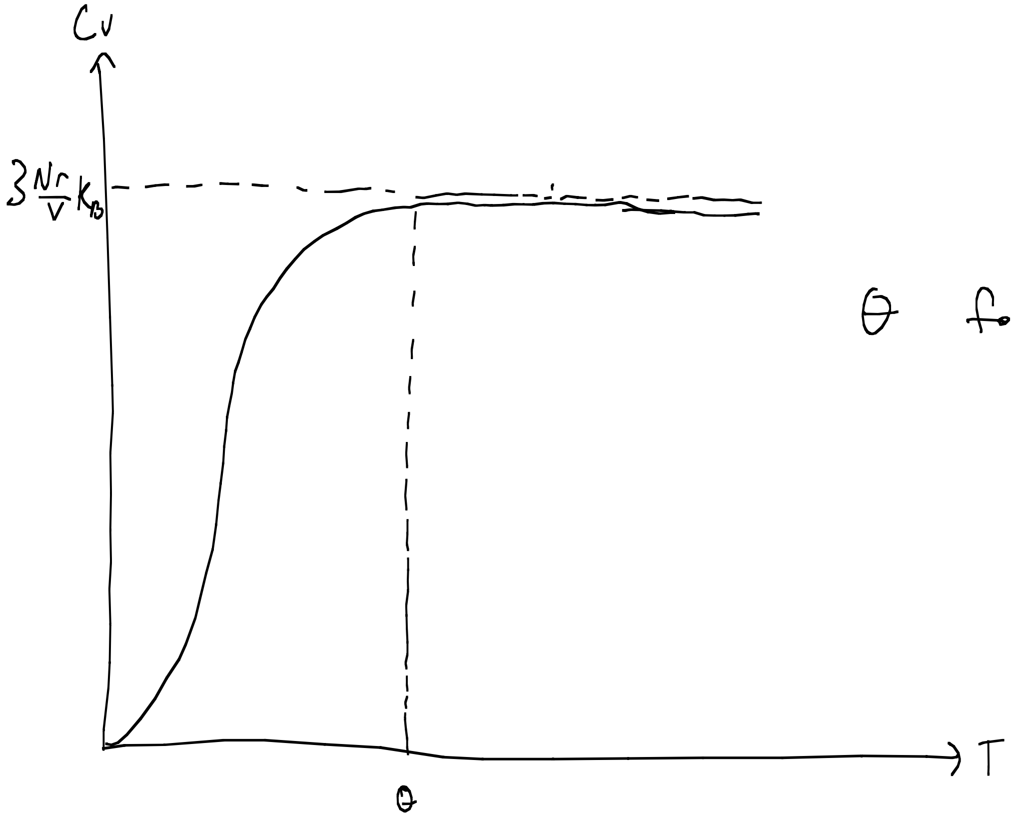
$$C_V \propto T^3\int_0^{\Theta/T}\frac{(1+y)\,y^4\,dy}{y^2} = T^3\int_0^{\Theta/T}(1+y)\,y^2\,dy \sim T^3\,y^3\Big|_0^{\Theta/T} \rightarrow \text{const!} = 3\frac{rN}{V}k$$

This matches classical Dulong-Petit prediction of equipartition of $\frac{1}{2}kT$ energy per degree of freedom (3x for K.E. / 3 for P.E.)

Low-Temperature specific heat capacity

In low temp limit $T << \theta$, $\frac{\theta}{T} \rightarrow \infty$ so our integral $\int_0^\infty \frac{e^y y^4\, dy}{(e^y-1)^2}$ is just a number $\left(\frac{4\pi^4}{15}\right)$ no temp. dependence, and $C_V = \frac{3rNk}{V} \frac{4\pi^4}{5} \left(\frac{T}{\theta}\right)^3$

This explains the very small low-temperature heat capacity of solids.



θ for Cu ~ 340K

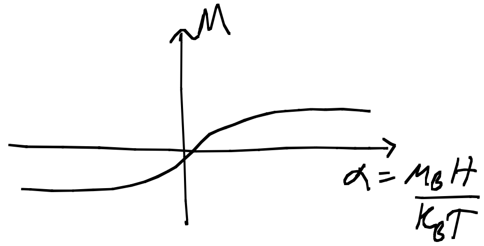
Au ~ 165K

Fe ~ 467K

Interactions: ordered magnetic states

First: local magnetic moments, paramagnetism $\mathcal{H} = -\sum_i \mu_i \cdot H$

$$M = N\langle \mu \rangle = N\,\frac{+\mu_B e^{-(-\mu_B H)/k_BT} + (-\mu_B)e^{-\mu_B H/k_BT}}{e^{-(-\mu_B H)/k_BT} + e^{-\mu_B H/k_BT}} = N\mu_B \tanh\frac{\mu_B H}{k_BT}$$



In the limit of small H or high T, $\alpha \to 0$ and we approx. $\tanh\alpha \sim \alpha$

$$M \sim N\mu_B \frac{\mu_B H}{k_BT} = \frac{\frac{N\mu_B^2}{k_B}}{T} H \qquad \text{so susceptibility} \quad \chi = \frac{C}{T}$$

"Curie's law"

Now, with interaction, $\mathcal{H} = -\sum_i \mu_i \cdot H - J\sum_i S_i\cdot S_{i+\delta}$ ($\delta = \pm 1$ – nearest neighbors)

$$= -\sum_i \mu_i \cdot H - \frac{J\hbar^2}{g^2\mu_B^2}\sum_i \mu_i \cdot \mu_{i+\delta}$$

$$\xrightarrow[\substack{\mu_{i+\delta} = \langle \mu_{i+\delta}\rangle \\ \text{and } M \propto \langle \mu_{i+\delta}\rangle}]{\text{mean field approx}} \; = -\sum_i \mu_i \cdot (H + wM)$$

"molecular field"
"crystal field"

Ferromagnetism : non zero M when $H=0$!

$M = N\mu_B \tanh\alpha' \simeq N\mu_B\left(\alpha' - \frac{\alpha'^3}{3} + \ldots\right)$ where $\alpha' = \frac{\mu_B}{k_B T}(H + wM)$, not valid for small T where α' large

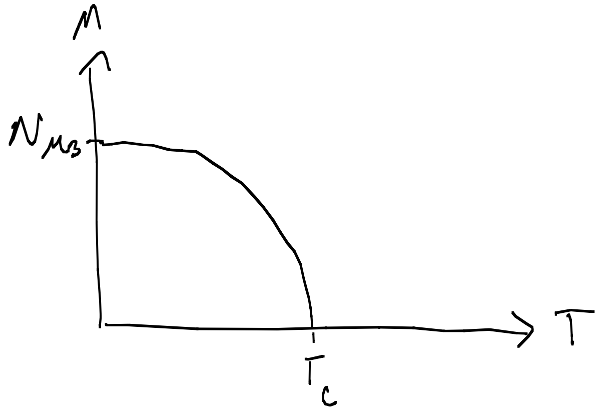
If $H=0$, Then

$$M \simeq N\mu_B\left(\gamma M - \frac{\gamma^3 M^3}{3}\right) \rightarrow M = \sqrt{\frac{3}{\gamma^3}\left(\gamma - \frac{1}{N\mu_B}\right)} \qquad \left(\gamma \equiv \frac{\mu_B w}{k_B T}\right)$$

Note that $M>0$ for $\gamma > \frac{1}{N\mu_B}$ so $\frac{\mu_B w}{k_B T} > \frac{1}{N\mu_B} \rightarrow T < \frac{N\mu_B^2 w}{k_B} = T_c$ "Curie Temp"

Just below T_c, $M = \frac{\sqrt{3}}{\gamma}\left(1 - \frac{1}{N\gamma\mu_B}\right)^{1/2} = \frac{\sqrt{3}}{\gamma}\left(1 - \frac{k_B T}{N\mu_B^2 w}\right)^{1/2} = \frac{\sqrt{3}}{\gamma}\left(1 - \frac{T}{T_c}\right)^{1/2}$

For $T \rightarrow 0$, $\tanh\alpha' \rightarrow 1$ so $M \rightarrow N\mu_B$

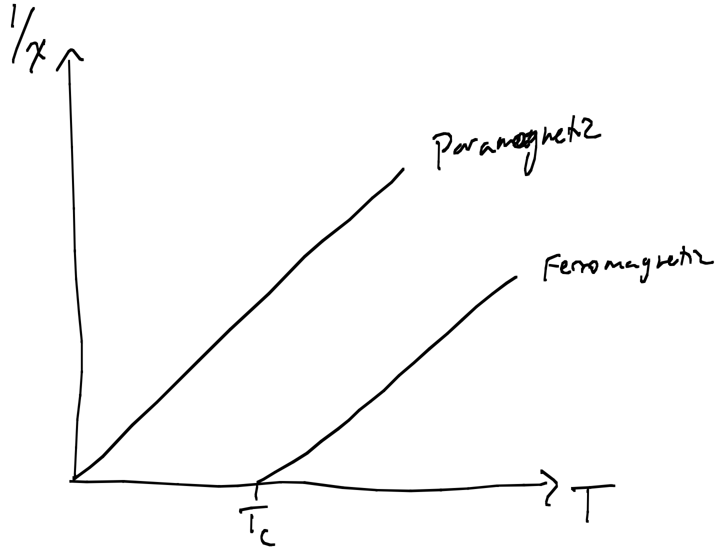


Above T_c

$$M = N\mu_B \tanh \alpha' \sim N\mu_B \frac{(H + wM)\mu_B}{k_B T}$$ to first order

Solution:

$$M = \frac{\frac{N\mu_B^2}{k_B}}{T - \frac{N\mu_B^2}{k_B}w} H = \frac{C}{T-T_c} H \rightarrow \chi = \frac{C}{T-T_c}$$ "Curie-Weiss Law"



But what does this local moment model have to do with the free electron gas? How does exchange interaction of <u>delocalized</u> electron planewaves occur?

Free electron gas: Exchange

2-electron pair wavefunction must be spatially antisymmetric (for electrons w/ same spin)

$$\Psi_{ij} \propto \varphi_{k_i}(r_i)\,\varphi_{k_j}(r_j) - \varphi_{k_i}(r_j)\,\varphi_{k_j}(r_i)$$

$$\propto e^{ik_ir_i}e^{ik_jr_j} - e^{ik_ir_j}e^{ik_jr_i} = e^{ik_ir_i}e^{ik_jr_j}\left(1-e^{-i(k_i-k_j)(r_i-r_j)}\right)$$

From this, calculate probability density $(r \equiv r_i - r_j)$

$$|\Psi_{ij}|^2 \propto 1-\cos(k_i-k_j)r$$

Net effect is calculated from average over Fermi sphere:

$$\rho_\uparrow = \frac{ne}{2}\,\frac{\iint\left[1-\cos(\vec{k}_i-\vec{k}_j)r\right]d^3k_i\,d^3k_j}{\left(\frac{4}{3}\pi k_F^3\right)^2}$$

$$= \frac{ne}{2}\left[1-\frac{\int\cos\vec{k}_i\cdot\vec{r}\,d^3k_i\int\cos\vec{k}_j\cdot\vec{r}\,d^3k_j}{\left(4/3\,\pi k_F^3\right)^2}\right]$$

$$\cos(k_i-k_j) = \cos k_i\cos k_j + \cancelto{0}{\sin k_i}\,\cancelto{0}{\sin k_j}$$

integrating over symmetric sphere gives zero contribution for antisymmetric sine

Fourier Transform of Fermi sphere

$$\int_{\substack{\text{Fermi}\\\text{sphere}}} \cos \vec{k}\cdot\vec{r}\; d^3k = 2\pi \int_0^{k_F}\int_0^{\pi} \cos(kr\cos\theta)\,\sin\theta\, k^2\, d\theta\, dk$$

$$= 2\pi \int_0^{k_F} \frac{\sin(kr\cos\theta)}{kr}\Bigg|_{\theta=0}^{\pi} k^2\, dk = \frac{4\pi}{r}\int_0^{k_F} k \sin kr\, dk =$$

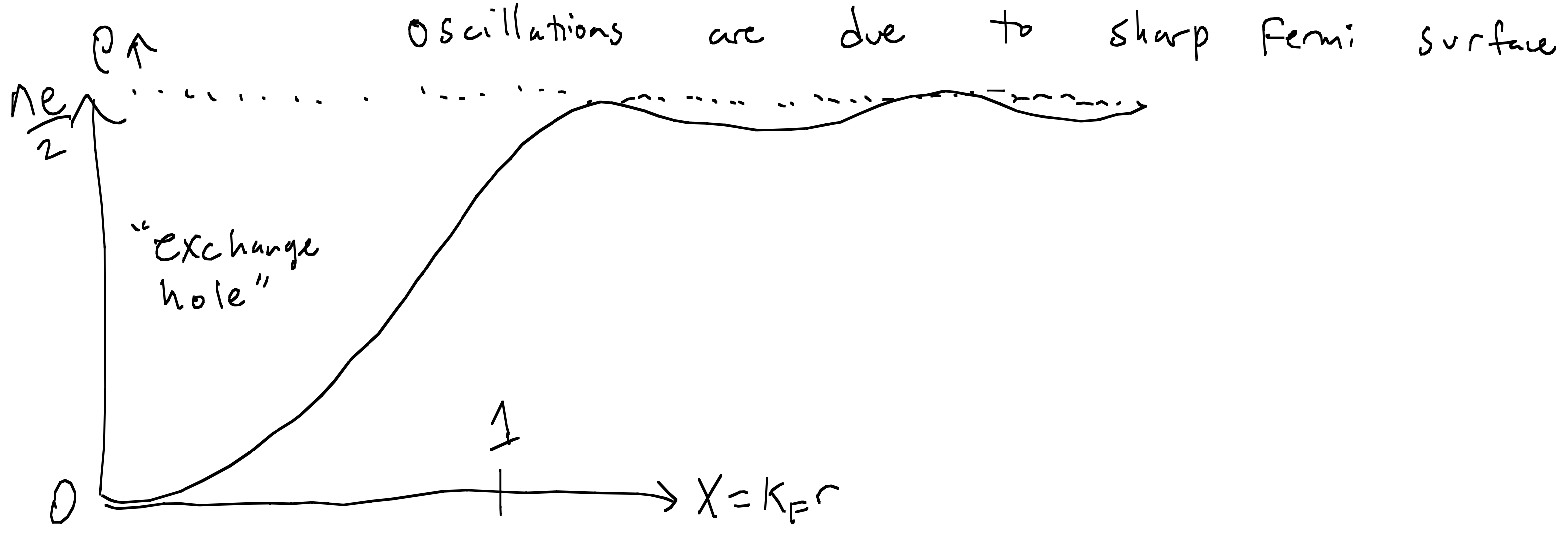
$$= \frac{4\pi}{r}\left(\frac{1}{r^2}\sin kr - \frac{k}{r}\cos kr\right)\Bigg|_0^{k_F} = \frac{4\pi}{r^3}\left(\sin k_F r - k_F r\cos k_F r\right)$$

So
$$\rho_\uparrow = \frac{n_e}{2}\left(1 - \frac{\left[\frac{4\pi}{r^3}\left(\sin k_F r - k_F r\cos k_F r\right)\right]^2}{\left(4/3\,\pi k_F^3\right)^2}\right) = \frac{n_e}{2}\left(1 - 9\left[\frac{\sin k_F r - k_F r\cos k_F r}{(k_F r)^3}\right]^2\right)$$

Note: $\sin x \sim x - \frac{x^3}{3!} + \ldots$, $\cos x \sim 1 - \frac{x^2}{2!} + \ldots$ so

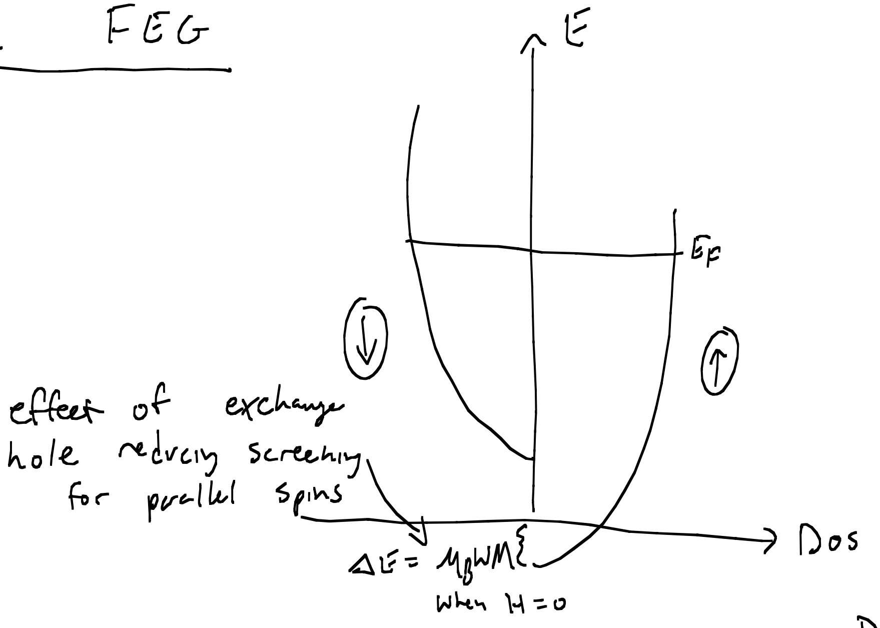
$$1 - 9\left(\frac{\sin x - x\cos x}{x^3}\right)^2 \sim 1 - 9\left(\frac{\left(x - \frac{x^3}{3!}\right) - x\left(1 - \frac{x^2}{2!}\right)}{x^3}\right)^2 = 1 - 9\left(\frac{1}{3}\right)^2 = 0 \leftarrow$$

all other
parallel spin
electrons
completely avoid
electron k_i
at $r=0$



$\Rightarrow$ The exchange hole reduces the screening of crystal potential and lowers the electron energy → energy is lowest if all electrons have same spin so Ferromagnetism is favored.

Ferromagnetism in the FEG



bulk magnetization:

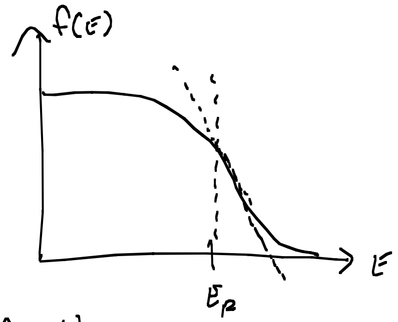
$$M = \mu_B (n_\uparrow - n_\downarrow) = \mu_B \left[\frac{1}{2}\int_{-\infty}^{\infty} g\left(E + \mu_B(H+wM)\right) f(E)\, dE - \frac{1}{2}\int_{-\infty}^{\infty} \overset{\text{DOS}}{g}\left(E - \mu_B(H+wM)\right) \overset{\text{Fermi-Dirac}}{f(E)}\, dE \right]$$

Make change of variables $E' = E + \Delta E$, $E' = E - \Delta E$ as appropriate $\left(\Delta E \equiv \mu_B(H+wM)\right)$

$$M = \frac{\mu_B}{2}\left(\int_{-\infty}^{\infty} g(E) f(E-\Delta E)\, dE - \int_{-\infty}^{\infty} g(E) f(E+\Delta E)\, dE \right) \sim \frac{\mu_B}{2} g(E_F) \int_{-\infty}^{\infty} \left[f(E-\Delta E) - f(E+\Delta E) \right] dE$$

Taylor expand integrand: $f(E+\Delta E) = f(E) + \Delta E\, f'(E) + \frac{\Delta E^2}{2!} f''(E) + \frac{\Delta E^3}{3!} f'''(E) + \cdots$

Stoner criterion for Ferromagnetism



$$M \sim \frac{\mu_B g(E_F)}{2} \int_{-\infty}^{\infty} \left(-2\Delta E\, f'(E) - \frac{2}{3!} \Delta E^3 f'''(E) \right) dE$$

Note that $f'(E) < 0$ and $f'''(E) > 0$. Then, for $M > 0$ and $H = 0$,

$$M + \mu_B g(E_F)\, w M \mu_B \cancelto{-1}{\int_{-\infty}^{\infty} f'(E)\, dE} < 0 \longrightarrow 1 - \mu_B^2 g(E_F)\, w < 0 \rightarrow g(E_F)\, w > \frac{1}{\mu_B^2}$$

Even without satisfying this condition, we still have $M = 2\Delta E \frac{g(E_F)}{2} \mu_B$ (just like paramagnetic susceptibility where $\Delta E = \mu_B H$) Now, $\Delta E = \mu_B (H + wM)$ so

$$M = \mu_B^2 g(E_F)(H + wM) = \chi_0 (H + wM) \longrightarrow M(1 - w\chi_0) = \chi_0 H$$

$$M = \frac{\chi_0}{1 - w\chi_0} H$$

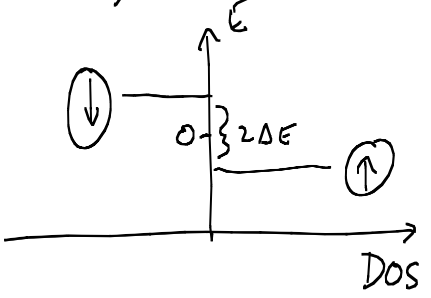
This explains enhanced paramagnetic susceptibility of "nearly FM" Rh, Pd, Pt

Transition Temperature:

Approx. continuous FEG DOS w/ discrete model (e.g. d-electrons in transition metals)

$$M = \mu_B (n_\uparrow - n_\downarrow) = \mu_B \left(\frac{1}{1+e^{-\mu_B w M / k_B T}} - \frac{1}{1+e^{\mu_B w M/k_B T}} \right) = \mu_B \tanh\left(\frac{\mu_B w M}{2 k_B T} \right)$$

$$\frac{M}{\mu_B} = \tanh\left(\frac{\left(\frac{\mu_B^2 w}{2k_B}\right)}{T} \cdot \frac{M}{\mu_B} \right) = \tanh\left(\frac{T_c}{T} \cdot \frac{M}{\mu_B} \right)$$



Asymptotic behavior:

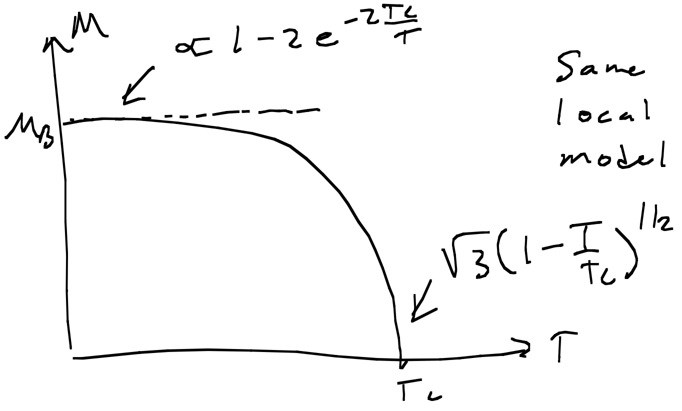
For $T \to 0$, $M \to \mu_B$, Approaching low temp limit,

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{1-e^{-2x}}{1+e^{-2x}} \sim \left(1-e^{-2x}\right)^2 = 1 - 2e^{-2x}$$ so $$\frac{M}{\mu_B} \sim 1 - 2e^{-2\frac{T_c}{T}\frac{M}{\mu_B}} \sim 1 - 2e^{-2\frac{T_c}{T}}$$ (since $M \to \mu_B$)

For $T \to T_c$, $\frac{M}{\mu_B} \sim \tanh \frac{M}{\mu_B}$ so $M \to 0$. Approaching from below,

$$\tanh(x) \sim x - \frac{x^3}{3}$$ so

$$\frac{T}{T_c} x = x - \frac{x^3}{3} \longrightarrow x \sim \frac{M}{\mu_B} = \sqrt{3}\left(1 - \frac{T}{T_c}\right)^{1/2}$$



Same as local moment model!

For $T > T_c$

Expand Fermi function: $\frac{1}{e^{-x}+1} - \frac{1}{e^{x}+1} \sim \frac{1}{2-x} - \frac{1}{2+x} \sim \frac{1}{2}\left[\left(1+\frac{x}{2}\right) - \left(1-\frac{x}{2}\right)\right] = \frac{x}{2}$

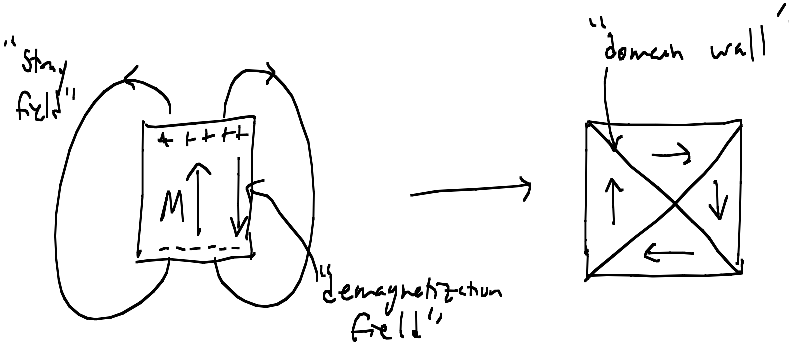
So $M = \mu_B\left(\frac{1}{e^{-x}+1} - \frac{1}{e^{x}+1}\right)$ is

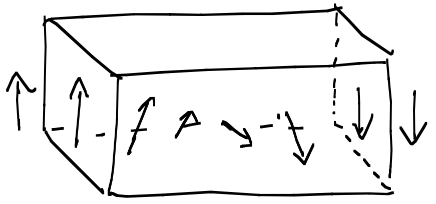
$x \equiv \frac{\mu_B(H+wM)}{k_BT}$

$M \sim \frac{\mu_B^2(H+wM)}{2k_BT} \longrightarrow M \sim \frac{\frac{\mu_B^2}{2k_BT}}{1-\frac{\mu_B^2 w}{2k_BT}} H = \frac{C}{T-T_c}$ "Curie-Weiss Law" again!

Ferromagnetic domains

System can minimize total energy, eliminating magnetostatic stray field by fracturing into magnetic domains. This process is a competition between magnetostatic energy and the exchange energy associated w/ wall formation




"Bloch Wall"

moment rotation along axis perp. to wal

Wall energy

Nearest-neighbor exchange $E = -\beta \mu_1 \mu_2 \cos\theta \sim -\beta \mu_1 \mu_2 \left(1 - \frac{\delta\theta^2}{2}\right) = C + \frac{\beta \mu^2}{2} \delta\theta^2$

Since we can redefine zero energy, and $\delta\theta = \frac{\pi}{N}$, (wall is N moments thick)

Energy density $u = \frac{\beta \mu^2}{2a^3}\left(\frac{\pi}{N}\right)^2$ ($a \equiv$ spacing between μ's)

so areal energy density is $u \cdot Na = \frac{\beta\mu^2}{2a^3}\left(\frac{\pi}{N}\right)^2 Na = A\frac{\pi^2}{aN}$ ($A \equiv \frac{\beta\mu^2}{2a}$ "exchange constant")

This obviously favors wide walls (large N)

Crystal anisotropy

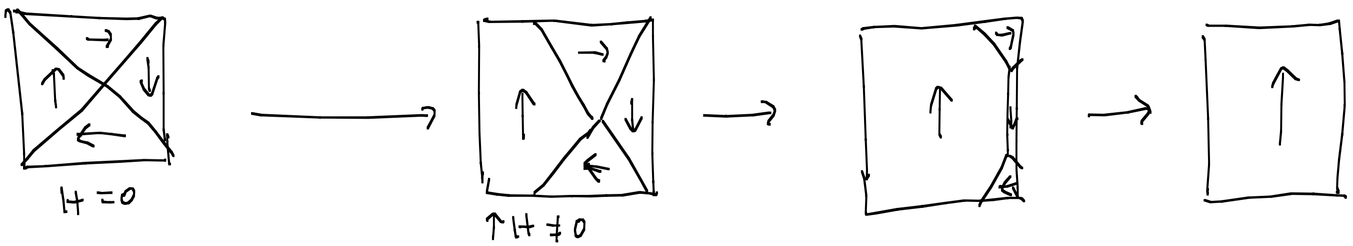
Spin-orbit interaction tends to align moments along crystal axis, so we must pay an energetic price to have moments in the wall oriented at intermediate directions. This obviously favors thin domain walls. Total energy is:

$$E_{wall} = KNa + A\frac{\pi^2}{Na}$$

Minimize with: $\frac{dE_{wall}}{dN} = 0 \longrightarrow Ka - A\frac{\pi^2}{N^2 a} = 0$. $Na = \sqrt{A\frac{\pi^2}{K}}$

Example: $A \sim 10^6 \, eV/cm$ and $K \sim \frac{10^{18} \, eV}{cm^3}$ so $Na \sim 10^{-6} \, cm = 10 \, nm$

Magnetization of FM: Domain wall movement.

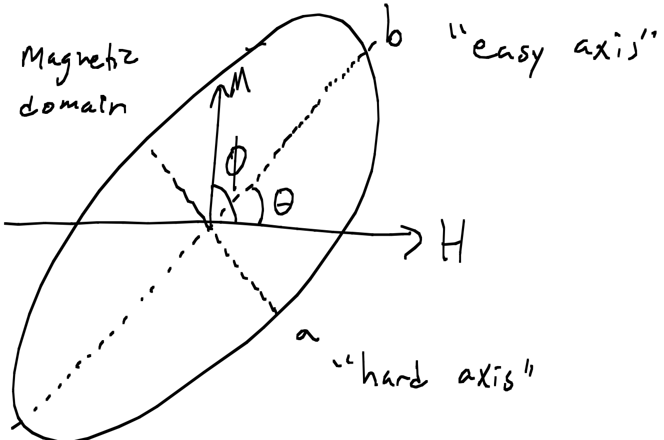


"Barkhausen noise":

Discontinuous change in magnetization when domain walls move past pinning defects

But, this is not the only way to "magnetize" bulk FM!

Coherent rotation in magnetic field



$D_a > D_b$

$$E = \underbrace{\frac{1}{2}M^2\left(D_b\cos^2(\phi-\theta) + D_a\sin^2(\phi-\theta)\right)}_{\text{Uniaxial anisotropy}} - \underbrace{HM\cos\phi}_{\text{Zeeman}}$$

Using $\cos^2 x = \frac{1}{2}(1+\cos 2x)$ and $\sin^2 x = \frac{1}{2}(1-\cos 2x)$

$$E = \frac{1}{4}M^2(D_a+D_b) - \frac{1}{4}M^2(D_a-D_b)\cos\left(2(\phi-\theta)\right) - HM\cos\phi$$

Equilibrium orientation ϕ given by

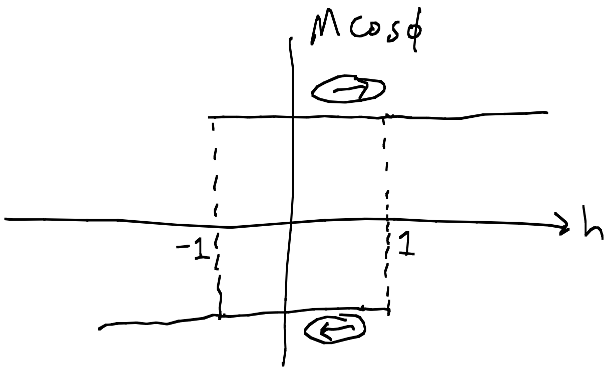
$$\frac{dE}{d\phi} = \frac{1}{2}M(D_a-D_b)\sin\left(2(\phi-\theta)\right) + H\sin\phi = 0$$

Hard! Special cases follow:

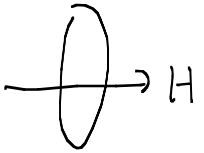
For $\theta = 0$

$\frac{1}{2}\sin 2\phi + h\sin\phi = 0 \longrightarrow$ only has solution $\phi = 0$ or π

$h \equiv \frac{H}{(D_a-D_b)M}$ "reduced field"



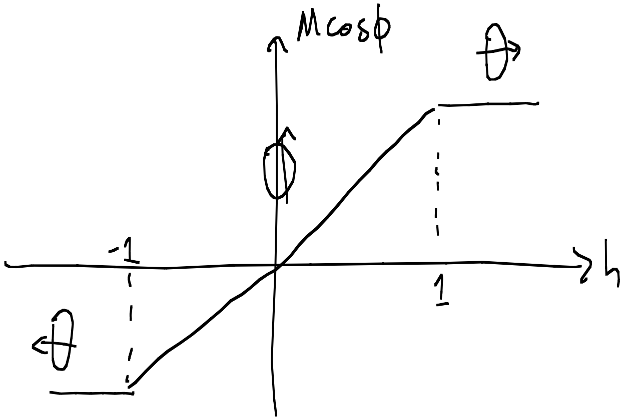
For $\theta = \frac{\pi}{2}$



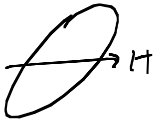
$$\frac{1}{2}\sin 2\left(\phi - \frac{\pi}{2}\right) + h\sin\phi = 0$$

$$-\frac{1}{2}\sin 2\phi = -h\sin\phi$$

$$\cancel{\sin\phi}\cos\phi = h\,\cancel{\sin\phi}$$



For $\theta = \frac{\pi}{4}$



$$\frac{1}{2}\sin 2\left(\phi - \frac{\pi}{4}\right) + h\sin\phi = 0$$

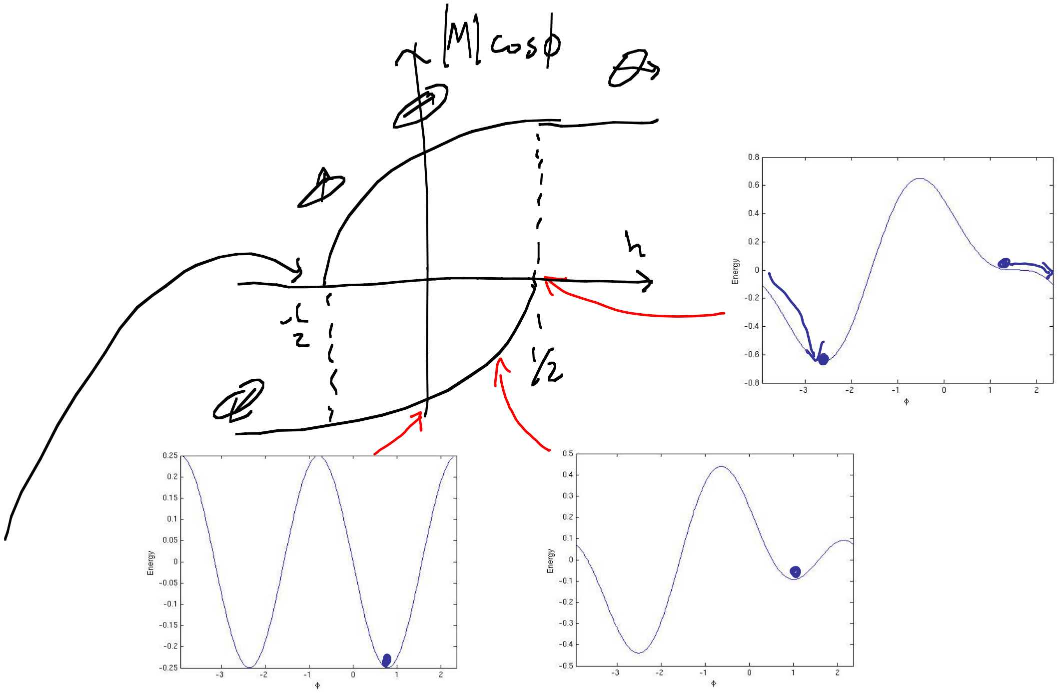
$$\frac{1}{2}\sin\left(2\phi - \frac{\pi}{2}\right) = -h\sin\phi$$

$$-\frac{1}{2}\cos 2\phi = -h\sin\phi$$

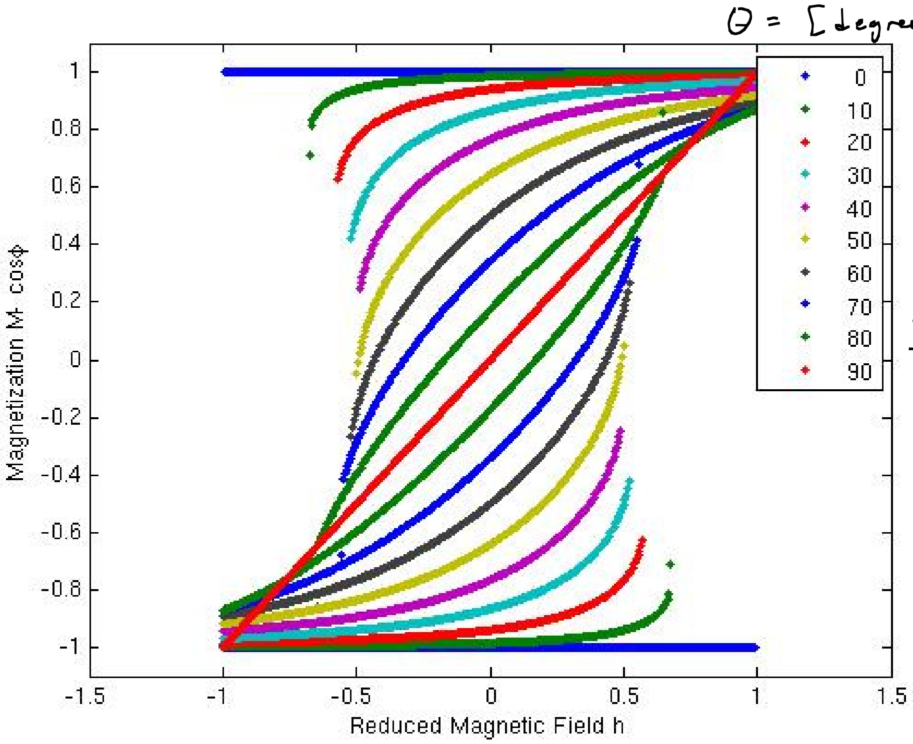
Solution; if $h = -\frac{1}{2}$

$\phi = \frac{\pi}{2}$ (where $\cos\phi = 0$)

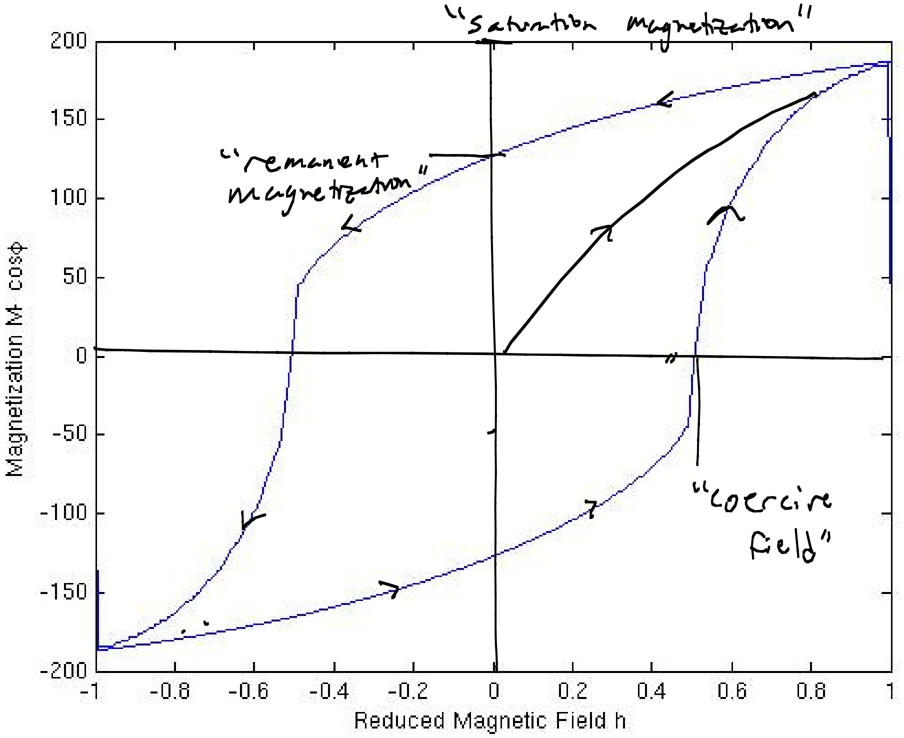
or if $h = 1/2$, $\phi = \frac{3\pi}{2}$



Ensemble average over $0 < \theta < \frac{\pi}{2}$: hysteresis loop



$200 \times \theta$ values →



To magnetize a randomly-oriented ensemble w/ $M=0$, just increase H past coercive field.

To demagnetize sample, just oscillate H from large amplitude to small.

As we pass to lower field amplitude, the coercive field is not exceeded and the domain is stuck in random orientation!

Applications of Ferromagnetism : Remanance ≡ "Memory"

Information is encoded into the $+M=$"1" and $-M=$"0" states at $H=0$.

But, one must consider long-term stability against thermal fluctuations:

Stability of magnetic state determined by Arrhenius Law $t = t_0 e^{E_a/k_BT}$ $(t_0 \sim 1\,ns)$

For $t = 10$ yrs, then $E_a \cong 40 k_BT = \overset{\text{anisotropy const}}{K}\underset{\text{volume}}{V}$. If volume small enough, $E_a \sim k_BT$

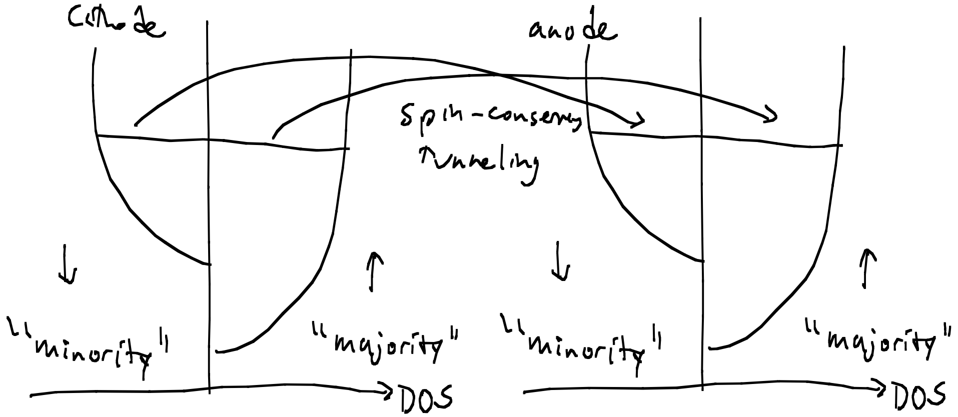
and "superparamagnetism" results → magnetic fluctuation pinned by external field (not anisotropy) so remanance (and hence memory) is lost.

This limits conventional information density on hard drive to ~100Gb/in. Increasing K can increase this limit, but then the coercive field rises so it becomes harder to "write" information!

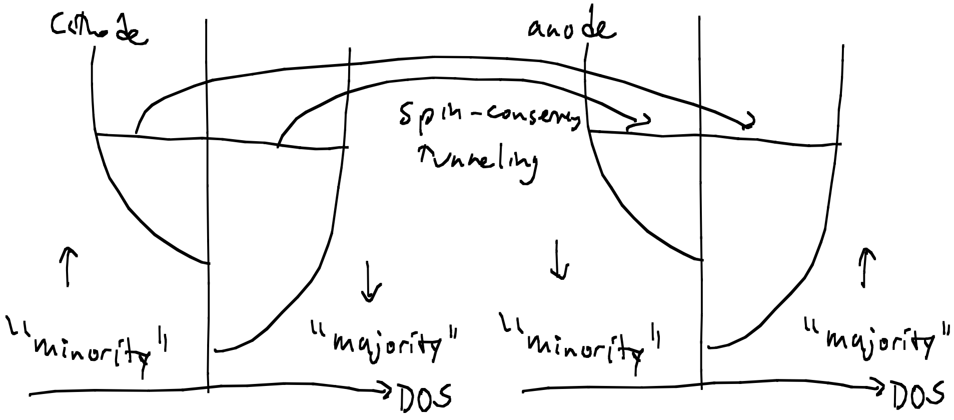
Tunnel Magnetoresistance (TMR)

Sensitive magnetic field sensors are required to "read" information encoded in magnetic state of a FM domain. TMR is the current technology in the "read head" floating above a spinning hard drive platter. The stray field from a "bit" on the platter manipulates the magnetization state of a "free" FM layer relative to a "fixed" layer, causing resistance change for transport of electrons from one (cathode) to the other (anode)

Parallel Magnetization



antiparallel magnetization



$$R_p = \frac{V}{I_p} \propto \frac{1}{MM+mm}$$

$M \equiv$ Majority DOS

$m \equiv$ minority DOS

$$R_{AP} = \frac{V}{I_{AP}} \propto \frac{1}{Mm+mM}$$

"Optimistic" magnetoresistance:

$$\frac{\Delta R}{R_p} = \frac{R_{AP}-R_p}{R_p} = \frac{\frac{1}{Mm+mM} - \frac{1}{MM+mm}}{\frac{1}{MM+mm}} = \frac{MM+mm-Mm-mM}{Mm+mM} = \frac{2(M-m)^2}{(M+m)^2-(M-m)^2} = \frac{2P^2}{1-P^2}$$

$P \equiv$ "Polarization"

$$= \frac{M-m}{M+m} = \frac{K_\uparrow - K_\downarrow}{K_\uparrow + K_\downarrow}$$

~ 0.5 for Ni, Co, Fe

so $\Delta R/R \sim 67\%$

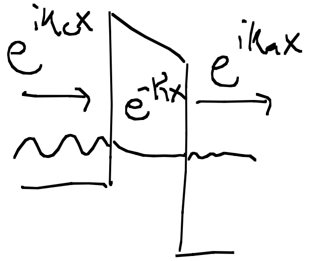
Tunnel Polarization

We considered only spin asymmetry caused by initial and final DOS, but did not consider the tunnel process in determining transport asymmetry.

Transmission coefficient can be approximated by incoherent product of interfacial transmission coefs:

$$T \sim \overbrace{\frac{4 k_c \kappa}{k_c^2 + \kappa^2}}^{\text{cathode-barrier}} \ \overbrace{\frac{4 k_a \kappa}{k_a^2 + \kappa^2}}^{\text{barrier-anode}}$$

where $k_c = k_\uparrow$ or $k_\downarrow$



tunnel spin polarization:

$$P = \frac{T_\uparrow - T_\downarrow}{T_\uparrow + T_\downarrow} = \frac{\frac{k_\uparrow}{k_\uparrow^2+\kappa^2} - \frac{k_\downarrow}{k_\downarrow^2+\kappa^2}}{\frac{k_\uparrow}{k_\uparrow^2+\kappa^2} + \frac{k_\downarrow}{k_\downarrow^2+\kappa^2}} = \frac{k_\uparrow(k_\downarrow^2+\kappa^2) - k_\downarrow(k_\uparrow^2+\kappa^2)}{k_\uparrow(k_\downarrow^2+\kappa^2) + k_\downarrow(k_\uparrow^2+\kappa^2)}$$

$$= \frac{k_\uparrow - k_\downarrow}{k_\uparrow + k_\downarrow} \ \frac{\kappa^2 - k_\uparrow k_\downarrow}{\kappa^2 + k_\uparrow k_\downarrow}$$ "Slonczewski Polarization" (c.f. $P = \frac{k_\uparrow - k_\downarrow}{k_\uparrow + k_\downarrow}$ above)

This tunnel-dependent polarization is especially important when considering spin transport (in addition to charge) from a FM to a normal conductor.

First, we need to generalize Ohm's law $J = \sigma E$.

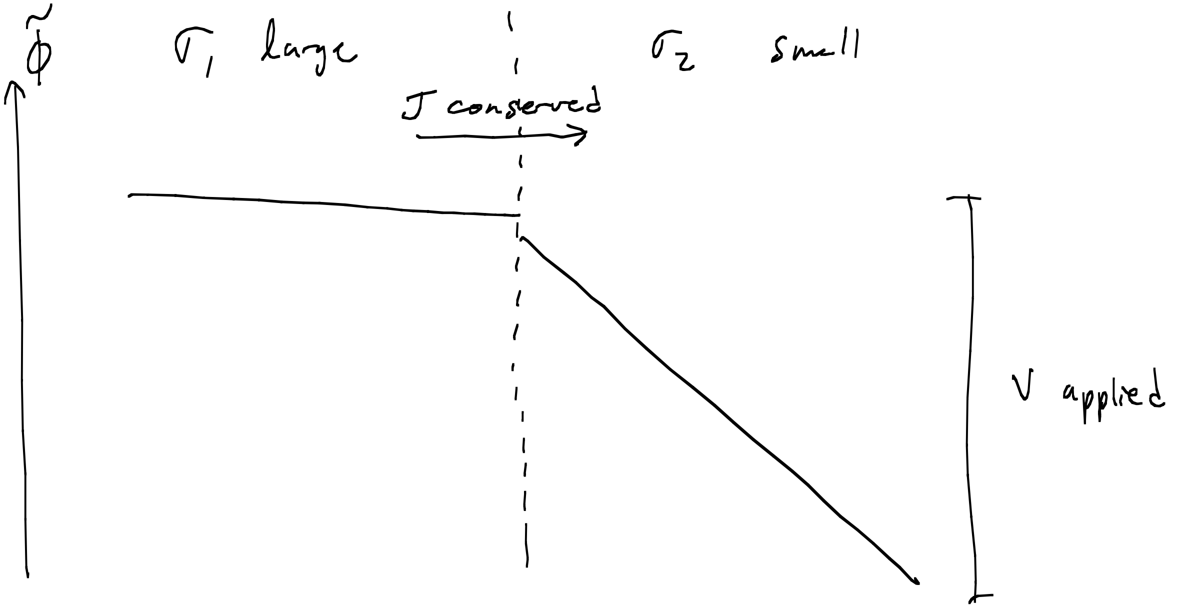
Generalization of Ohm's Law: inclusion of diffusion current

Electric field drives a "drift" current proportional to conductivity σ, but concentration gradient drives a "diffusion" current proportional to Diffusion coef. D:

$$J = \overbrace{\sigma \mathcal{E}}^{\text{drift}} - \overbrace{e\underset{\substack{\uparrow \\ \text{diffusion const.}}}{D}\nabla n}^{\text{diffusion}} = \sigma\left(\nabla(-\phi) - \frac{eD}{\sigma}\nabla n\right) = \sigma\left(\nabla(-\phi) - \frac{eD}{ne\mu}\nabla n\right) = \sigma\nabla(-\tilde{\phi})$$

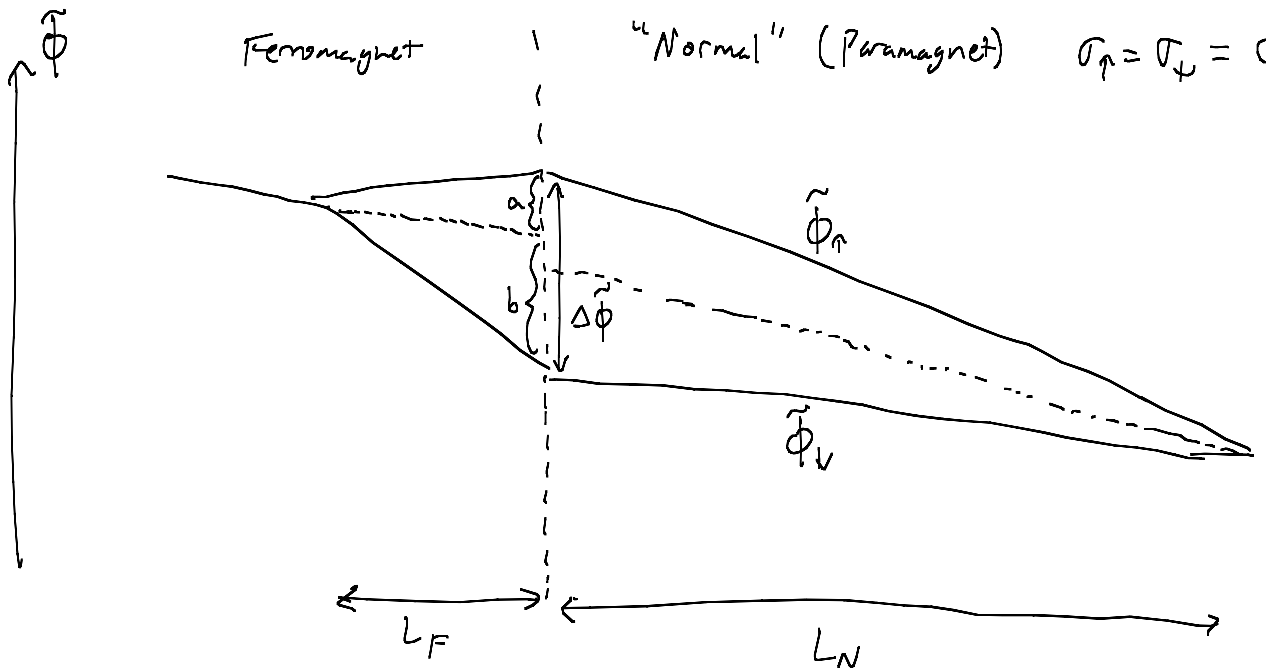
$\tilde{\phi} \equiv \phi + \frac{D}{\mu}\ln\frac{n}{n_0}$ "electrochemical potential" (Note, $D/\mu = \frac{k_B T}{e}$ for nondegenerate electron gas)

At an interface with $\sigma_1 \neq \sigma_2$:



Spin dependent ohmic transport

$J_\uparrow = \sigma_\uparrow(-\nabla\tilde\Phi_\uparrow)$, $J_\downarrow = \sigma_\downarrow(-\nabla\tilde\Phi_\downarrow)$



$\sigma_\uparrow = \sigma_\downarrow = \sigma_N/2$

We want Polarization in normal metal $P = \frac{J_\uparrow - J_\downarrow}{J_\uparrow + J_\downarrow} = \frac{J_\uparrow - J_\downarrow}{J} \neq 0$ so $\nabla\tilde\Phi_\uparrow \neq \nabla\tilde\Phi_\downarrow$!

This causes splitting $\Delta\tilde\Phi$ at interface.

Note: $J_\uparrow = J\left(\frac{1+P}{2}\right)$ $J_\downarrow = J\left(\frac{1-P}{2}\right)$

Likewise, in Fm we have bulk polarization $\beta = \frac{\sigma_\uparrow - \sigma_\downarrow}{\sigma_\uparrow + \sigma_\downarrow}$

so that $\sigma_\uparrow = \sigma_F\left(\frac{1+\beta}{2}\right)$, $\sigma_\downarrow = \sigma_F\left(\frac{1-\beta}{2}\right)$ where $\sigma_F = \sigma_\uparrow + \sigma_\downarrow$

Can $P = \beta$?

Normal side: $J_\uparrow = \frac{J}{2} + \frac{\sigma_N}{2}\frac{\frac{\Delta\tilde{\phi}_N}{2}}{L_N}$ and $J_\downarrow = \frac{J}{2} - \frac{\sigma_N}{2}\frac{\frac{\Delta\tilde{\phi}_N}{2}}{L_N}$ so $P = \frac{\sigma_N \Delta\tilde{\phi}_N}{2 L_N J}$

But what is $\Delta\tilde{\phi}_N$?

FM side: $J_\uparrow = \sigma_\uparrow\left[\frac{J}{\sigma_F} - \frac{a}{L_F}\right]$ and $J_\downarrow = \sigma_\downarrow\left[\frac{J}{\sigma_F} + \frac{b}{L_F}\right]$

so
$$\Delta\tilde{\phi}_F = a+b = L_F\left[\left(\frac{J}{\sigma_F} - \frac{J_\uparrow}{\sigma_\uparrow}\right) + \left(\frac{J_\downarrow}{\sigma_\downarrow} - \frac{J}{\sigma_F}\right)\right] = L_F\left[\frac{J_\downarrow}{\sigma_\downarrow} - \frac{J_\uparrow}{\sigma_\uparrow}\right]$$

$$= L_F\left[\frac{J\left(\frac{1-P}{2}\right)}{\sigma_F\left(\frac{1-\beta}{2}\right)} - \frac{J\left(\frac{1+P}{2}\right)}{\sigma_F\left(\frac{1+\beta}{2}\right)}\right] = J\frac{L_F}{\sigma_F}\,\frac{(1-P)(1+\beta) - (1+P)(1-\beta)}{1-\beta^2} = J\frac{L_F}{\sigma_F}\,\frac{\beta-P}{1-\beta^2}$$

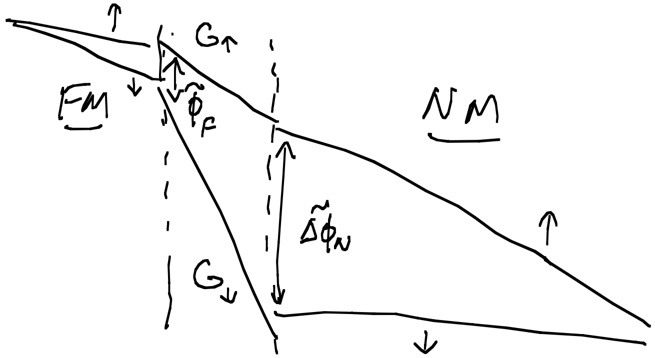
Equating $\Delta\tilde{\phi}_F = \Delta\tilde{\phi}_N$,

$$\frac{2 L_N P}{\sigma_N}\cancel{J} = \cancel{J}\frac{L_F}{\sigma_F}\,\frac{\beta-P}{1-\beta^2} \longrightarrow P = \frac{\beta\eta}{1+\eta-\beta^2} \quad \text{where} \quad \eta = \frac{L_F\sigma_N}{\sigma_F L_N}$$

$\Rightarrow$ only If $\beta = 1$ (perfect "half metallic" FM) does $P = \beta$ independent of η.

But, $\beta \sim 0.5$ for Ni, Fe, Co. Then η dominates; unfortunately, $L_F \ll L_N$ for typical metals, and (especially if the nonmagnet is a semiconductor), $\sigma_F \gg \sigma_N$ so η and hence P is small!

Relaxation of electrochemical continuity



The problem is driven by $\Delta\tilde{\phi}$ on the FM side, opposing flow of spin up!

The solution is to minimize the splitting w/ intermediate layer.

$$\Delta\tilde{\phi}_N - \Delta\tilde{\phi}_F = \left(\frac{J_\downarrow}{G_\downarrow} - \frac{J_\uparrow}{G_\uparrow}\right)$$

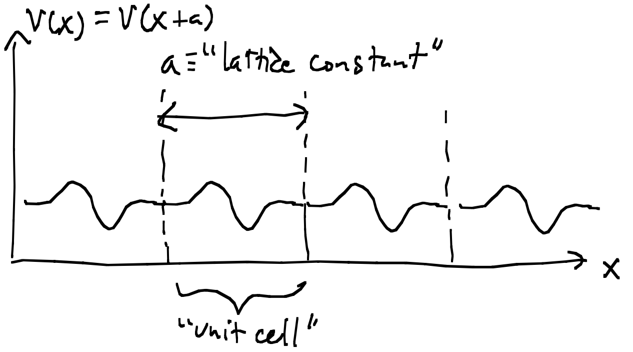
using expressions previously derived, ($G \equiv$ barrier conductance)

$$\Rightarrow \qquad P = \frac{\beta\eta\left(1 + \frac{1}{4\beta}\frac{\sigma_F}{L_F}\left(\frac{1}{G_\downarrow} - \frac{1}{G_\uparrow}\right)(1-\beta^2)\right)}{1+\eta-\beta^2 + \left(\frac{\sigma_N}{4L_N}\left(\frac{1}{G_\downarrow} + \frac{1}{G_\uparrow}\right)(1-\beta^2)\right)}$$

In low G limit, $P \simeq \frac{G_\uparrow - G_\downarrow}{G_\uparrow + G_\downarrow}$, so an ohmic, nonmagnetic intermediate layer (with $G_\uparrow = G_\downarrow$) only makes the problem worse!

Tunneling (not ohmic transport) gives $G_\uparrow \neq G_\downarrow$ because $G \propto$ Transmission. Therefore Slonczewski's result saves the day for spin injection!

Electrons in 1D periodic potential



Schrödinger equation: $-\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = E\psi$

Write V(x) as Fourier series:

$$V(x) = \sum_G V_G e^{iGx}, \quad G = G_n = n\frac{2\pi}{a} = 0, \pm\frac{2\pi}{a}, \pm\frac{4\pi}{a}\ldots$$ → "reciprocal lattice numbers"

"Bloch's theorem": Solution $\psi = e^{ikx}u(x)$ "Bloch wave", where $u(x) = \sum_G C_G e^{iGx}$

Substitute ψ into Schrodinger Eqn: $-\frac{\hbar^2}{2m}\left(e^{ikx}u\right)'' + Ve^{ikx}u = Ee^{ikx}u$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(u'' + 2iku' - k^2u\right) + Vu = Eu \longrightarrow -\frac{\hbar^2}{2m}\left(\frac{d}{dx} + ik\right)^2 u + Vu = Eu$$

Note that since $p = \frac{\hbar}{i}\frac{d}{dx}$, This reduces to

$$\frac{(p+\hbar k)^2}{2m}u + Vu = Eu \longrightarrow \Big[\underbrace{\frac{p^2}{2m} + V}_{H_0} + \underbrace{\frac{\hbar^2k^2}{2m} + \frac{\hbar}{m}k\cdot p}_{H_p}\Big]u = Eu \rightarrow \left[H_0 + H_p\right]u = Eu$$

This suggests a route to solution using perturbation theory ("k-dot-p") using knowledge of $k=0$ wavefunctions. But, not yet!

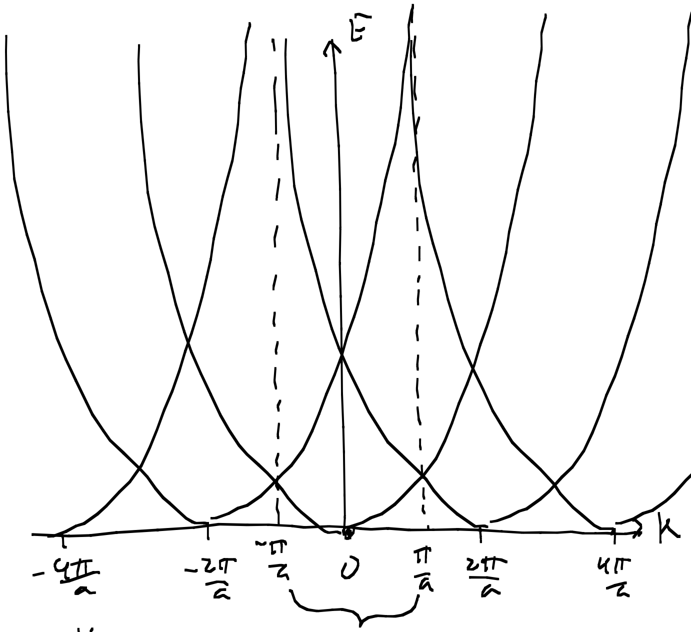
Fourier representation

In this representation, $\frac{d}{dx} \rightarrow iG$, so our Schrodinger equation becomes

$$\frac{\hbar^2}{2m}\sum_G (k+G)^2 C_G e^{iGx} + \sum_{G'} V_{G'} e^{iG'x}\sum_G C_G e^{iGx} = E\sum_G C_G e^{iGx}$$

If $V_G = 0$ for all G $(V(x)=0)$:

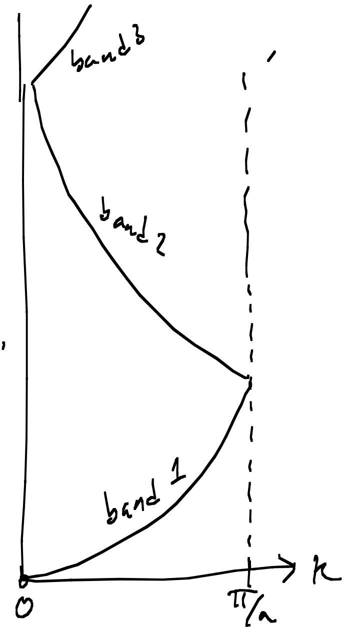
$$\frac{\hbar^2}{2m}(k+G_h)^2 = E \qquad (\text{for all } h)$$



"unit cell" in reciprocal space = "Brillouin zone"

"extended zone scheme" (redundant) $\xrightarrow[\text{symmetry}]{\text{periodic, inversion}}$ "reduced zone scheme"

"Band structure"



"Irreducible Brillouin zone"

Nonzero Potential $V(x)$

Potential energy term in Schrödinger Eqn is (using integer label h):

$$\sum_{G'} V_{G'} e^{iG'x} \sum_{G} C_G e^{iGx} = \sum_{h'} V_{h'} e^{iG_{h'}x} \sum_{h} C_h e^{iG_h x} = \sum_{h}\sum_{h'} V_{h'} C_h e^{i(G_h+G_{h'})x} = \sum_{h}\sum_{h'} V_{h'} C_h e^{iG_{h+h'}x}$$

Now, after variable substitution $h+h' \longrightarrow h$, we have $= \sum_{h}\sum_{h'} V_{h'} C_{h-h'} e^{iG_h x}$

and the sums in our Schrödinger equation can be unified:

$$\sum_{h}\left[\frac{\hbar^2}{2m}(K+G_h)^2 C_h + \sum_{h'} V_{h'} C_{h-h'}\right] e^{iG_h x} = \sum_{h} E C_h e^{iG_h x}$$

Since the $e^{iG_h x}$ basis functions are orthonormal, each coefficient must separately satisfy

$$\frac{\hbar^2}{2m}(K+G_h)^2 C_h + \sum_{h'} V_{h'} C_{h-h'} = E C_h \qquad \text{(for all } h\text{)}$$

This is an infinite system of linear equations, which invites solution via matrix manipulation!

Infinite matrix eigenvalue problem: $\frac{\hbar^2}{2m}(k+G_h)^2 C_h + \sum_{h'} V_{h'} C_{h-h'} = E C_h$

$$\vdots$$

$$(h=-1)\quad \cdots + V_1 C_{-2} + \frac{\hbar^2}{2m}(k+G_{-1})^2 C_{-1} + V_0 C_{-1} + V_{-1} C_0 + V_{-2} C_1 + \cdots = E C_{-1}$$

$$(h=0)\quad \cdots + V_2 C_{-2} + V_1 C_{-1} + \frac{\hbar^2}{2m}(k+G_0)^2 C_0 + V_0 C_0 + V_{-1} C_1 + \cdots = E C_0$$

$$(h=1)\quad \cdots + V_3 C_{-2} + V_2 C_{-1} + V_1 C_0 + \frac{\hbar^2}{2m}(k+G_1)^2 C_1 + V_0 C_1 + \cdots = E C_1$$

$$\vdots$$

This is equivalent to:

$$\begin{bmatrix} \ddots & & \vdots & & \\ V_1 & \frac{\hbar^2}{2m}(k+G_{-1})^2+V_0 & V_{-1} & V_{-2} & \cdots \\ \cdots V_2 & V_1 & \frac{\hbar^2}{2m}(k+G_0)^2+V_0 & V_{-1} & V_{-2} \cdots \\ \cdots & V_2 & V_1 & \frac{\hbar^2}{2m}(k+G_1)^2+V_0 & V_{-1} \cdots \\ & & \vdots & & \ddots \end{bmatrix} \begin{bmatrix} \vdots \\ C_{-1} \\ C_0 \\ C_1 \\ \vdots \end{bmatrix} = E \begin{bmatrix} \vdots \\ C_{-1} \\ C_0 \\ C_1 \\ \vdots \end{bmatrix} \Rightarrow$$

just eigenvalue problem

$$\mathcal{H}\Psi = E\Psi$$

Note that a real $V(x)$ gives $V_G = V_{-G}^*$, hence $\mathcal{H}$ is hermitian and E is real!

Finite Matrix Eigenvalue problem

But we can't solve eigenvalues of an infinite matrix!

Cutoff values of G to finite number → equivalent to finite resolution in x : $x \longrightarrow n\frac{a}{N}$ where n is an integer and N is total # of Gs

Then $e^{i(G_{h'}+G_h)x} = e^{i(h+h')\frac{2\pi}{\cancel{a}} n \frac{\cancel{a}}{N}}$ → periodic in $h+h'$ w/ period N

So V_h values "wrap around" along row in Hamiltonian!

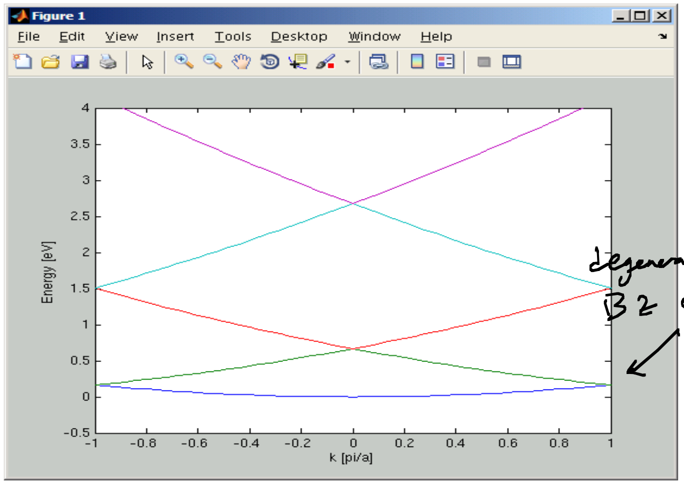
Example: $N=3$ $h=-1,0,1$

$$\begin{bmatrix} \frac{\hbar^2}{2m}(K+G_{-1})^2+V_0 & V_{-1} & V_1 \\ V_1 & \frac{\hbar^2}{2m}(K+G_0)^2+V_0 & V_{-1} \\ V_{-1} & V_1 & \frac{\hbar^2}{2m}(K+G_1)^2+V_0 \end{bmatrix} \begin{bmatrix} C_{-1} \\ C_0 \\ C_1 \end{bmatrix} = E \begin{bmatrix} C_{-1} \\ C_0 \\ C_1 \end{bmatrix}$$

Now we can diagonalize our finite hermitian matrix $\mathcal{H}$!

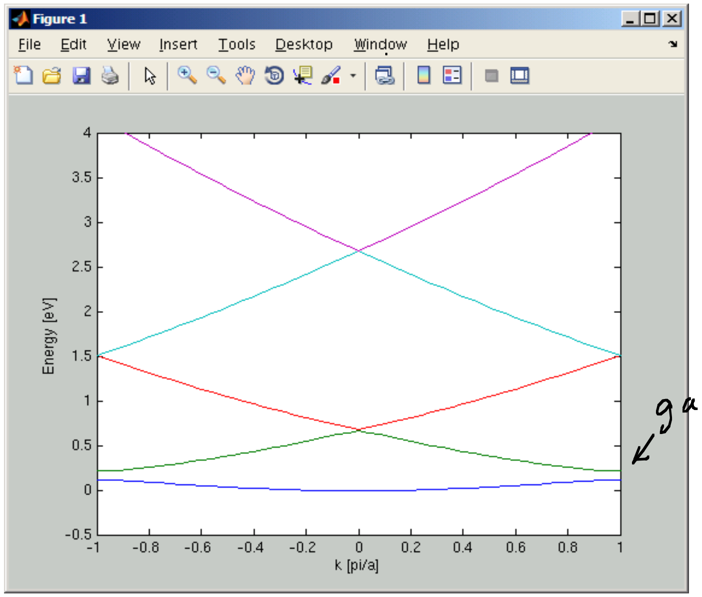
Numerical Diagonalization

V=0, "free electron" dispersion:

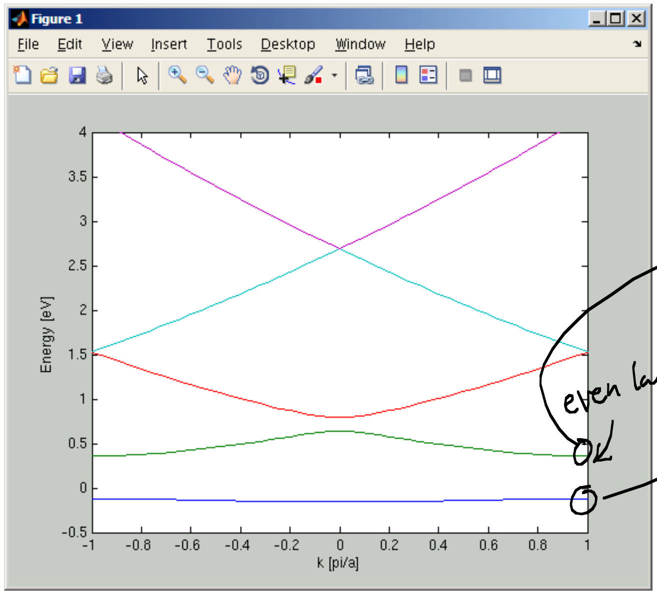


The broken continuous translational symmetry induced by V(x) Consequently breaks band degeneracy at BZ edge. This results in "bandgaps", which can be further understood by inspecting the alignment of probability density $\psi^*\psi$ w.r.t. the potential V(x) for k at the BZ edge.

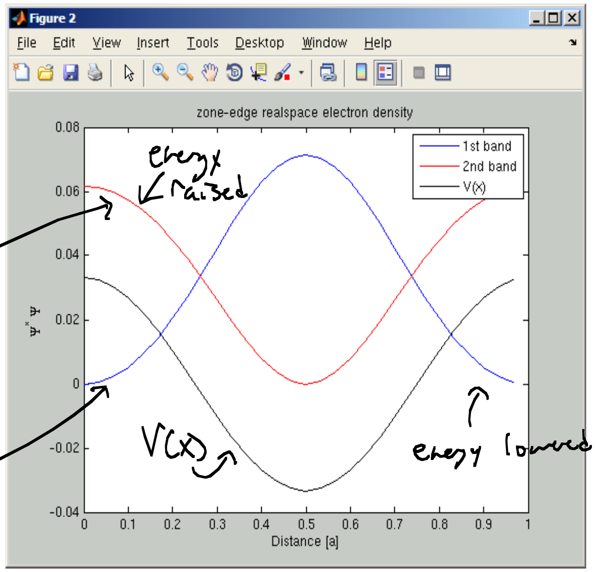
$V = 0.1\overset{eV}{} \cos \frac{2\pi x}{a}$: (a = 1.5nm)



$V = 0.5 \cos \frac{2\pi x}{a}$:



wave function density $\psi^*\psi$



Band gaps

Why are bandgaps induced by nonzero potential giving off-diagonal elements of $\mathcal{H}$?

Consider a 2-band model Hamiltonian:

$$\mathcal{H} = \begin{bmatrix} E_1 & \Delta \\ \Delta^* & E_2 \end{bmatrix} :$$

parabolic dispersion $\frac{\hbar^2}{2m}(K+G_2)^2$

At the BZ edge, $E_1 = E_2$ so

$$\mathcal{H} = E_{1,2}\mathbb{1} + \begin{bmatrix} 0 & \Delta \\ \Delta^* & 0 \end{bmatrix} \Rightarrow$$

eigenvalues are $E_{1,2}$ + roots of $\{E^2 - |\Delta|^2 = 0\}$

so potential splits eigenvalues to $E_{1,2} \pm |\Delta|$ giving a "gap" of $2|\Delta|$!

The bandgap gives an explanation for the existence of insulators:

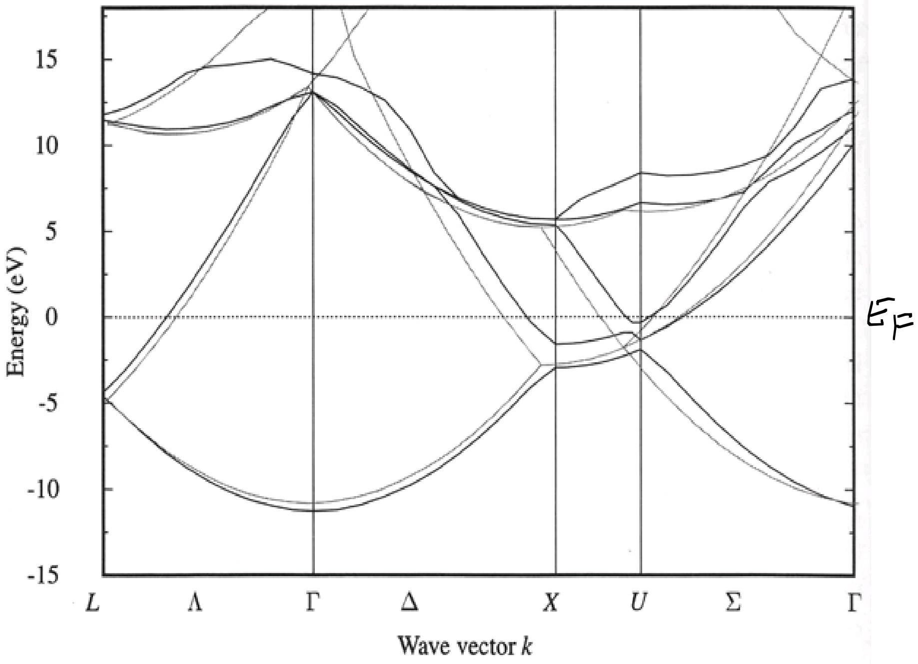
The absence of available (unoccupied) states near E_F as in Sommerfeld model means that distributions asymmetric in $\vec{k}$ are impossible and despite large densities of electrons, no current can flow!

Fermi Energy

Fermi energy is determined by accounting for every electron in unit cell, 2 electrons per band. If the last filled band is just below a bandgap, the material is an "insulator" (or semiconductor as explained later). Otherwise, half-filled bands give "metals" and zero gap gives "semimetal".

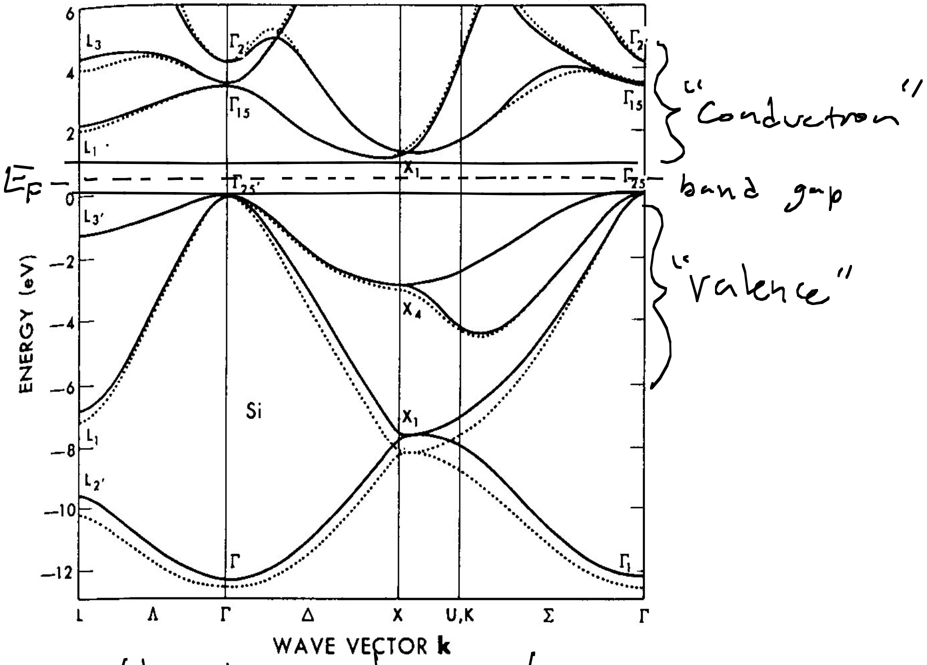
Examples:

Aluminum ($Z = 13$) (a metal)



3 valence electrons w/ 1 atom in unit cell: 1.5 filled bands

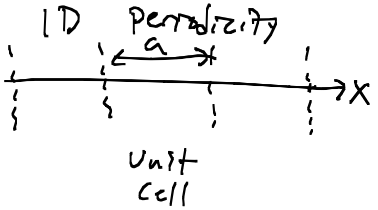
Silicon ($Z = 14$) (an insulator/semiconductor)



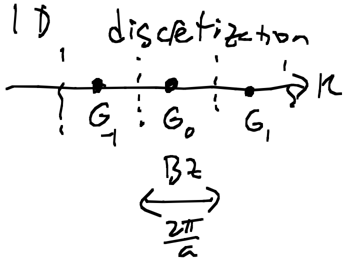
4 valence electrons w/ 2 atoms in unit cell so 4 filled bands

Bandstructure beyond 1 dimension: How to interpret 3D bandstructures above?

1D:



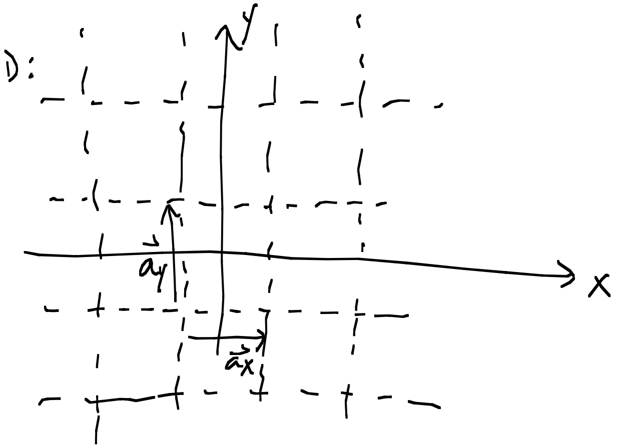
$\Longrightarrow$



G_h "reciprocal lattice numbers" $= h\frac{2\pi}{a}$ h an integer

2D periodicity (square lattice)

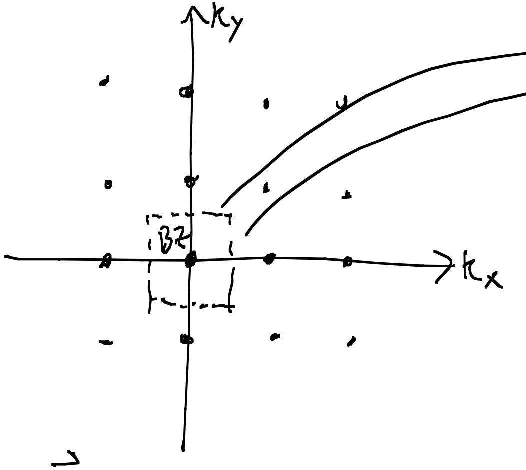
2D:



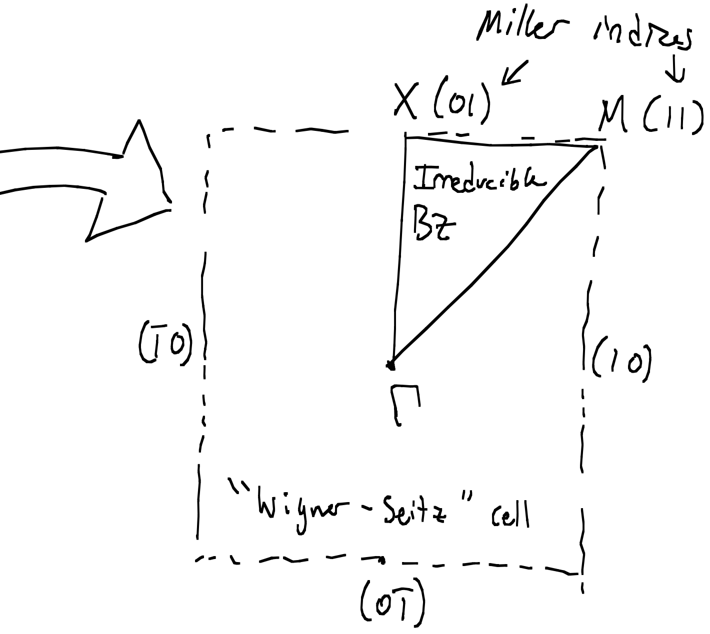
$\vec{a}_x, \vec{a}_y$ "primitive lattice vectors"

$\Longrightarrow$

2D discretization

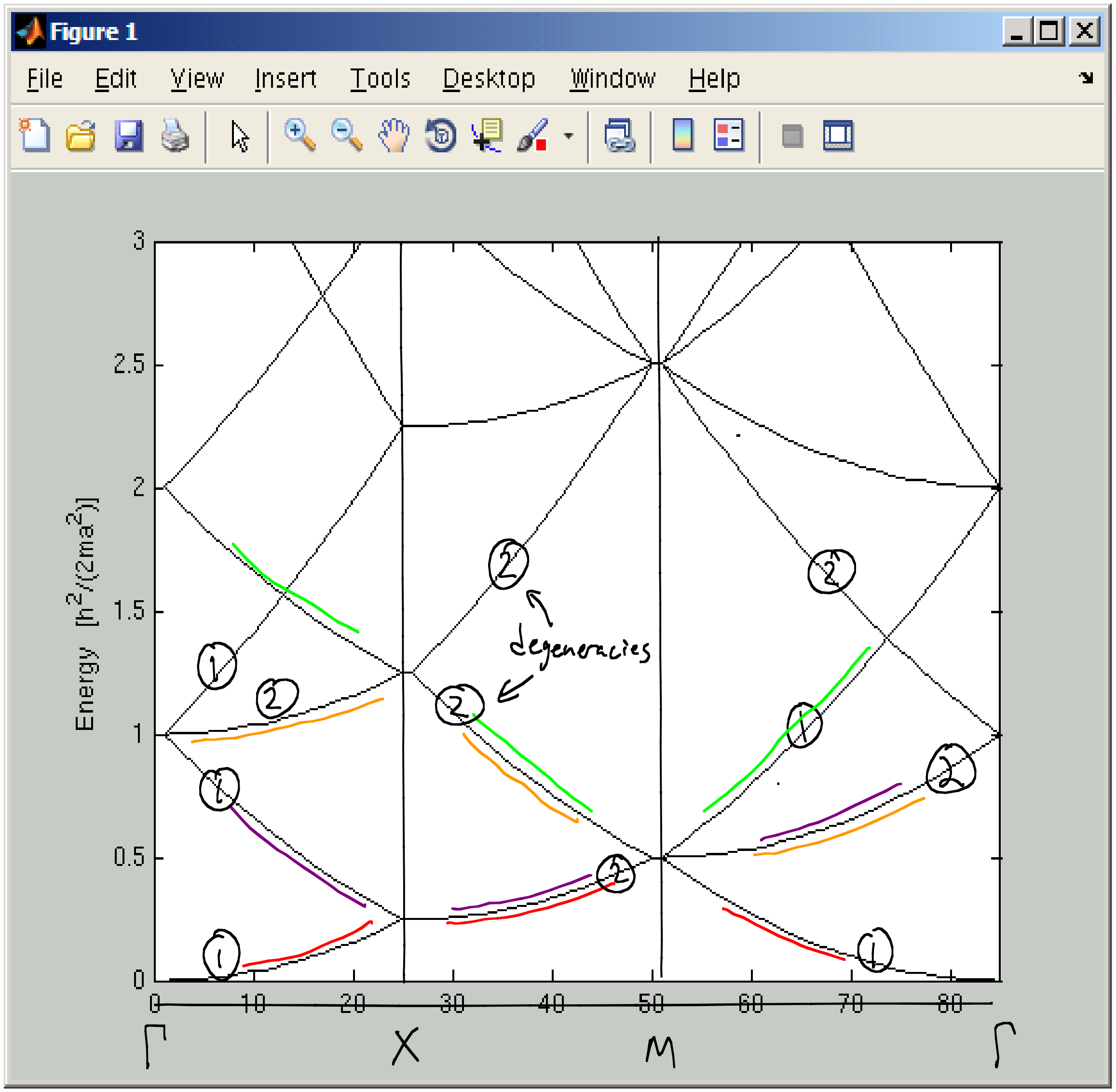


$$\vec{G} = h\frac{2\pi}{|a_x|}\hat{x} + l\frac{2\pi}{|a_y|}\hat{y}$$

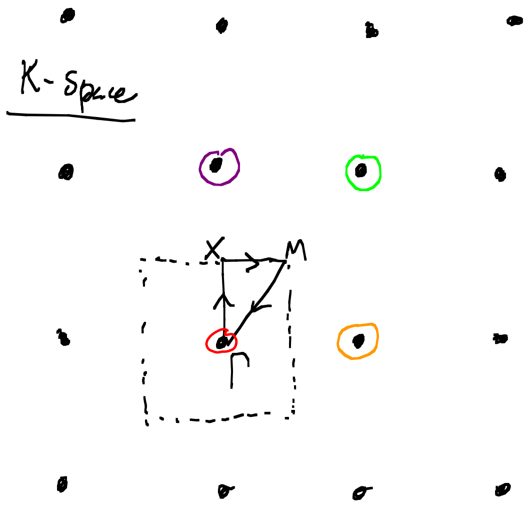


The BZ can be reduced to the irreducible BZ by eliminating redundancies caused by symmetry. The Bandstructure is calculated on the perimeter of the IBZ, where points of high symmetry are labeled by Roman letters (BZ boundary) or Greek letters (interior pts).

2D Square lattice: "Nearly-free electron" bandstructure



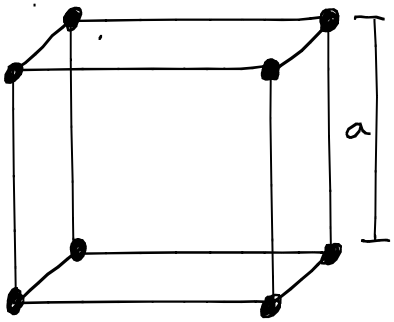
A paraboloid $\frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2$ sits on every reciprocal lattice point $\vec{G}$ and crosses our path along the IBZ perimeter



Note: on the BZ boundary, bands must cross at a degeneracy, or have zero slope due to a gap (by symmetry)

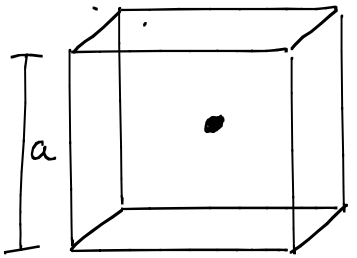
3 dimensions: primitive unit cell

primitive = includes only 1 lattice point. For example, a primitive unit cell for the "simple cubic" lattice might be chosen w/ the "conventional" unit cell.

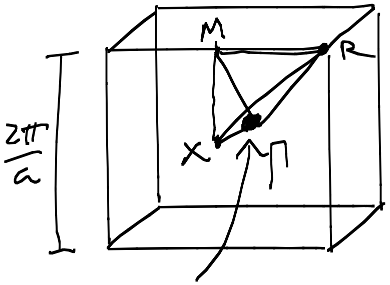


Each lattice point is shared w/ 8 unit cells so this contains $8 \times 1/8 = 1$ total lattice points. However, it is more convenient to choose the Wigner-Seitz unit cell w/ one lattice point at the center so that constructing the BZ is straightforward:

real (x) space Wigner-Seitz cell:



reciprocal (k) space Brillouin Zone:

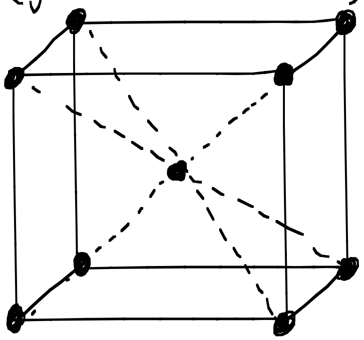


Irreducible BZ (here, 1/48th of BZ volume) is an irregular polyhedron defined by lattice symmetries

related lattices (conventional unit cells):

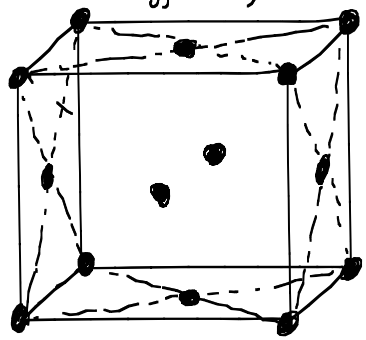
body-centered cubic (bcc)

(e.g. alkali metals)



face-centered cubic (fcc)

(e.g. Cu, Ag, Au)

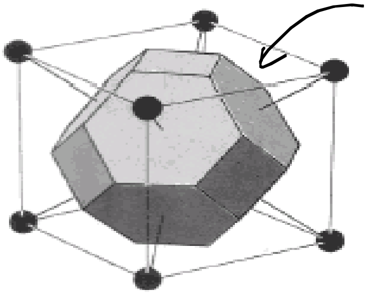


BZs in 3 dimensions: bcc and fcc

real-space lattice

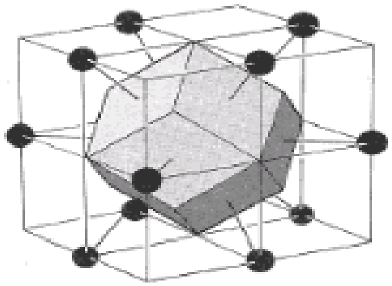
reciprocal lattice

bcc:



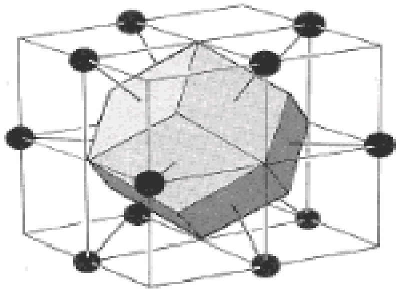
"Wigner-Seitz" primitive cell

(planes halfway between origin + nearest lattice point)

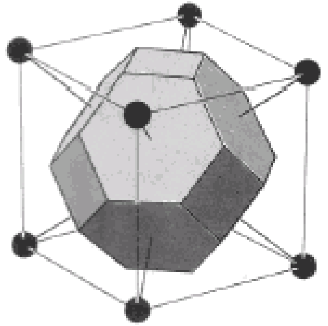


Note that bcc BZ in k-space is same as fcc W-S cell in x-space, and vice-versa.

fcc:



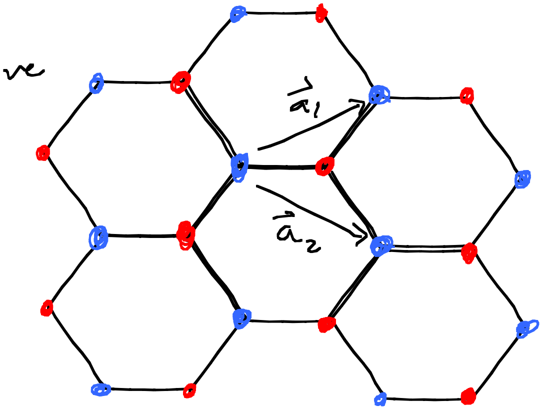
(primitive cell contains 1 lattice point)



These are examples of "Bravais lattices": All lattice points are equivalent.
Note, however, that NOT ALL lattices are Bravais!

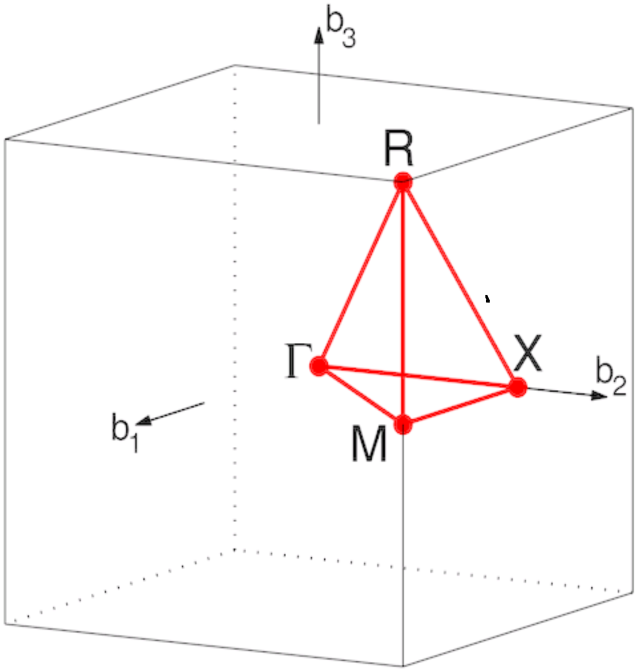
Example: Honeycomb (e.g. graphene): red and blue lattice points are not the same.

But this is same as triangular lattice with "basis" $d=\vec{0}$ and $\frac{1}{3}(\vec{a}_1+\vec{a}_2)$



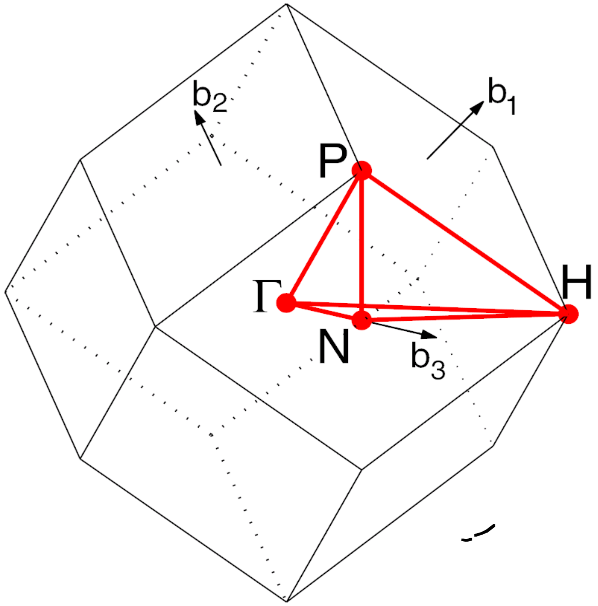
IBZs of Cubic lattices

http://en.wikipedia.org/wiki/Brillouin_zone



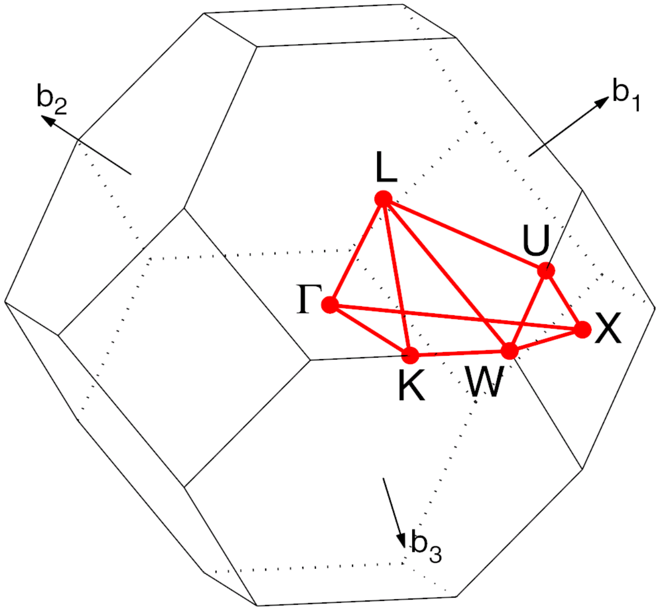
CUB path: Γ-X-M-Γ-R-X|M-R

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]



BCC path: Γ-H-N-Γ-P-H|P-N

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

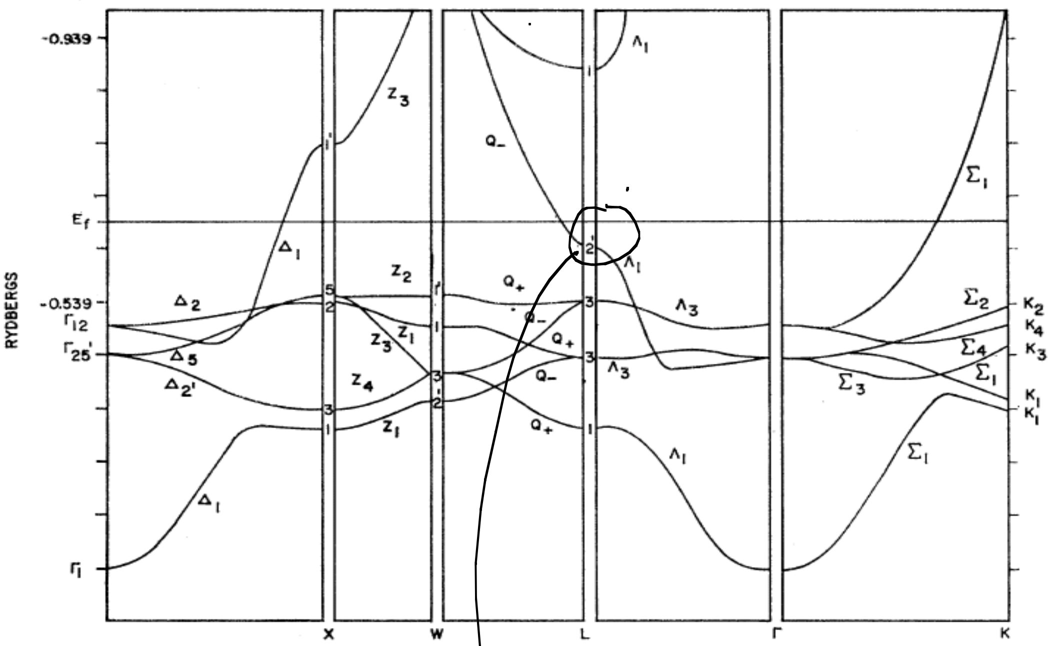


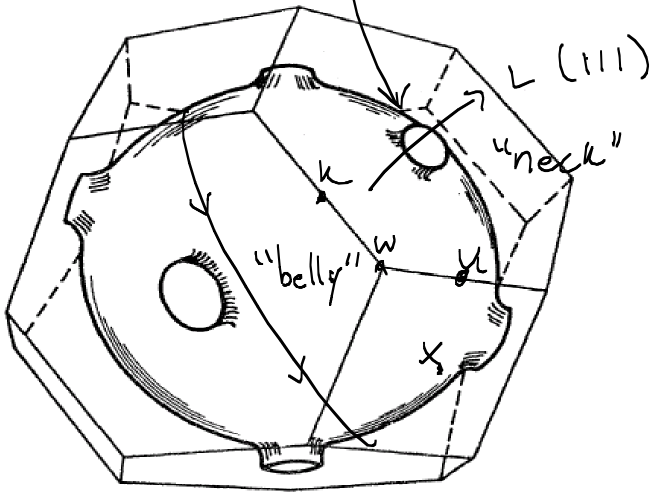
FCC path: Γ-X-W-K-Γ-L-U-W-L-K|U-X

[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

Fermi Surface

Example: Copper (FCC)



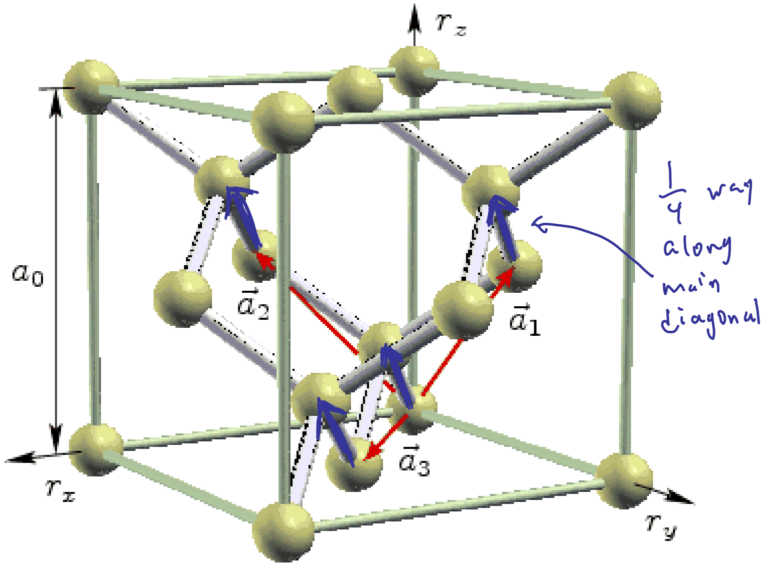


The nearly-free electron bands always meet in degeneracies at the BZ boundary, so the Fermi surface is a sphere (as in the Sommerfeld model neglecting periodicity).

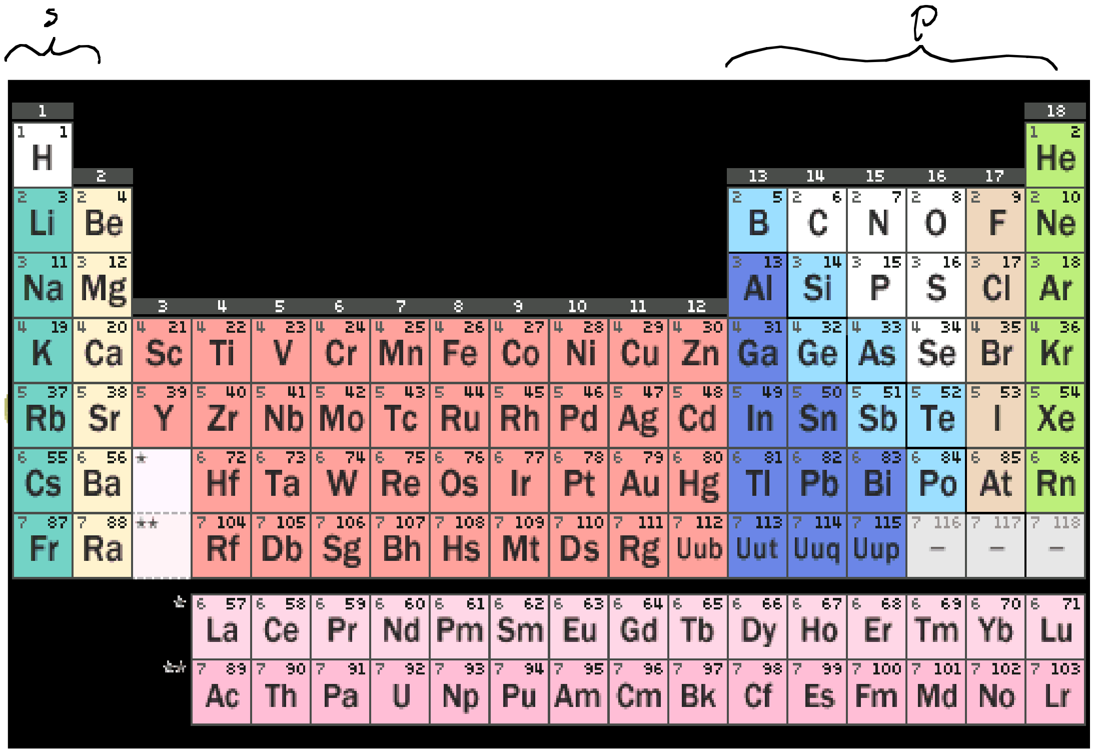
For bands where potential $V(\vec{r})$ has been taken into account, this is obviously not the case due to off-diagonal matrix elements and degeneracy splitting.

For Cu, we have valence $[Ar]\,4s^1 3d^{10}$, so with 11 electrons, we fill 5-½ bands to find the Fermi energy. This line intersects a partially filled band along Γ–X, but NOT along Γ-L (111 dir). The resulting Fermi surface merges with another sphere in an adjacent BZ, forming a "neck" that can be seen in deHaas-van Alphen w/ H along (111). Two frequencies in 1/H from "neck" and "belly" result.

Diamond / Zincblende lattice



(a) Conventional cubic cell.



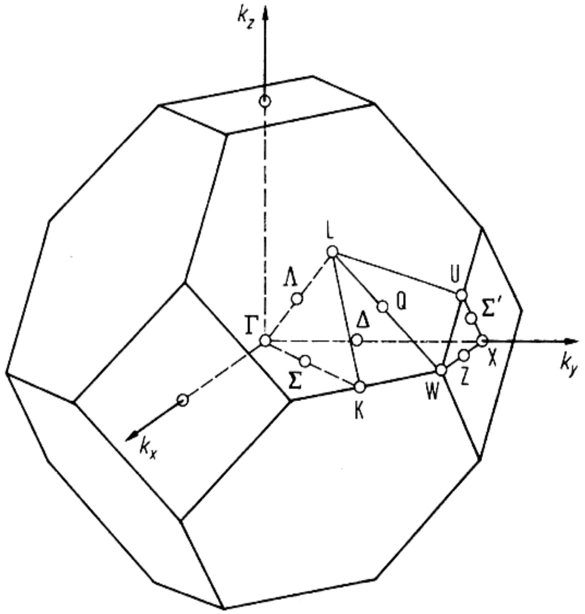
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 –	117 –	118 –

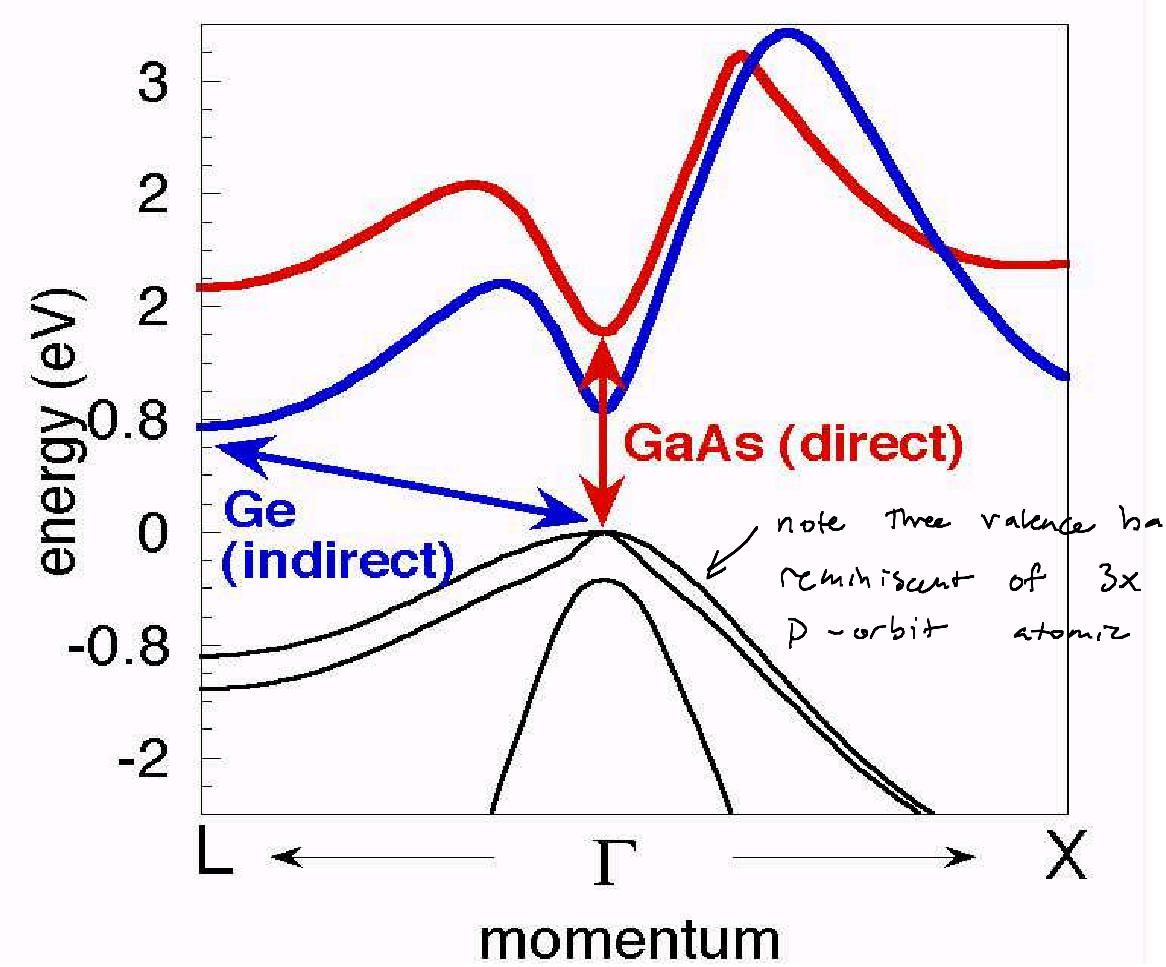
*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

each atom in group IV (C, Si, Ge) has 4x equivalent sp^3 hybridized bonds equally distributed in space. This tetragonal coordination leads to diamond lattice: 2 interpenetrating fcc lattices, separated by 1/4 distance along main diagonal.

Zincblende is formed by putting inequivalent atoms (e.g. from groups III and V or II and VI) on the fcc lattices. The BZ is identical to fcc BZ since it is the underlying Bravais lattice (with basis $\vec{d} = \vec{0}$ and $\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$)

Types of Bandgaps



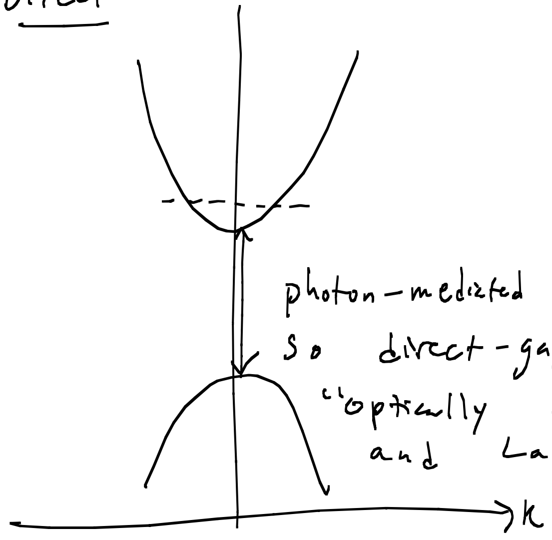


note Three valence bands reminiscent of 3x degenerate p-orbit atomic states.

Although many small-gap insulators (semiconductors) have diamond/zincblende lattice, The bandstructure can be very different: varying bandgaps AND varying locations in k-space where conduction band is lowest. This defines two kinds of bandgaps: direct (e.g. GaAs, InP) and indirect (e.g. Si, Ge, GaP)

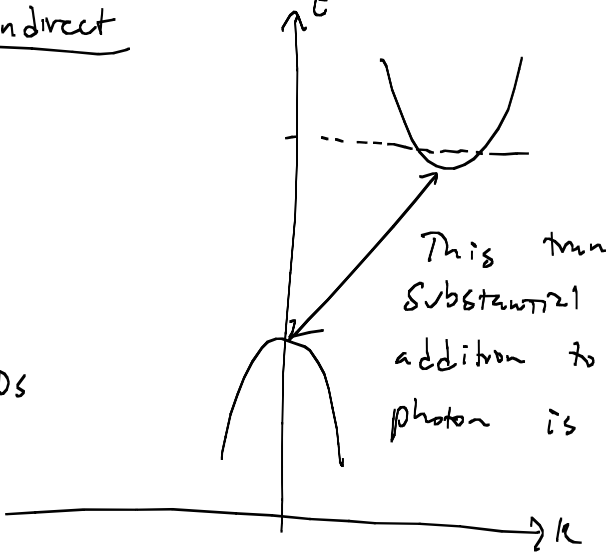
Constant energy surfaces

Direct



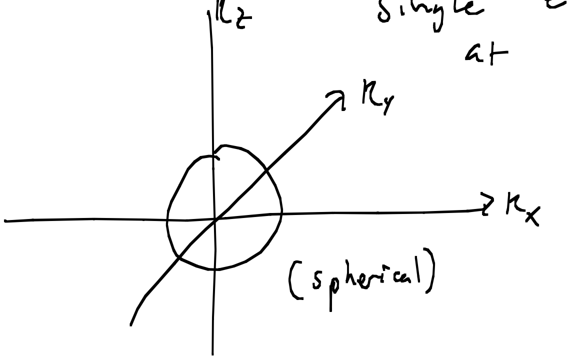
photon-mediated transition (no momentum)
So direct-gap materials good for "optically active" devices like LEDs and Lasers!

Indirect

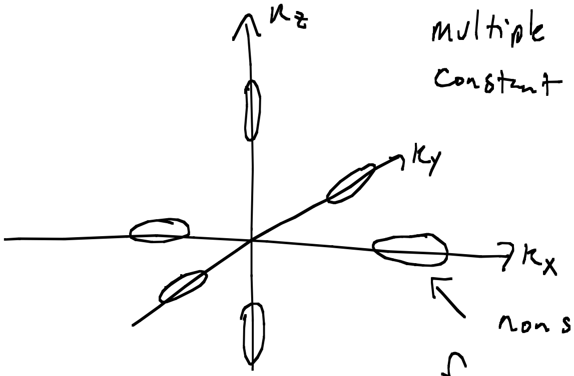


This transition needs substantial momentum in addition to energy E_g so photon is not enough!

Constant-energy surface of conduction band!



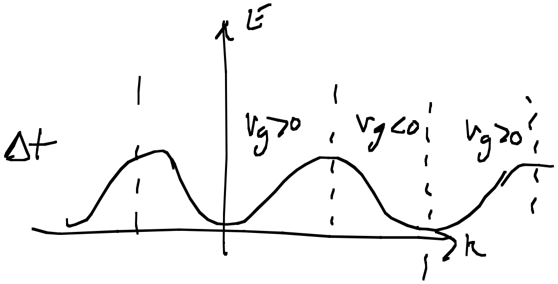
Single energy surface at zone center



multiple symmetry-related constant energy surfaces

nonspherical surfaces from anisotropic band curvature!

Electrons in Bands: Dynamics



velocity: $v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$. If $F = \frac{dp}{dt} = \hbar\frac{dk}{dt}$ Then $\Delta k = \frac{F}{\hbar}\Delta t$

It would seem that the periodic dispersion relation would allow a DC force (i.e. Coulomb force from electric field $\mathcal{E}$) to cause AC current.

We need $\Delta k > \frac{2\pi}{a}$ → $\frac{e\mathcal{E}}{\hbar}\tau > \frac{2\pi}{a}$ → $\mathcal{E} > \frac{h}{e}\frac{1}{a\tau}$ but scattering time τ small!

This "Bloch oscillation" only possible for large lattice const: periodic "superlattices"

acceleration: $a = \frac{dv_g}{dt} = \frac{d}{dt}\left(\frac{d\omega}{dk}\right) = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dt}\right) = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\frac{dk}{dt}\right) = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\frac{dp}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F$

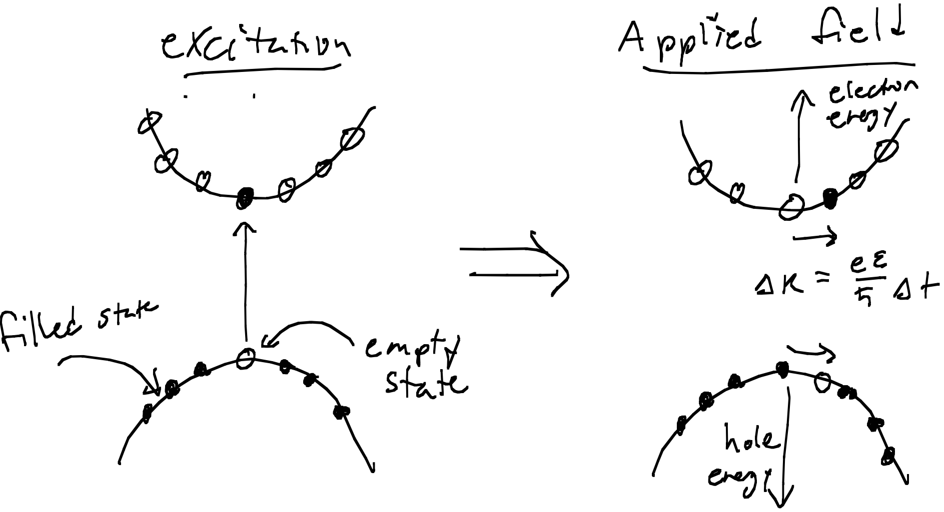
So $F = \frac{\hbar^2}{\frac{d^2E}{dk^2}}a = m^*a$ (m^* = "effective mass", due to similarity w/ Newton's 2nd law)

Check: for free electron $E = \frac{\hbar^2k^2}{2m}$, $\frac{d^2E}{dk^2} = \frac{\hbar^2}{m}$ so $m^* = m$ ✓

Valence band "holes"

Note that by this definition, valence band electrons have a negative mass and their mobility $\mu = \frac{e\tau}{m^*}$ is of opposite sign as conduction electrons! Does this mean current flows the "wrong" way? No!

$\Rightarrow$ Consider an excitation which promotes a valence electron to the conduction band, then response of all electrons to Coulomb force causing $\Delta k = \frac{e\mathcal{E}}{\hbar}\Delta t$:

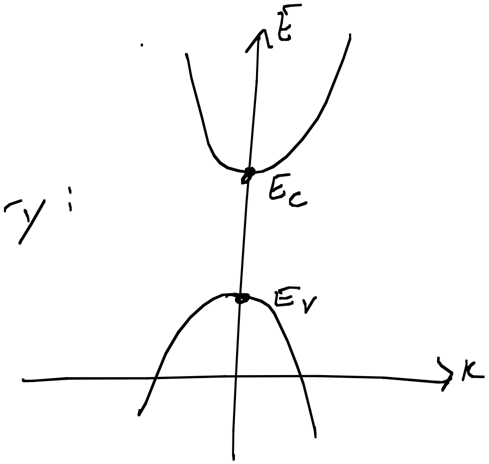


Now the contribution to current density $J = nev_g$ from the conduction band is $\propto \frac{dE}{dk} > 0$. The valence band is nearly filled except for the empty state @ $k = \Delta k$ w/ $v_g^{\text{empty}} \propto \frac{dE}{dk} < 0$, so the current density contribution from valence band states is:

$$J \propto \cancelto{0\ (\text{filled band})}{\sum_{i,\text{ all valence}} v_g} - v_g^{\text{empty}} > 0 .$$

Since this empty state has opposite v_g as a negative electron yet results in the same current flow due to the otherwise-filled valence background, it is convenient to consider it as a positive-charged particle with positive mass and group velocity: a "hole"!

Effective mass via perturbation Theory: K·p



If we know $E(k=0)=E_c$ and band-edge wavefunctions, we can calculate $E(k)$ using second-order Perturbation Theory:

$$E(k) = \overset{(0^{th})}{E(0)} + \overset{(1^{st})}{\langle \psi_c^0 | \mathcal{H}_p | \psi_c^0 \rangle} + \overset{(2^{nd})}{\sum_n \frac{|\langle \psi_c^0 | \mathcal{H}_p | \psi_n^0 \rangle|^2}{E_c - E_n}} + \cdots$$

only one term in sum for 2-band model!

where $\mathcal{H}_p = \frac{\hbar^2 k^2}{2m} + \frac{\hbar}{m}\vec{k}\cdot\vec{p}$

for conduction band:

$$E_c(k) = E_c + \frac{\hbar^2k^2}{2m}\cancelto{1}{\langle \psi_c^0 | \psi_c^0 \rangle} + \cancelto{=0\text{ (bottom of band, deriv zero)}}{\langle \psi_c^0 | \frac{\hbar}{m} k\cdot p | \psi_c^0 \rangle} + \frac{\frac{\hbar^2k^2}{2m}\cancelto{=0\text{ (orthogonality)}}{|\langle \psi_c^0 | \psi_v^0 \rangle|^2}}{E_c - E_v} + \frac{|\langle \psi_c^0 | \frac{\hbar}{m} k\cdot p | \psi_v^0 \rangle|^2}{E_c - E_v}$$

$$= E_c + \frac{\hbar^2k^2}{2m} + \frac{\hbar^2k^2}{m^2}\frac{|\langle \psi_c^0 | p | \psi_v^0 \rangle|^2}{E_g}$$

$$= E_c + \frac{\hbar^2k^2}{2}\left(\frac{1}{m} + \frac{2\langle p \rangle^2}{m^2 E_g}\right) = E_c + \frac{\hbar^2k^2}{2m^*} \quad \text{where} \quad \frac{1}{m^*} = \frac{1}{m} + \frac{2\langle p \rangle^2}{m^2 E_g}$$

Clearly Then, smaller bandgaps give smaller effective mass m^*. This can be understood in terms of The second-order perturbation term, which is stronger when E_g is small. Large corrections bend The bands upward, causing more curvature and hence smaller m^*. For $E_v(k)$, $E_v - E_c < 0$ so correction is negative!

Approximate Calculation of $\langle p\rangle^2 = |\langle \varphi_c^0 | p | \varphi_v^0\rangle|^2$

In 1D, we saw that the zone-edge wavefunctions above and below a bandgap were merely shifted in phase. Using $\varphi_c^0 \propto \cos\frac{2\pi x}{a}$ and $\varphi_v^0 \propto \sin\frac{2\pi x}{a}$,

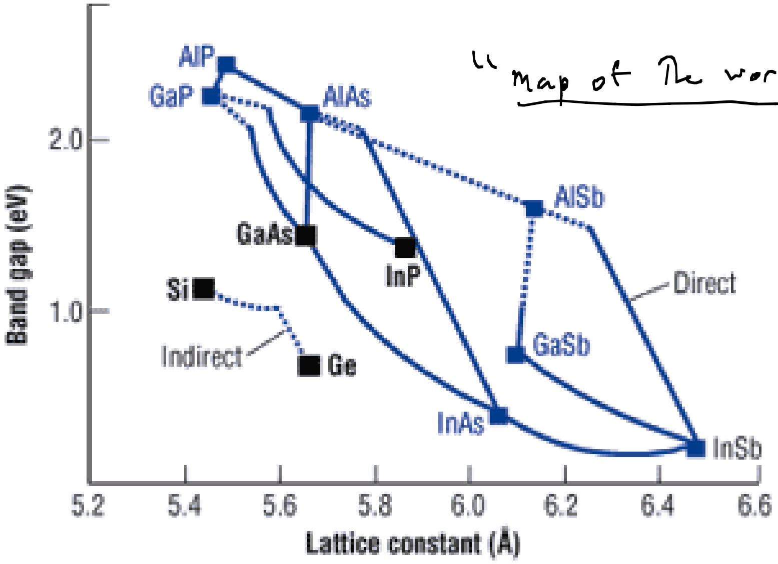
$$\langle \varphi_c^0 | \frac{\hbar}{i}\frac{d}{dx} | \varphi_v^0\rangle = \frac{\hbar}{i}\cdot\frac{2\pi}{a}\cdot\langle\varphi_c^0|\varphi_c^0\rangle$$

Therefore, $\langle p\rangle^2 \sim \frac{h^2}{a^2}$. Since typical lattice constants $a\sim 5\,Å$, we have

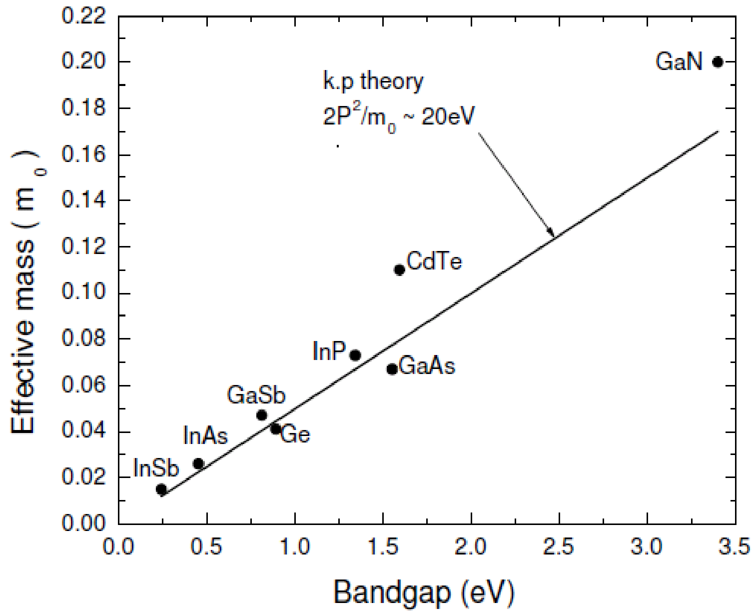
$$\frac{2\langle p\rangle^2}{m} \sim \frac{2\,(4\times10^{-15}\,eV\cdot s)^2}{5\times10^5\,eV/c^2\cdot(5\times10^{-8}\,cm)^2} \sim 20\,eV.$$

Since $E_g \ll 20\,eV$, approx.

$$\frac{1}{m^*} \sim \frac{2\langle p\rangle^2}{m}\cdot\frac{1}{mE_g} \Longrightarrow \frac{m^*}{m}\sim\frac{E_g}{20\,eV}$$



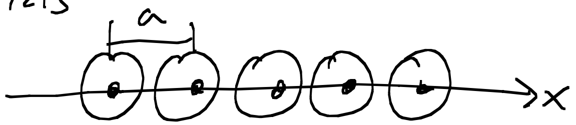
"map of the world"



"Tight-binding" or "LCAO" bandstructure calculation

Construct wavefunction from isolated atomic orbitals

Example: 1 atomic s-orbital, 1-D lattice



$$\psi(r) = \sum_m c_m |\phi_s(r-R_m)\rangle$$ (c_m's have same magnitude, orbitals on different sites orthogonal)

Bloch condition: $\psi(r+a) = e^{ika}\psi(r)$ so $\psi(r) = \sum_m \frac{e^{ikR_m}}{\sqrt{N}} |\phi_s(r-R_m)\rangle$

$$\psi(r+a) = \sum_m \frac{e^{ikR_m}}{\sqrt{N}} |\phi_s(r+a-R_m)\rangle \xrightarrow{R_{m'} = R_m - a} \sum_{m'} \frac{e^{ik(R_{m'}+a)}}{\sqrt{N}} |\phi_s(r-R_{m'})\rangle = e^{ika} \sum_{m'} \frac{e^{ikR_{m'}}}{\sqrt{N}} |\phi_s(r-R_{m'})\rangle$$

$$= e^{ika}\psi(r) \checkmark$$

Substitute into Schrödinger Eqn:

$$\sum_m \frac{e^{ikR_m}}{\sqrt{N}} \mathcal{H} |\phi_s(r-R_m)\rangle = E \sum_m \frac{e^{ikR_m}}{\sqrt{N}} |\phi_s(r-R_m)\rangle$$ ($\mathcal{H}$ includes atomic potential + <u>interactions</u>)

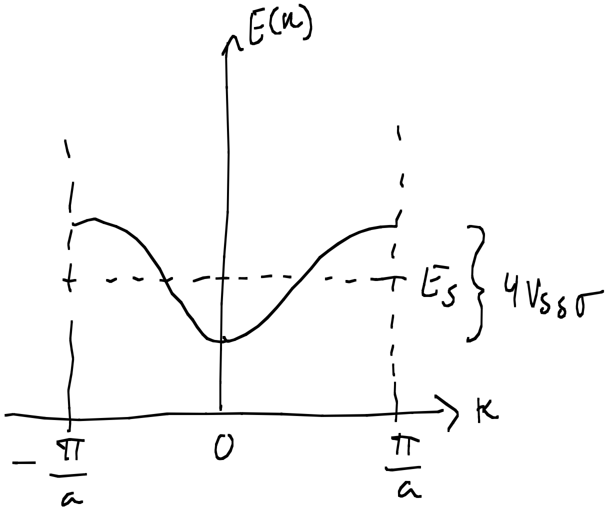
Energy of one unit cell from projection onto $\langle\phi_s(r)|$

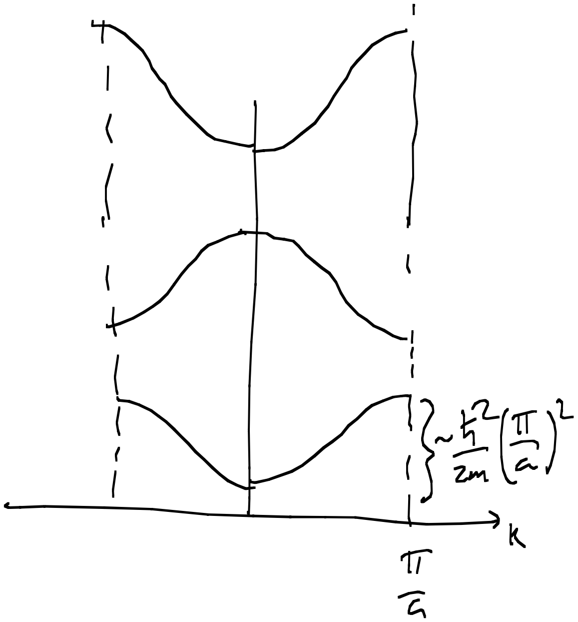
$$\frac{e^{ika}}{\sqrt{N}} \underbrace{\langle\phi_s(r)|\mathcal{H}|\phi_s(r-a)\rangle}_{-V_{ss\sigma}} + \frac{1}{\sqrt{N}} \underbrace{\langle\phi_s(r)|\mathcal{H}|\phi_s(r)\rangle}_{E_s} + \frac{e^{-ika}}{\sqrt{N}} \underbrace{\langle\phi_s(r)|\mathcal{H}|\phi_s(r+a)\rangle}_{-V_{ss\sigma}} = \frac{E}{\sqrt{N}} \cancelto{1}{\langle\phi_s(r)|\phi_s(r)\rangle}$$

+ 0 from orthogonal basis states

This gives dispersion directly: $E(k) = E_s - 2V_{ss\sigma}\cos(ka)$

Comparison with Nearly-free-electron bands





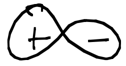
So we expect the magnitude of coupling term $V_{ss\sigma} \sim \frac{\hbar^2}{ma^2}$

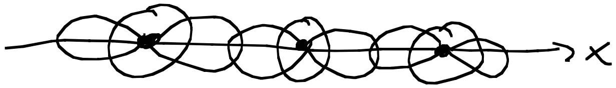
But how to reproduce the higher-energy bands?

Add more orbitals!

2-band LCAO: s-p model

two orbitals :





$$\Psi(r) = \sum_m \frac{e^{ikR_m}}{\sqrt{N}} \left[c_s|\phi_s(r-R_m)\rangle + c_p|\phi_p(r-R_m)\rangle \right]$$

Substitute into Schrödinger eqn:

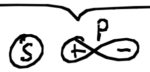
$$\sum_m \frac{e^{ikR_m}}{\sqrt{N}} \mathcal{H} \left[c_s|\phi_s(r-R_m)\rangle + c_p|\phi_p(r-R_m)\rangle \right] = E \sum_m \frac{e^{ikR_m}}{\sqrt{N}} \left[c_s|\phi_s(r-R_m)\rangle + c_p|\phi_p(r-R_m)\rangle \right]$$

project onto $\langle\phi_s(r)|$, keeping interactions (diagonal matrix elements) w/ nearest neighbors

$$\langle\phi_s(r)| \times \frac{1}{\sqrt{N}} \left[\begin{array}{l} e^{ika}\mathcal{H}|\phi_s(r-a)\rangle c_s + e^{ika}\mathcal{H}|\phi_p(r-a)\rangle c_p \\ + e^{-ika}\mathcal{H}|\phi_s(r+a)\rangle c_s + e^{-ika}\mathcal{H}|\phi_p(r+a)\rangle c_p = E|\phi_s(r)\rangle c_s \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + \text{orthogonal states} \\ + \mathcal{H}|\phi_s(r)\rangle c_s + \mathcal{H}|\phi_p(r)\rangle c_p \end{array} \right]$$

this term contributes zero since there is no on-site interaction between orbitals

$$\left[E_s - 2V_{ss\sigma}\cos ka\right]c_s + \left[e^{ika}\underbrace{\langle\phi_s(r)|\mathcal{H}|\phi_p(r-a)\rangle}_{= V_{sp\sigma}} + e^{-ika}\underbrace{\langle\phi_s(r)|\mathcal{H}|\phi_p(r+a)\rangle}_{= -V_{sp\sigma}}\right]c_p = E c_s$$



$= V_{sp\sigma}$

$= -V_{sp\sigma}$

$$\left[E_s - 2V_{ss\sigma}\cos ka\right]c_s + \left[2iV_{sp\sigma}\sin ka\right]c_p = E c_s$$

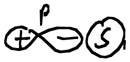
p-state projection

projecting onto $\langle \phi_p(r)|$ gives

$$\langle \phi_p(r)| \times \frac{1}{\sqrt{N}} \left[\begin{array}{l} e^{ika}\mathcal{H}|\phi_s(r-a)\rangle c_s + e^{ika}\mathcal{H}|\phi_p(r-a)\rangle c_p \\ + e^{-ika}\mathcal{H}|\phi_s(r+a)\rangle c_s + e^{-ika}\mathcal{H}|\phi_p(r+a)\rangle c_p = E\,|\phi_p(r)\rangle c_p \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{+ orthogonal states} \\ + \overset{\text{contributes zero since no interaction}}{\mathcal{H}|\phi_s(r)\rangle c_s} + \mathcal{H}|\phi_p(r)\rangle c_p \end{array} \right]$$

$$\underbrace{\langle \phi_p(r)|\mathcal{H}|\phi_p(r)\rangle}_{E_p} c_p + e^{ika}\underbrace{\langle \phi_p(r)|\mathcal{H}|\phi_p(r-a)\rangle}_{= V_{pp\sigma}} + e^{-ika}\underbrace{\langle \phi_p(r)|\mathcal{H}|\phi_p(r+a)\rangle}_{V_{pp\sigma}}$$

$$+ e^{ika}\underbrace{\langle \phi_p(r)|\mathcal{H}|\phi_s(r-a)\rangle}_{= -V_{sp\sigma}} + e^{-ika}\underbrace{\langle \phi_p(r)|\mathcal{H}|\phi_s(r+a)\rangle}_{= V_{sp\sigma}} = E c_p$$



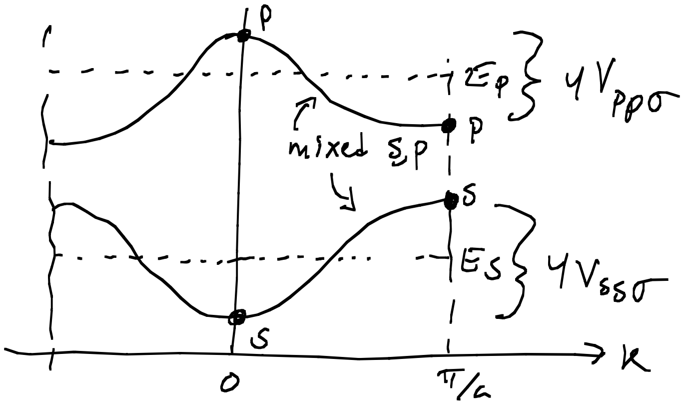
This results in

$$\left[E_p + 2V_{pp\sigma}\cos ka\right]c_p + \left[-2i\,V_{sp\sigma}\sin ka\right]c_s = E c_p$$

2x2 Matrix eigenvalue problem

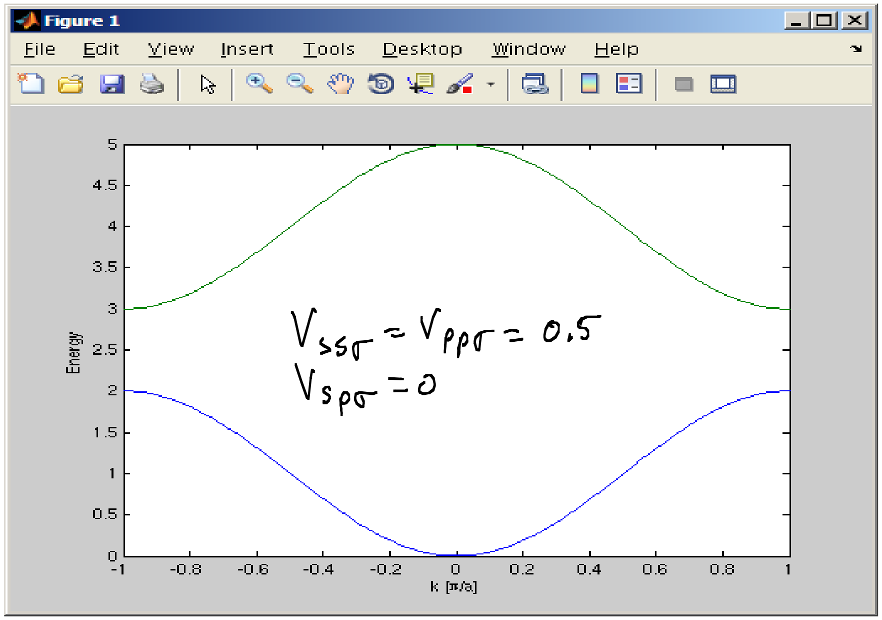
These two linear equations are equivalent to:

$$\begin{bmatrix} E_s - 2V_{ss\sigma}\cos ka & 2iV_{sp\sigma}\sin ka \\ -2iV_{sp\sigma}\sin ka & E_p + 2V_{pp\sigma}\cos ka \end{bmatrix}\begin{bmatrix} C_s \\ C_p \end{bmatrix} = E\begin{bmatrix} C_s \\ C_p \end{bmatrix}$$



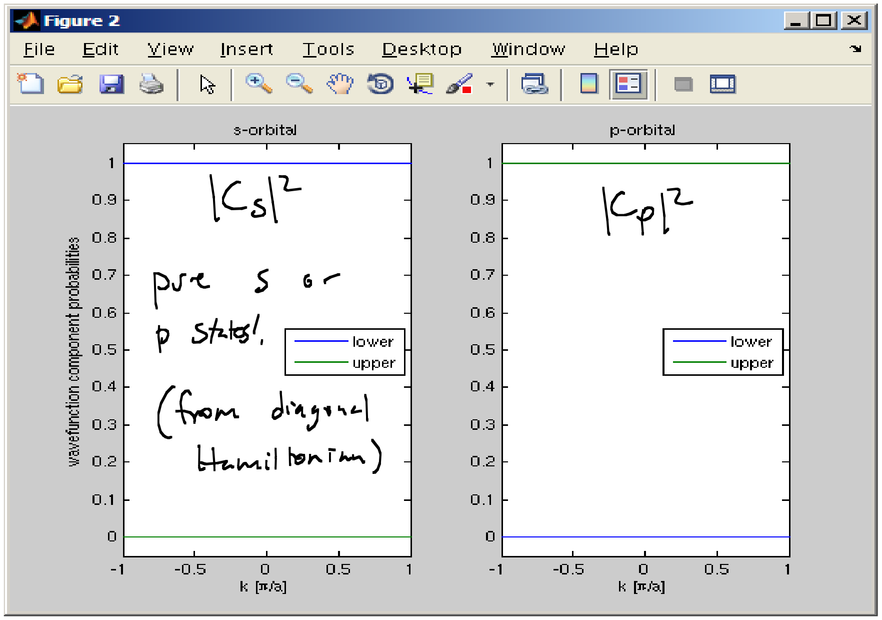
Note that the Hamiltonian matrix is hermitian so E is real, and for $k=0$ and $\frac{\pi}{a}$, (IBZ boundaries) it is diagonal. There, the eigenvectors are $\begin{bmatrix}1\\0\end{bmatrix}$ and $\begin{bmatrix}0\\1\end{bmatrix}$, so the wavefunctions are purely s- or p- orbital character. In the interior of the BZ, ψ is a mixture.

Numerical Results



$V_{ss\sigma} = V_{pp\sigma} = 0.5$

$V_{sp\sigma} = 0$

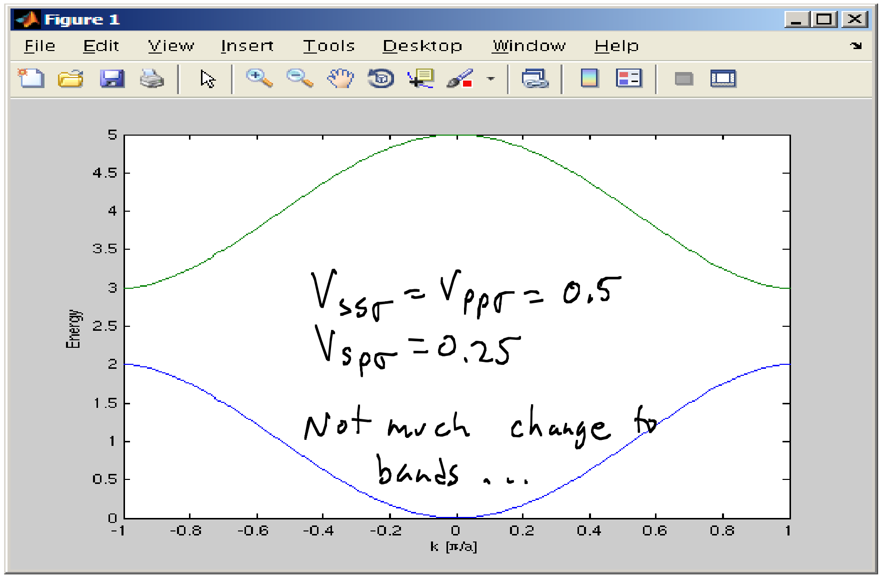


$|C_s|^2$

$|C_p|^2$

pure s or p states!

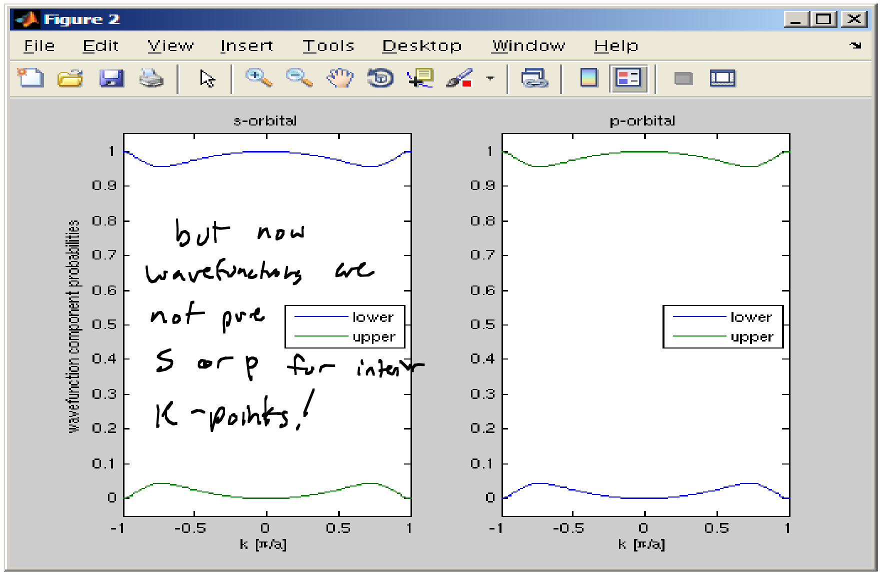
(from diagonal Hamiltonian)



$V_{ss\sigma} = V_{pp\sigma} = 0.5$

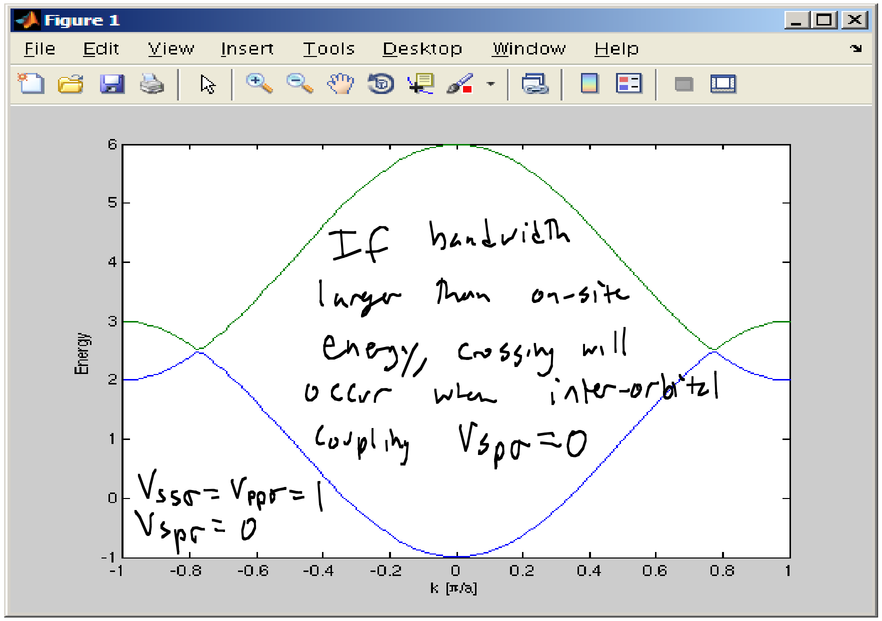
$V_{sp\sigma} = 0.25$

Not much change to bands ...



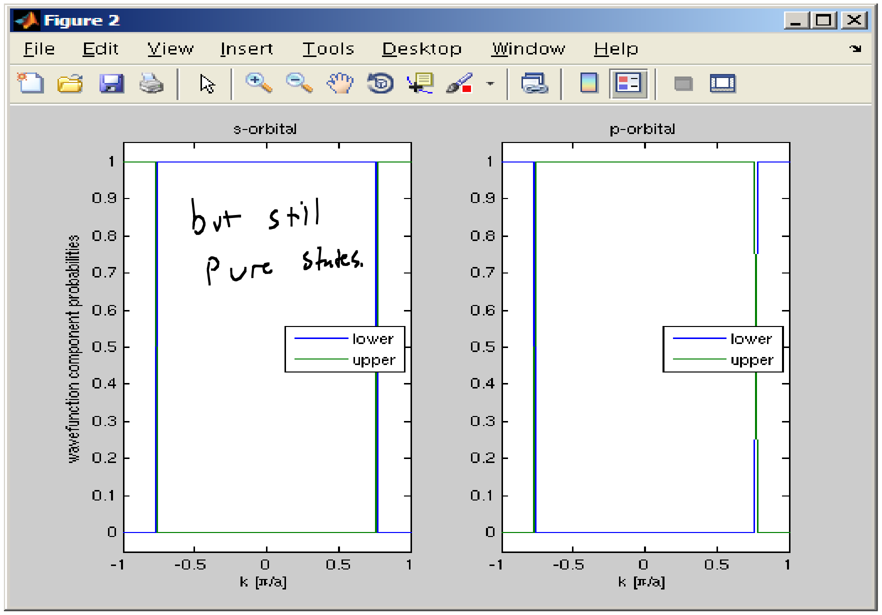
but now wavefunctions are not pure s or p for interior k-points!

Band mixing and band extrema at interior k points

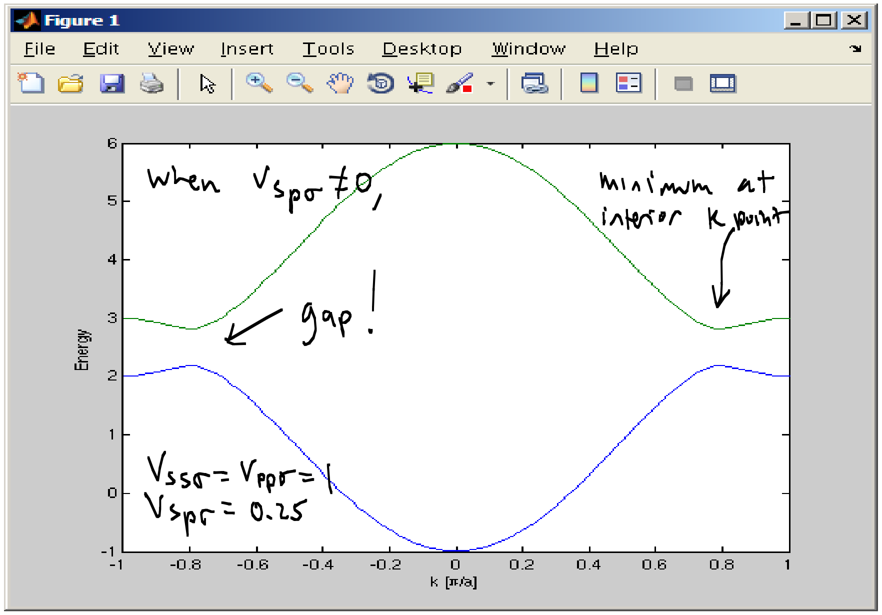


If bandwidth larger than on-site energy, crossing will occur when inter-orbital coupling $V_{sp\sigma}=0$

$V_{ss\sigma}=V_{pp\sigma}=1$
$V_{sp\sigma}=0$



but still pure states.

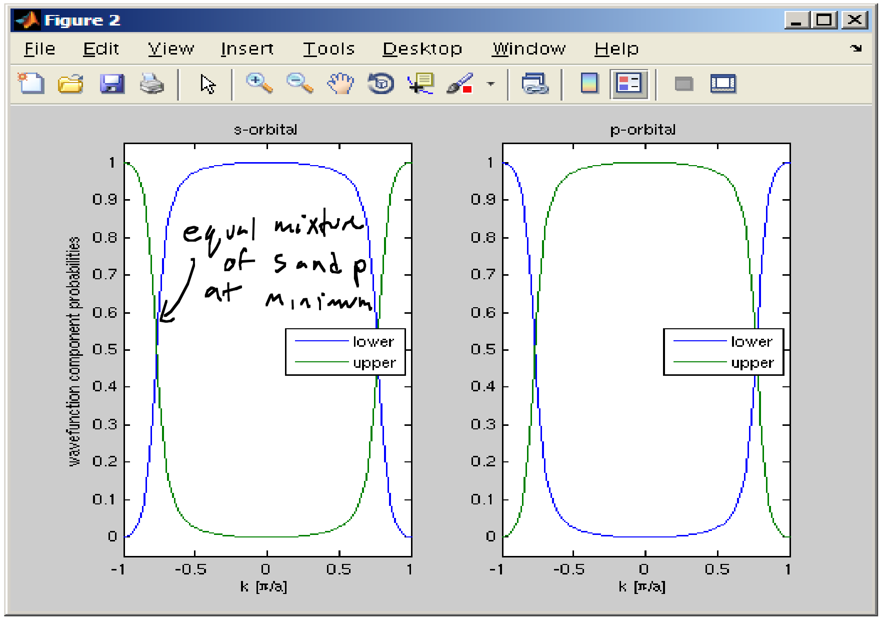


when $V_{sp\sigma}\neq 0$,

gap!

minimum at interior k point

$V_{ss\sigma}=V_{pp\sigma}=1$
$V_{sp\sigma}=0.25$



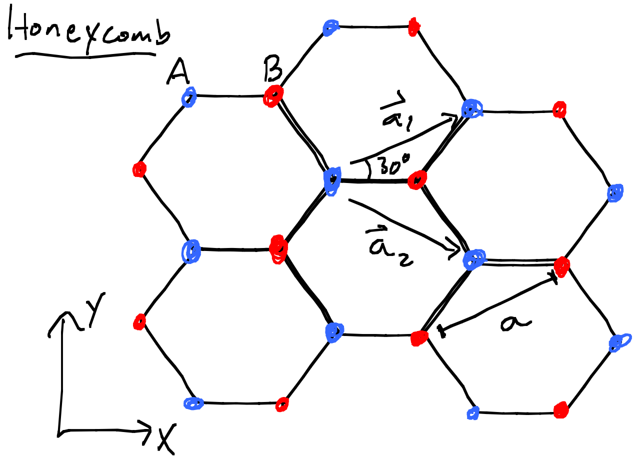
equal mixture of s and p at minimum

Tight binding bandstructure in 2D: lattice w/ basis (graphene)

lattice vectors

$$\vec{a}_1 = \frac{\sqrt{3}}{2} a\hat{x} + \frac{a}{2}\hat{y}$$

$$\vec{a}_2 = \frac{\sqrt{3}}{2} a\hat{x} - \frac{a}{2}\hat{y}$$

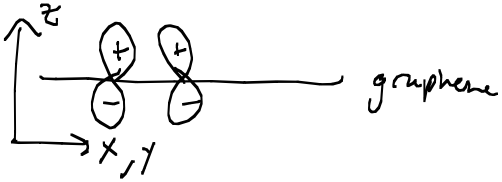


basis vectors

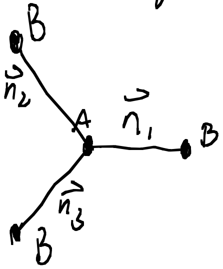
$$\vec{d}_1 = \vec{0}$$

$$\vec{d}_2 = \frac{a}{\sqrt{3}}\hat{x}$$

⇒ Each Group IV carbon atom hybridizes 2 p and one s orbital to form 3 sp^2 bonds in the x-y plane, leaving one p_z orbital out of plane. These two atoms per unit cell (A and B) form "π bond"



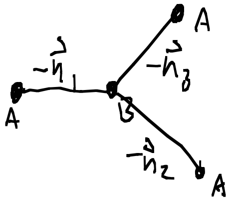
⇒ nearest neighbor vectors:



$$\vec{n}_1 = \vec{d}_2$$

$$\vec{n}_2 = \vec{d}_2 - \vec{a}_2$$

$$\vec{n}_3 = \vec{d}_2 - \vec{a}_1$$



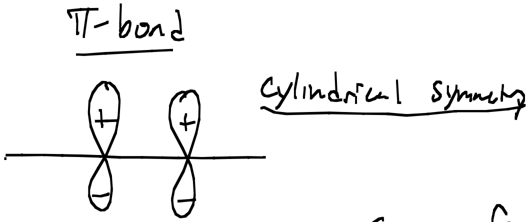
note vector signs reversed for B-lattice atoms!

Tight-binding wave function

$$\Psi = \sum_m \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\left[c_A e^{i\vec{k}\cdot\vec{d}_1}\phi_{pA}(\vec{r}-\vec{R}_m-\vec{d}_1) + c_B e^{i\vec{k}\cdot\vec{d}_2}\phi_{pB}(\vec{r}-\vec{R}_m-\vec{d}_2)\right]$$

Include only nearest neighbors in Schrodinger Eqn, project onto $\langle\phi_{pA}|$ and $\langle\phi_{pB}|$, use orthonormality

$$\langle\phi_{pA}|\times\left[\frac{\mathcal{H}}{\sqrt{N}}\left\{\begin{array}{l} e^{i\vec{k}\cdot\vec{n}_1}c_B|\phi_{pB}(\vec{r}-\vec{n}_1)\rangle \\ + e^{i\vec{k}\cdot\vec{n}_2}c_B|\phi_{pB}(\vec{r}-\vec{n}_2)\rangle \\ + e^{i\vec{k}\cdot\vec{n}_3}c_B|\phi_{pB}(\vec{r}-\vec{n}_3)\rangle \\ \\ + c_A|\phi_{pA}(\vec{r})\rangle \end{array}\right\} = E\Psi\right] = E\frac{c_A}{\sqrt{N}}\cancelto{1}{\langle\phi_{pA}|\phi_{pA}\rangle}$$



Define $\langle\phi_{pA}(r)|\mathcal{H}|\phi_{pA}(r)\rangle \equiv E_p$ and $\langle\phi_{pA}(r)|\mathcal{H}|\phi_{pB}(r-n)\rangle \equiv -V_{pp\pi}$ ← Same for all nearest neighbors

Matrix eigenvalue problem

$$E_p C_A - f(k) V_{pp\pi} C_B = E C_A \qquad \text{where} \qquad f(k) = e^{i\vec{k}\cdot\vec{n}_1} + e^{i\vec{k}\cdot\vec{n}_2} + e^{i\vec{k}\cdot n_3}$$

Project onto B-site p_z orbital $\langle \phi_{pB}(\vec{r})| \rightarrow$ reversal of nerest-neighbor vectors!

$$E_p C_B - f^*(k) V_{pp\pi} C_A = E C_B$$

These two Eqns equivalent to

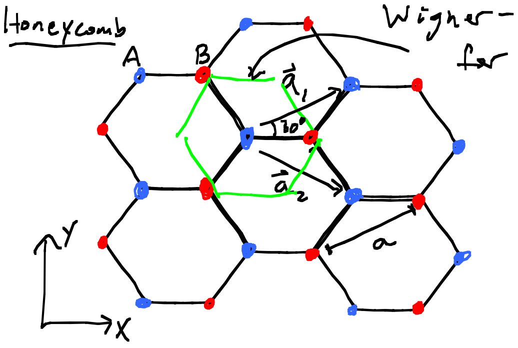
$$\begin{bmatrix} E_p & -V_{pp\pi} f(k) \\ -V_{pp\pi} f^*(k) & E_p \end{bmatrix} \begin{bmatrix} C_A \\ C_B \end{bmatrix} = E \begin{bmatrix} C_A \\ C_B \end{bmatrix}$$

Eigenvalues: $(E_p - E)^2 - V_{pp\pi}^2 |f(k)|^2 = 0 \Rightarrow E = E_p \pm V_{pp\pi} |f(k)|$

We just need to find the k's along the perimeter of the IBZs and then we can calculate bandstructure!

Reciprocal lattice

real-space lattice:



Wigner-Seitz unit cell for triangular lattice

lattice vectors

$$\vec{a}_1 = \frac{\sqrt{3}}{2} a \hat{x} + \frac{a}{2} \hat{y}$$

$$\vec{a}_2 = \frac{\sqrt{3}}{2} a \hat{x} - \frac{a}{2} \hat{y}$$

reciprocal lattice vectors $\vec{b}$ satisfy $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

$$\Rightarrow \quad a_1^x b_1^x + a_1^y b_1^y = 2\pi$$

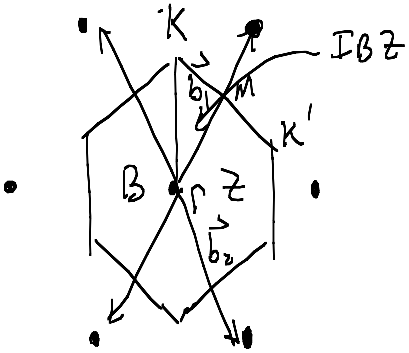
$$a_1^x b_2^x + a_1^y b_2^y = 0 \qquad \text{etc.}$$

$$\begin{bmatrix} a_1^x & a_1^y & 0 & 0 \\ 0 & 0 & a_2^x & a_2^y \\ 0 & 0 & a_1^x & a_1^y \\ a_2^x & a_2^y & 0 & 0 \end{bmatrix} \begin{bmatrix} b_1^x \\ b_1^y \\ b_2^x \\ b_2^y \end{bmatrix} = \begin{bmatrix} 2\pi \\ 2\pi \\ 0 \\ 0 \end{bmatrix}$$

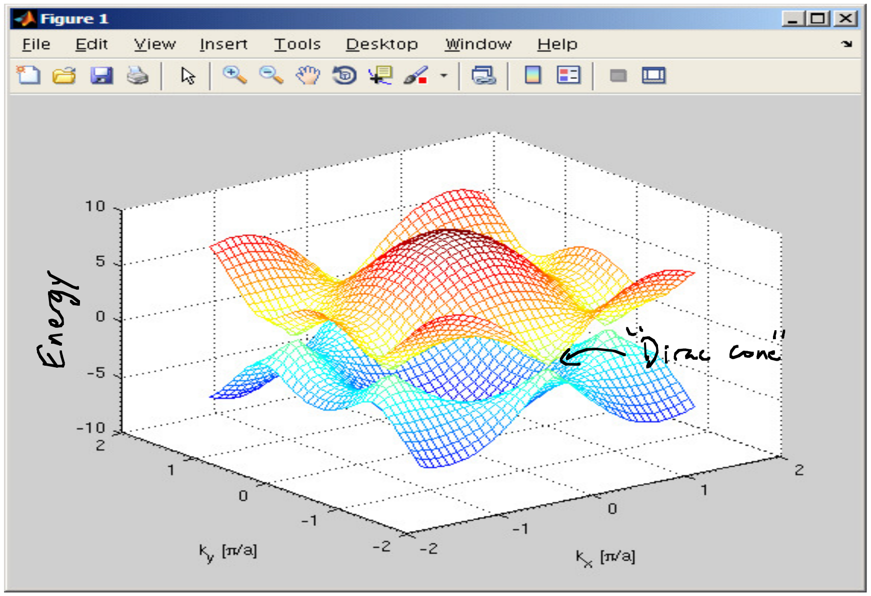
$$\vec{b}_1 = \left(\frac{1}{\sqrt{3}} \hat{x} + \hat{y} \right) \frac{2\pi}{a} = \left(\frac{1}{2} \hat{x} + \frac{\sqrt{3}}{2} \hat{y} \right) \frac{4\pi}{\sqrt{3} a}$$

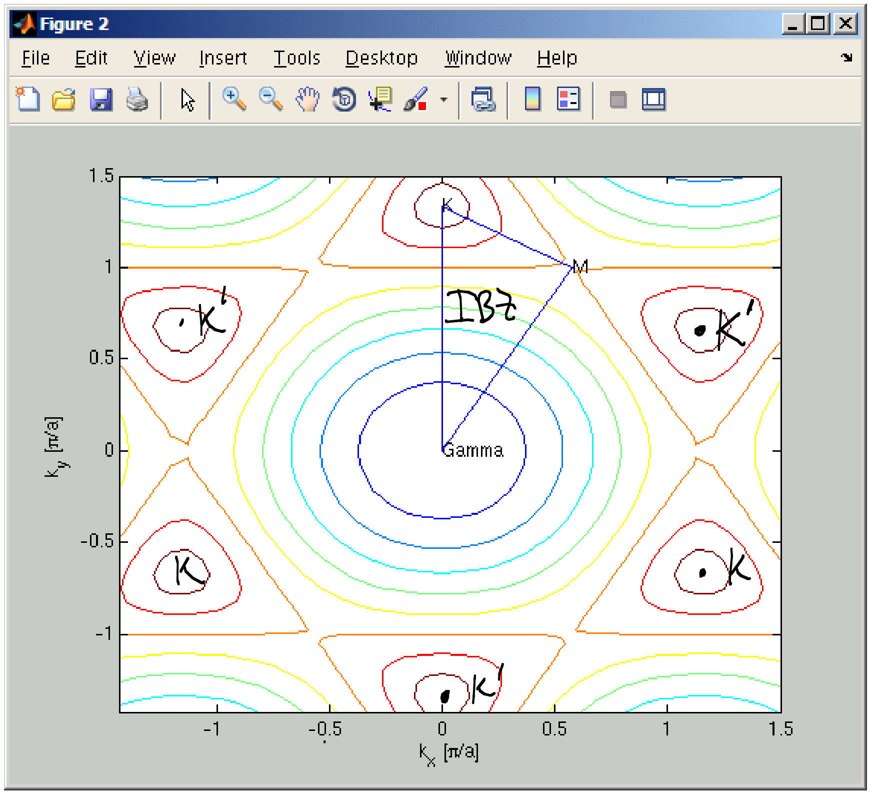
$$\vec{b}_2 = \left(\frac{1}{\sqrt{3}} \hat{x} - \hat{y} \right) \frac{2\pi}{a} = \left(\frac{1}{2} \hat{x} - \frac{\sqrt{3}}{2} \hat{y} \right) \frac{4\pi}{\sqrt{3} a}$$

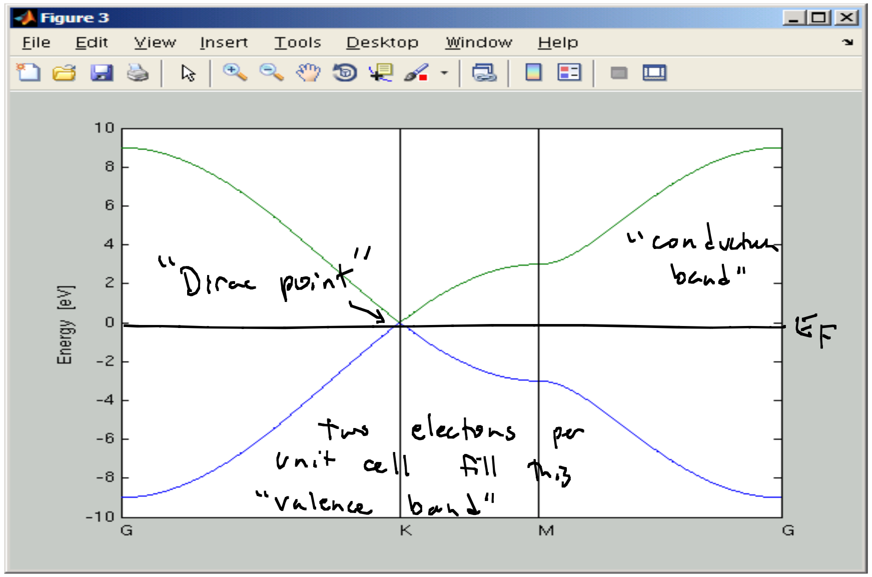
So the reciprocal lattice is rotated by 30° relative to the real-space lattice! ⟶



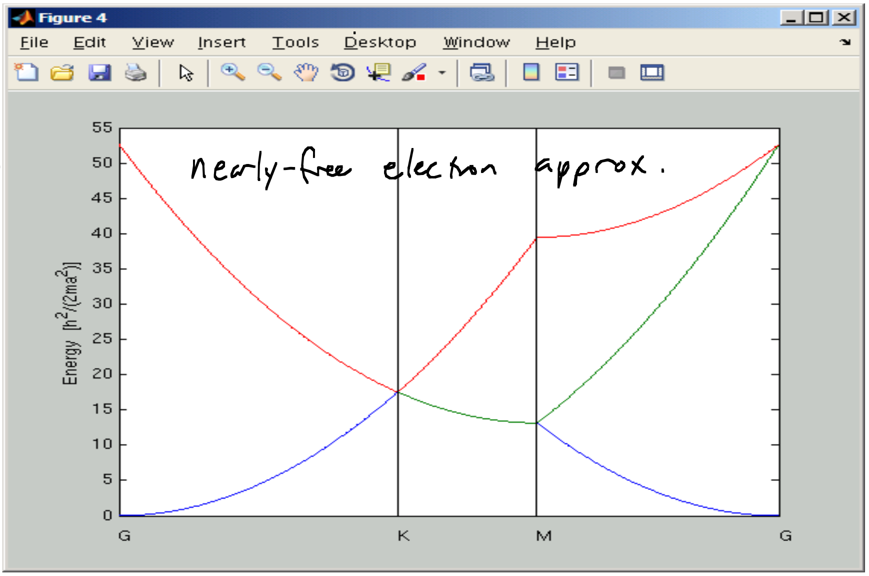
Numerical Results







So intrinsic graphene is a "zero-gap insulator" or "semi metal"!



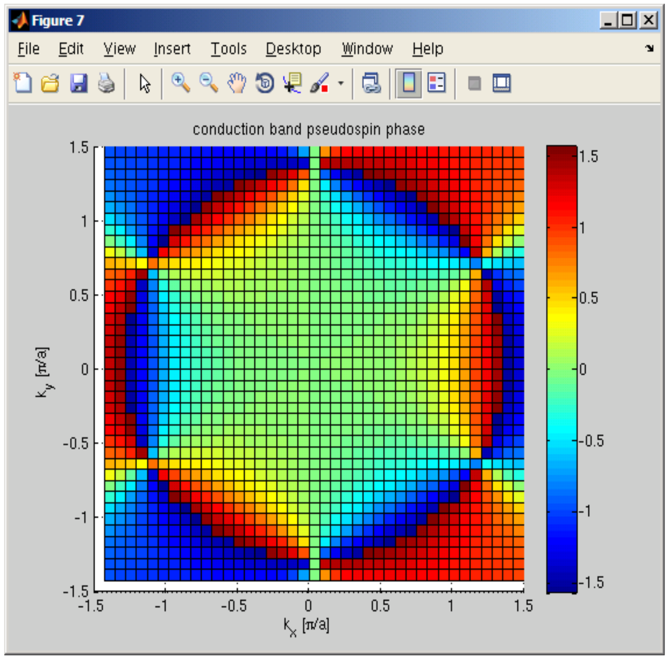
Wave functions

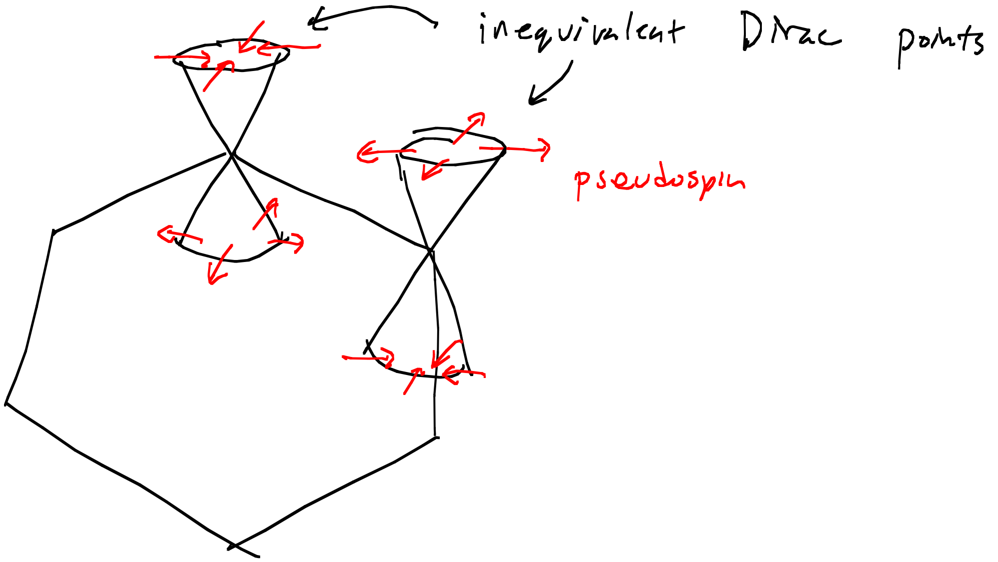
The two-component wavefunction eigenvectors have the form $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\ -f^*/|f|\end{bmatrix}$, $\frac{1}{2}\begin{bmatrix}1\\ \frac{f^*}{|f|}\end{bmatrix}$

If f^* real, these are $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\ -1\end{bmatrix}$ and $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\ 1\end{bmatrix}$. This is the same as eigenvectors of spin-$\frac{1}{2}$ pauli matrix $\sigma_x = \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$! ($|+x\rangle$ and $|-x\rangle$)

If f^* imaginary, they are $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\ -i\end{bmatrix}$ and $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\ i\end{bmatrix}$. These are eigenvectors of spin-$\frac{1}{2}$ pauli matrix $\sigma_y \begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}$! ($|+y\rangle$ and $|-y\rangle$)

For this reason, the p_z components from inequivalent lattice sites are said to constitute "pseudo spin":



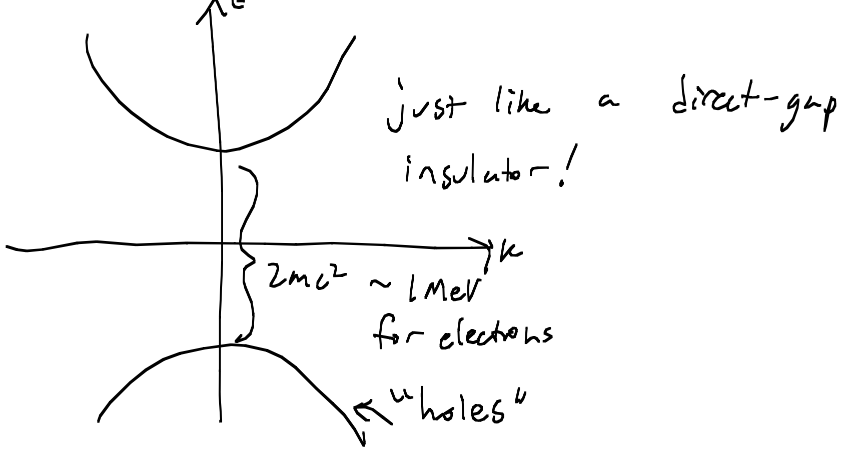


"Massless Dirac Fermions"

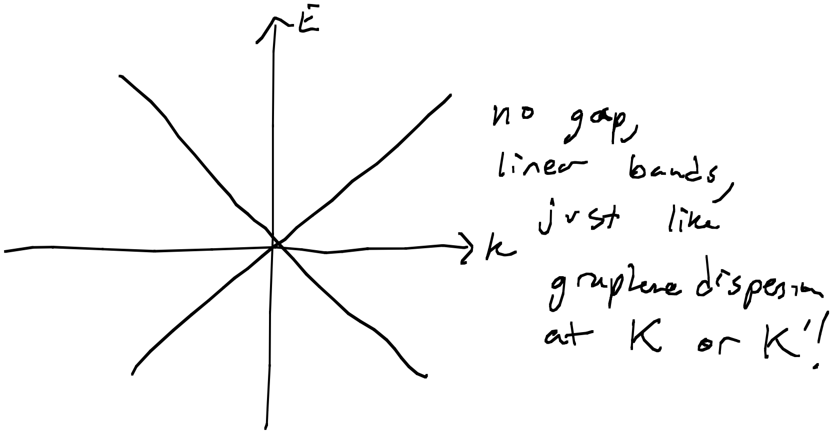
The total energy from solution of the relativistic Dirac Eqn is $E = \pm\sqrt{(mc^2)^2 + (pc)^2}$. For small momentum p, This can be expanded as $\pm mc^2\sqrt{1+\left(\frac{pc}{mc^2}\right)^2} \sim \pm mc^2\left(1 + \frac{p^2}{2m^2c^2} + \ldots\right) = \pm\left(mc^2 + \frac{p^2}{2m} + \ldots\right)$

This gives a dispersion

for $p=\hbar k$, $m \neq 0$ (like electrons):



for $m=0$ (like photons) $E = \pm pc$:



For photons, $V_g = \frac{1}{\hbar}\nabla_k E = c$. For electrons in graphene, lattice const $a \sim 2.5$Å so

$$V_g \sim \frac{1}{\hbar}\frac{10eV}{\pi/a} \sim \frac{10\,\cancel{eV}\cdot 2.5\times10^{-8}\,cm}{6.6\times10^{-16}\,\cancel{eV}\cdot s \quad \pi} \sim 10^8\ cm/s$$ (about $c/100$)

3D LCAO: Cubic Lattice

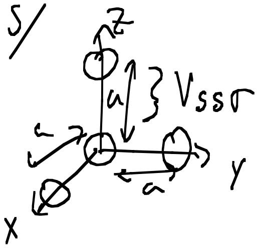
"Recipe":

1. Identify all orbitals in primitive unit cell (basis set)
2. Find all nearest neighbor vectors $\vec{n}_i$ for each orbital
3. Determine matrix elements (with appropriate phases) for each orbital combination

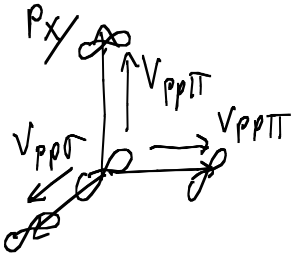
In the 3D cubic lattice w/ basis s, p_x, p_y, p_z we have the following:
$(\vec{n}_1 = a\hat{x}, \vec{n}_2 = a\hat{y}, \vec{n}_3 = a\hat{z})$

diagonal elements

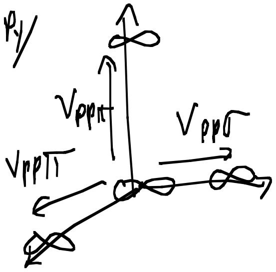
s/



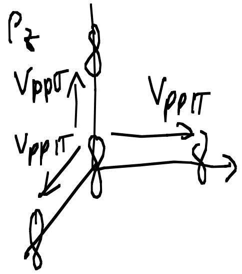
p_x/



p_y/

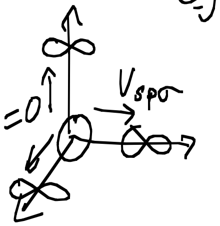


p_z

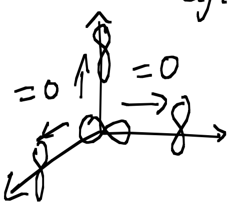


off-diagonal elements

e.g. $\langle s | H | p_y \rangle$



e.g. $\langle p_y | H | p_z \rangle$



Now incorporate phases $e^{i\vec{k}\cdot\vec{n}_i}$ in construction of Hamiltonian!

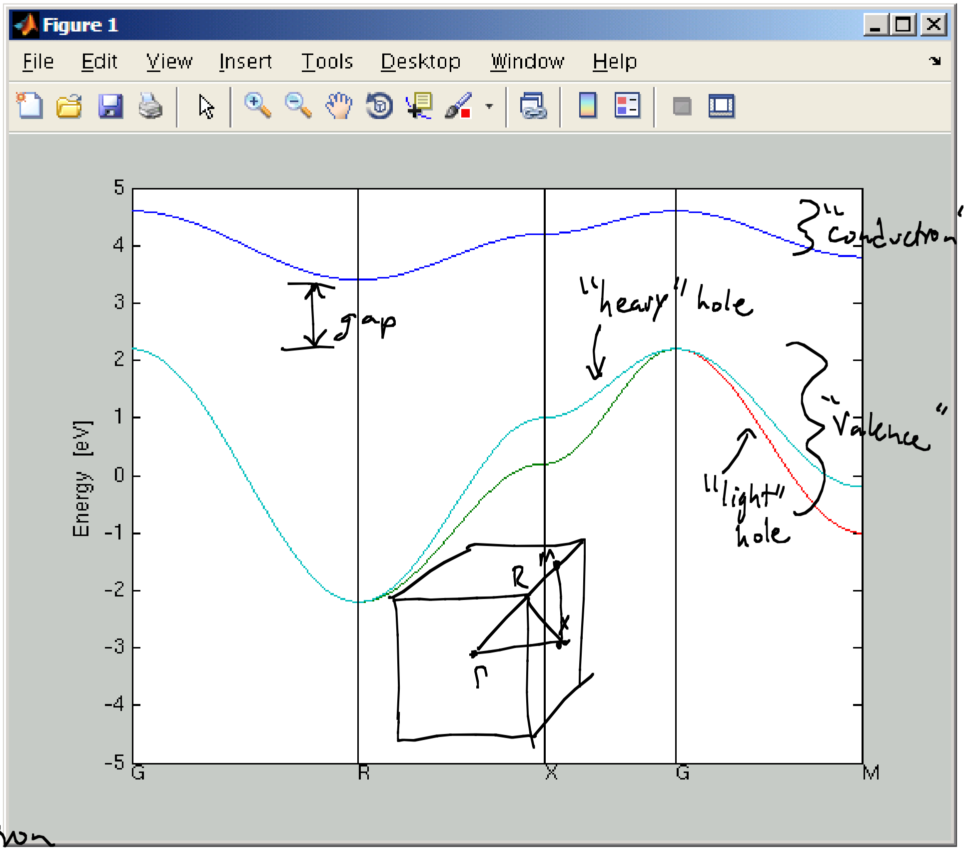
Hamiltonian Matrix

$$\begin{array}{c|cccc}
 & |s\rangle & |p_x\rangle & |p_y\rangle & |p_z\rangle \\
\hline
\langle s| & E_s + V_{ss\sigma}\big(e^{i\vec{k}\cdot a\hat{x}} + e^{-i\vec{k}\cdot a\hat{x}} + e^{i\vec{k}\cdot a\hat{y}} + e^{-i\vec{k}\cdot a\hat{y}} + e^{i\vec{k}\cdot a\hat{z}} + e^{-i\vec{k}\cdot a\hat{z}}\big) & V_{sp\sigma}\big(e^{i\vec{k}\cdot a\hat{x}} + e^{-i\vec{k}\cdot a\hat{x}}\big) & V_{sp\sigma}\big(e^{i\vec{k}\cdot a\hat{y}} + e^{-i\vec{k}\cdot a\hat{y}}\big) & V_{sp\sigma}\big(e^{i\vec{k}\cdot a\hat{z}} + e^{-i\vec{k}\cdot a\hat{z}}\big) \\
\langle p_x| & \dagger & E_p + V_{pp\sigma}\big(e^{i\vec{k}\cdot a\hat{x}} + e^{-i\vec{k}\cdot a\hat{x}}\big) + V_{pp\pi}\big(e^{i\vec{k}\cdot a\hat{y}} + e^{-i\vec{k}\cdot a\hat{y}} + e^{i\vec{k}\cdot a\hat{z}} + e^{-i\vec{k}\cdot a\hat{z}}\big) & 0 & 0 \\
\langle p_y| & & 0 & x \to y \quad y,z \Rightarrow x,z & 0 \\
\langle p_z| & & 0 & 0 & y \to z \quad x,z \to x,y
\end{array}$$

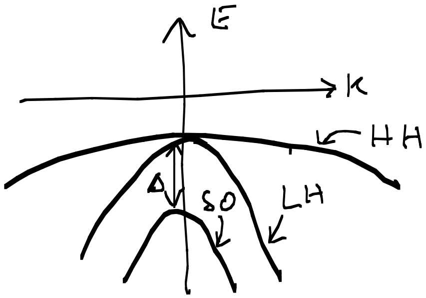
Using symmetry of the orbitals and lattice, we only needed to calculate 3 elements!

Cubic band structure

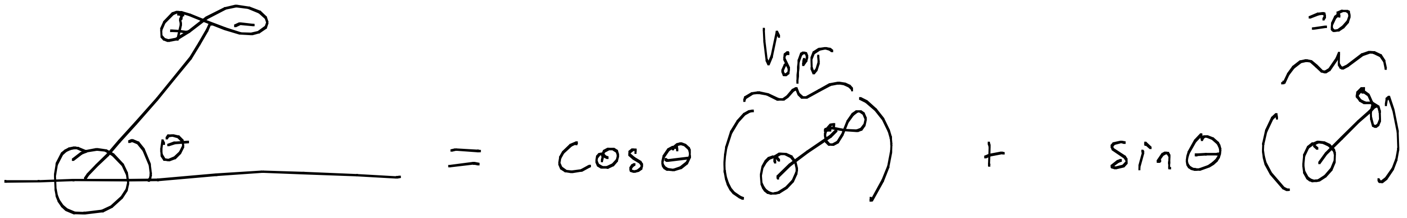
The valence band is 3x degenerate @ Γ point, but these split into two bands for $k \neq 0$: light and heavy holes, resulting from the different kind of orbital overlap in different directions for nonisotropic p orbitals.

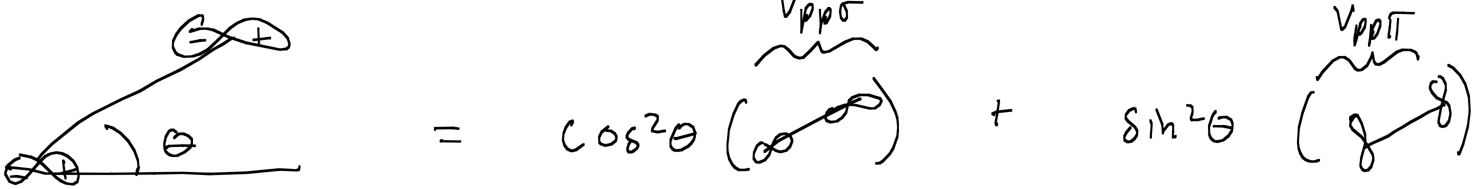


Note that the p-like valence band arises from atomic states w/ nonzero angular momentum $l=1$. When spin-orbit interaction is included, the $j = l + \frac{1}{2} = 3/2$ states $(m_J = \pm 3/2, \pm\frac{1}{2})$ have different energy than the $j = l - \frac{1}{2} = \frac{1}{2}$ states $(m_J = \pm 1/2)$. This is the reason for the split-off valence band!

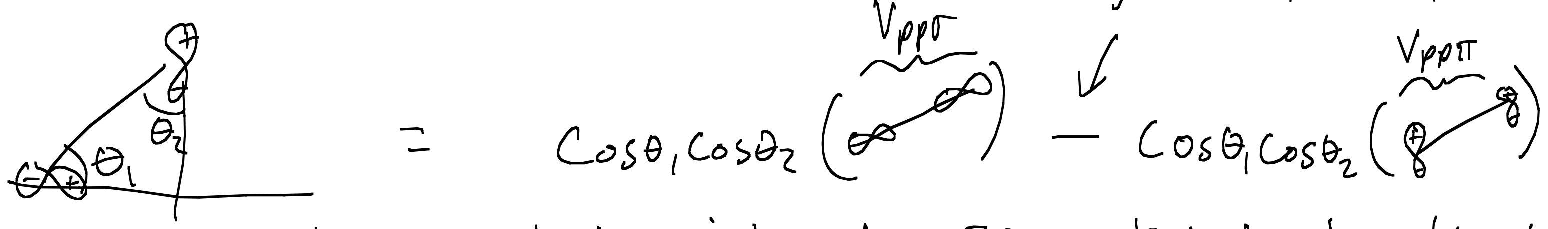


LCAO for non-Cartesian lattices (Slater + Koster, Phys Rev 94, 1498 (1954))

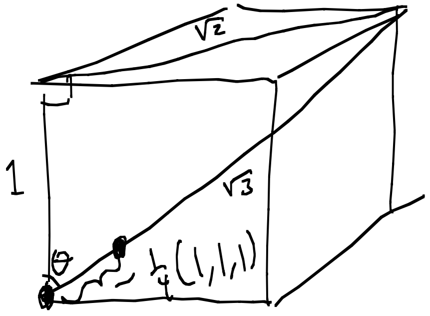




negative due to overlap of ⊕ and ⊖ lobes



For diamond/zincblende: 2 interpenetrating FCC, displaced by 1/4 distance along main diagonal



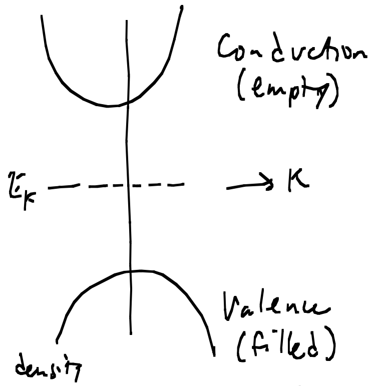
$\cos\theta = \frac{1}{\sqrt{3}}$, $\sin = \frac{\sqrt{2}}{\sqrt{3}}$ so often one defines:

$V_{sp} = \frac{1}{\sqrt{3}} V_{sp\sigma}$, $V_{xx} = \frac{1}{3} V_{pp\sigma} + \frac{2}{3} V_{pp\pi}$ (identical p orbitals)

$V_{xy} = \frac{1}{3}\left(V_{pp\sigma} - V_{pp\pi}\right)$ (p orbitals w/ different axes)

Carriers in Semiconductors

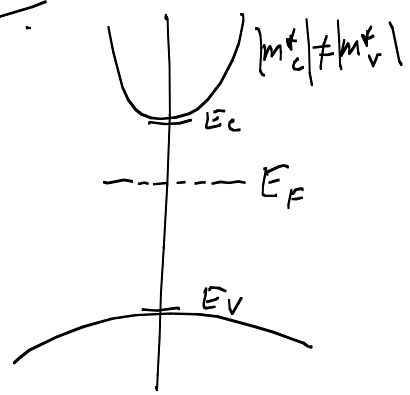
T=0



electron density
hole density

$$\sigma = \overset{\text{electron density}}{n_0} e \mu_e + \overset{\text{hole density}}{p_0} e \mu_p = 0 \quad (\text{insulator!})$$

T≠0



what is $n_0(T)$, $p_0(T)$?
(in Thermal equilibrium)

Then we can determine $\sigma(T)$

electrons in conduction band $n_0 = \int_0^\infty \overset{\text{FD}}{f(E)}\, \overset{\text{DOS}}{g(E)}\, dE$ (not constant like in metal!)

If E_F in gap, $(E-E_F)/k_BT >> 1$ and $f(E) = \frac{1}{e^{\frac{E-E_F}{k_BT}}+1} \sim e^{-\left(\frac{E-E_F}{k_BT}\right)}$ (Boltzmann)

Then,
$$n_0 = \int_0^\infty e^{-(E-E_F)/k_BT} \left(\frac{1}{2\pi^2}\right)\left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}\, dE = e^{E_F/k_BT}\left(\frac{1}{2\pi^2}\right)\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_0^\infty e^{-E/k_BT} E^{1/2}\, dE$$

transform $x = E/k_BT$, $dE = k_BT\, dx$

$$= e^{E_F/k_BT}\left(\frac{1}{2\pi^2}\right)\left(\frac{2m^*}{\hbar^2}\right)^{3/2} (k_BT)^{3/2} \overbrace{\int_0^\infty x^{1/2} e^{-x}\, dx}^{\sqrt{\pi}/2} = \overset{\text{"effective conduction band DOS"}}{N_c}\, e^{(E_F-E_c)/k_BT} \quad \left(E_F \text{ relative to } E_c\right)$$

Similarly, we can derive hole density $p_0 = N_v\, e^{(E_v-E_F)/k_BT}$ ← "effective valence band DOS"

Law of Mass Action

For "intrinsic" insulator/semiconductor, $n_0 = p_0$

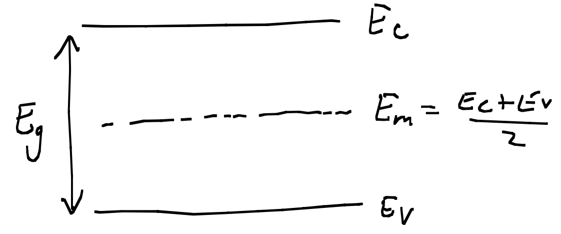
$$N_c e^{(E_F - E_c)/k_BT} = N_v e^{(E_v - E_F)/k_BT}$$

$$e^{(2E_F - (E_c + E_v))/k_BT} = \frac{N_v}{N_c} \Rightarrow e^{2(E_F - E_m)/k_BT} = \frac{N_v}{N_c}$$

$$E_F - E_m = \frac{k_BT}{2} \ln \frac{N_v}{N_c}$$

So as T rises, E_F moves toward band w/ lower m^*!

Note: we have reduced our system of a gapped parabolic dispersion to a simple 2-level spectrum!



Note that $n_0 p_0$ is independent of E_F:

$$n_0 p_0 = N_c N_v e^{-(E_c - E_v)/k_BT} = N_c N_v e^{-E_g/k_BT} = n_i^2$$ "intrinsic carrier concentration"

$$n_0 p_0 = n_i^2$$ "Law of Mass Action"

Example

In Si, $N_c = 3 \times 10^{19}\,\text{cm}^{-3}$ $N_v = 2 \times 10^{19}\,\text{cm}^{-3}$, $E_g \sim 1.1\,\text{eV}$ $(300\,\text{K} \rightarrow k_BT = 1/40\,\text{eV})$

$$n_i = \sqrt{N_c N_v}\, e^{-E_g/2k_BT} \sim 10^{19}\,\text{cm}^{-3} \cdot e^{-20} \sim 10^{10}\,\text{cm}^{-3}$$

$$\sigma = n_0 e \mu \sim 10^{10}\,\text{cm}^{-3} \cdot 10^{-19}\,\text{C} \cdot 10^{3}\,\frac{\text{cm}^2}{\text{V s}} = 10^{-6}\,\text{S cm}^{-1}$$ and even smaller as T decreases!

Controlling E_F: From intrinsic to extrinsic

How to gain more of one carrier in one band at the expense of opposite carriers in other band.

electrons: "donor" impurity doping → "n-type"

Substitute atoms w/ more valence electrons: group V in place of group IV (Si, Ge, C)
(P, As, Sb)

for compound III-V, group IV in place of group III atom

holes: "acceptor" impurity doping → "p-type"

Substitute atoms w/ less valence electrons: group III in place of group IV (Si, Ge, C)

for compound III-V, group IV in place of group V atom

Example: $n = \overset{\swarrow\,\text{donor concentration}}{N_D} = N_c e^{(E_F - E_c)/k_B T} \longrightarrow E_F - E_c = k_B T \ln \frac{N_D}{N_c}$

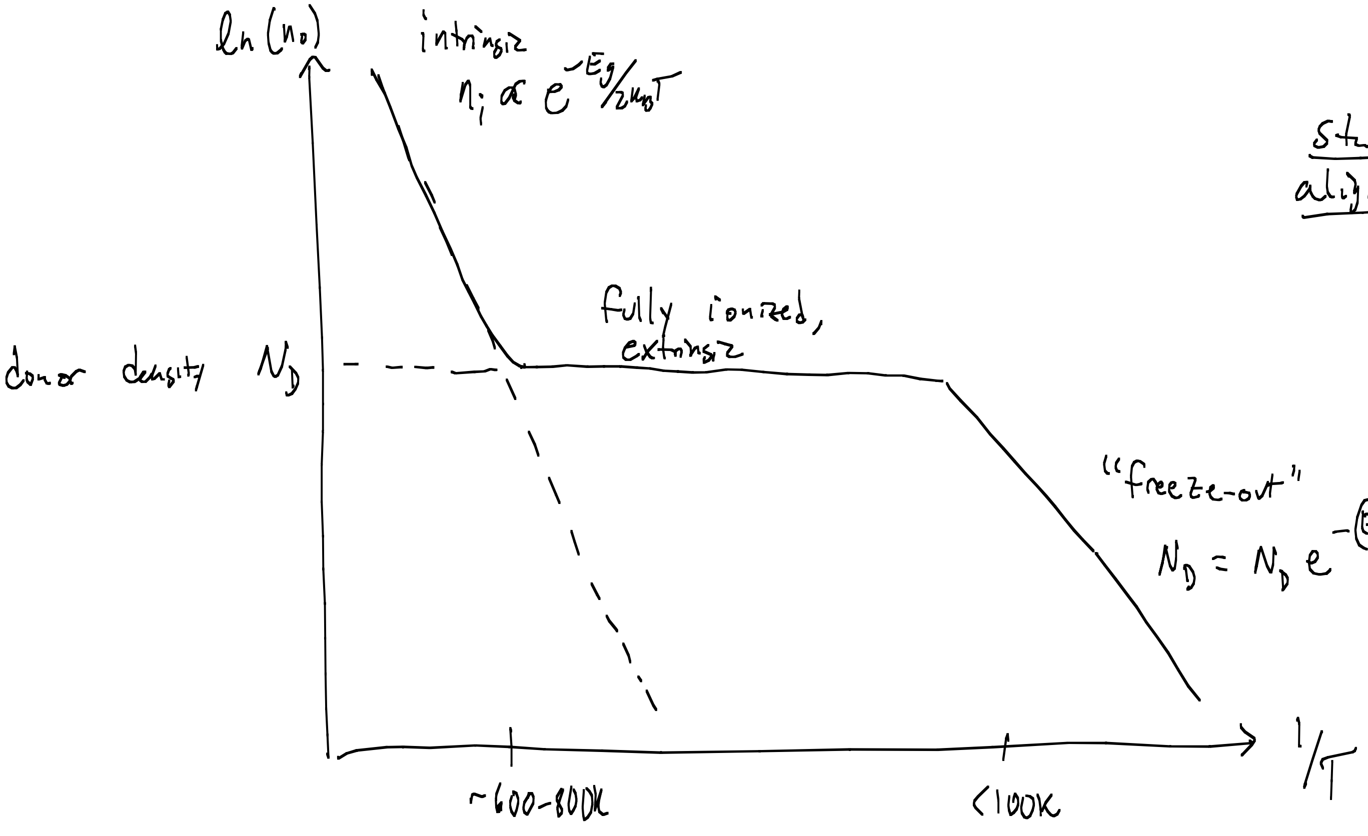
For $N_D = 10^{15}\ \text{cm}^{-3}$ and $N_c \sim 10^{19}$, $E_F - E_c \sim -0.26\ \text{eV}$ much closer to E_c for $E_g = 1.1\ \text{eV}$ (Si)! (This concentration gives resistivity $\rho = \frac{1}{\sigma} = \frac{1}{ne\mu} \sim 10\,\Omega\,\text{cm}$)

Impurity state

Donors leave behind positively charged immobile ion → hydrogenic spectrum

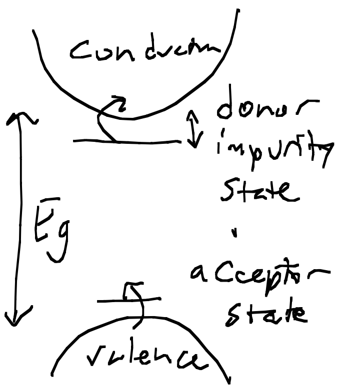
Bohr atom: $E = -\frac{1}{2}\alpha^2 mc^2 = -\frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2 mc^2 = -13.6\,\text{eV}$

Semiconductor: $E = -\frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2 mc^2\left(\frac{m^*}{m}\frac{1}{\epsilon_{rel}^2}\right) \xrightarrow{Si} -13.6\,\text{eV}\cdot\left(\frac{0.3}{12^2}\right) \sim -30\,\text{meV}$ (In gap, close to band and easily ionized @ RT)



$$N_D = N_D e^{-(E_F-\Delta)/k_BT} + N_c e^{-E_F/k_BT}$$

State alignment:



Metal - Insulator Transition

Can we dope to arbitrary concentration and still expect to see insulating behavior ("freezout") at low enough temperatures? NO!

At high enough carrier concentration, screening will diminish the attractive impurity potential to the point that no bound state is supported!

A crude approximation of this density is provided by the 3D spherical finite well of depth V_0 and radius a_0, where $V_0 a_0^2 > \frac{\hbar^2 \pi^2}{8m}$ must be satisfied to support a bound state.

Thomas-Fermi screening length gives $a_0^2 = \frac{\epsilon}{e^2 g(\epsilon_F)} = \frac{2\epsilon \epsilon_F}{3e^2 n} = \frac{2\epsilon \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}}{3e^2 n}$

So we must have

$$V_0 \frac{\cancel{2}\epsilon \frac{\cancel{\hbar^2}}{\cancel{2m}}(3\pi^2 n)^{2/3}}{3e^2 n} > \frac{\cancel{\hbar^2}\pi^2}{8\cancel{m}} \longrightarrow n^{1/3} < \frac{8V_0 \epsilon}{e^2(3\pi^2)^{1/3}} = \frac{8}{(3\pi^2)^{1/3}} \frac{V_0 \epsilon_{rel}}{\alpha \hbar c} \sim \frac{10^{-2}\,\text{eV} \cdot 10}{10^{-2} \quad 10^{-5}\,\text{eVcm}} = 10^6\,\text{cm}^{-1}$$

So for $N_d \gtrsim 10^{18}\,\text{cm}^{-3}$, we no longer expect insulating behavior → M.I.T.

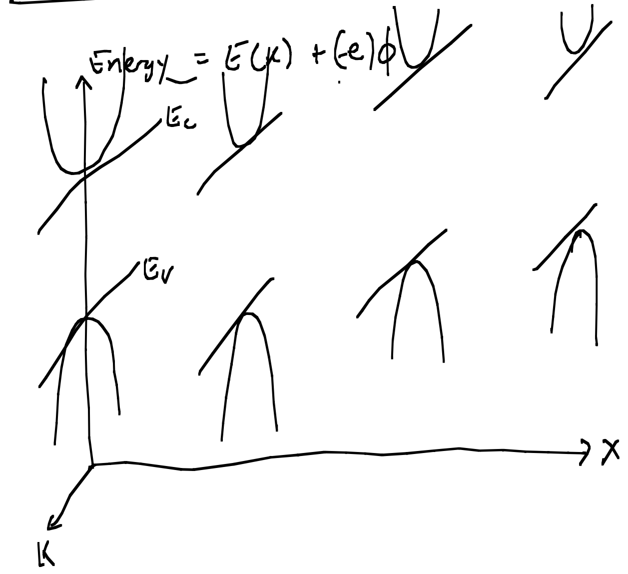
Band diagrams

Ability to dope semiconductors as a function of position allows for fabrication of useful devices! How to understand this spatial dependence + how it affects transport of charge?

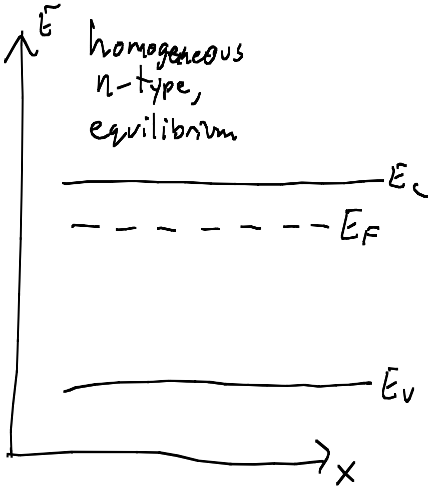
Kroemer's "Lemma of Proven ignorance":

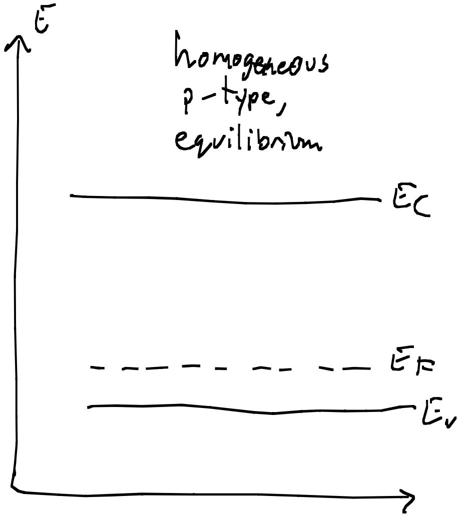
"If you can't draw Energy-band diagram, you don't know what you're talking about" – H. Kroemer RMP 73, 783 (2001) (Nobel Prize, 2000)

Band diagram: band extrema [from $E(k)$ and potential energy $(-e)\phi$] v.s. position



$\Longrightarrow$



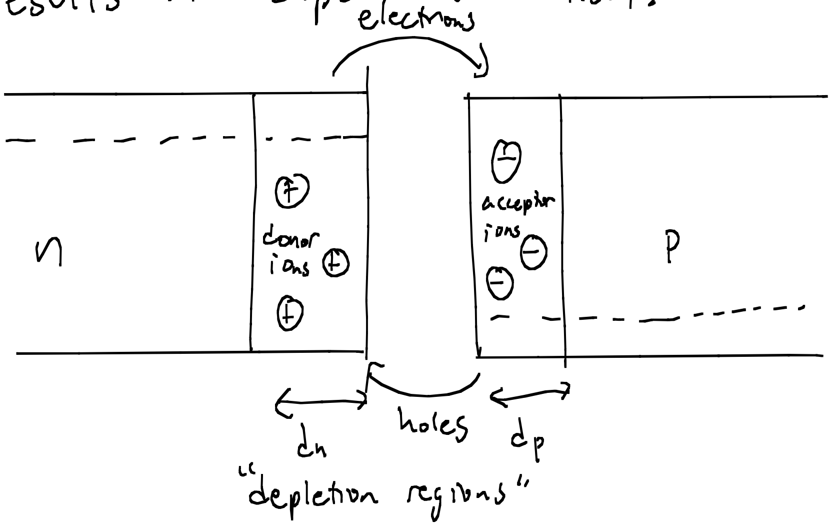


equilibrium ≡ Fermi level is constant

What happens at an interface between semiconductors of different doping?

p-n junction in equilibrium

Charge transfer to equalize chemical potential results in dipole formation:



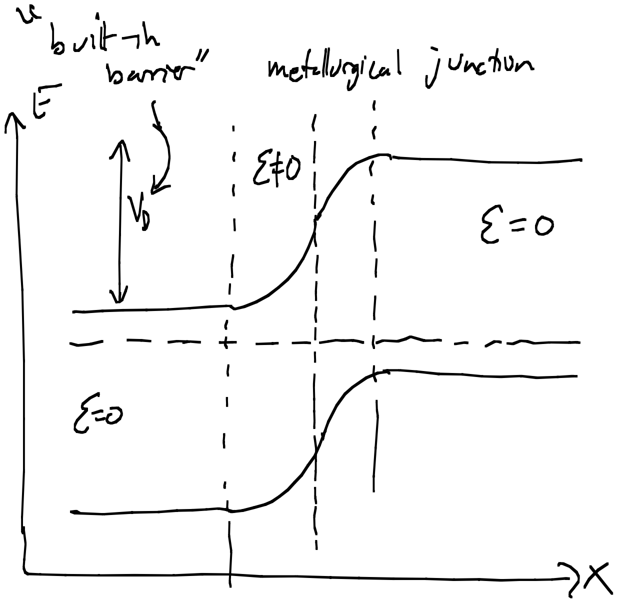
Poisson's eq.

$$-\nabla^2\phi = \frac{\rho}{\epsilon}$$

$$\Longrightarrow$$

constant space-charge density

$\Rightarrow$ quadratic $\phi(x)$



- Total charge neutrality $N_D d_n = N_A d_p$ gives depletion region depths inversely prop. to doping density: eg. $d_n = \left(\frac{2\epsilon V_D}{e}\frac{N_A/N_D}{N_A+N_D}\right)^{1/2}$
- Internal electric field results from spatially distributed dipole.
- Equilibrium maintained by equalizing drift and diffusion currents

What happens out of equilibrium (voltage bias)?

Drift - Diffusion Eq

particle current $J = \overset{\text{drift}}{\underbrace{nv}} - \overset{\text{diffusion}}{\underbrace{D\nabla n}}$

continuity equation $\frac{dn}{dt} = -\nabla \cdot J - \frac{n}{\tau}$ "minority carrier lifetime"

The $-\frac{n}{\tau}$ term is due to "recombination": annihilation of electron by hole via transition across gap. In direct bandgap, energy conservation can result in emission of photon w/ $\hbar\omega \sim E_g$.

Combining two above gives:

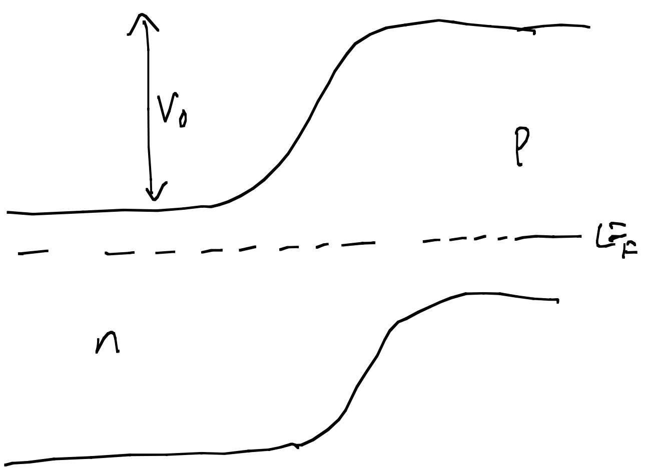
$\frac{dn}{dt} = D\nabla^2 n - v\cdot\nabla n - \frac{n}{\tau}$ "drift-diffusion equation" → governs spatio-temporal evolution of excess carriers!

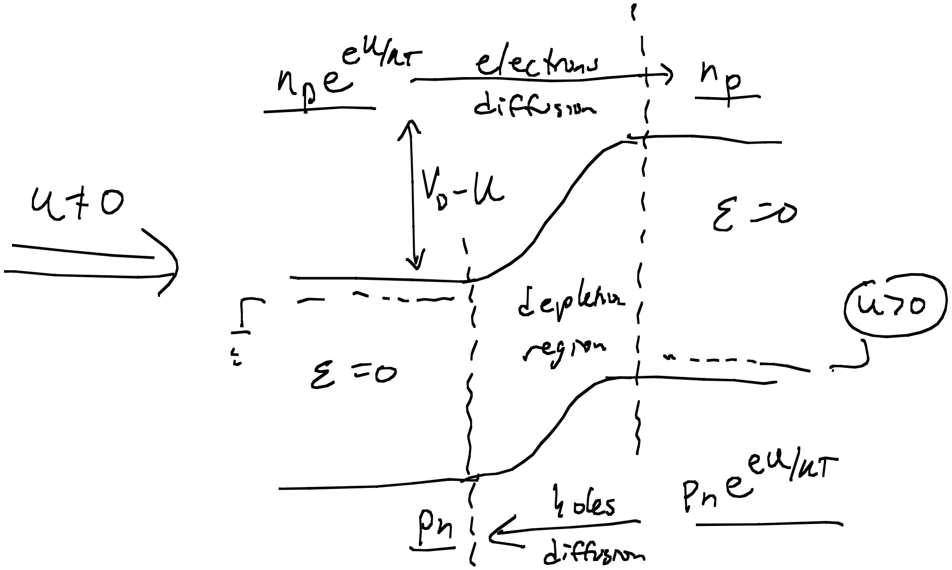
In steady-state, $\frac{dn}{dt} = 0$. For $v=0$, we have (in 1-D)

$$\frac{d^2n}{dx^2} = \frac{n}{D\tau} \Rightarrow n(x) = C_+ e^{+\frac{x}{L}} + C_- e^{-\frac{x}{L}}, \quad L = \sqrt{D\tau}$$ "diffusion length"

The coefs $C_{+/-}$ determined by B.C.'s. What are the B.C.'s for p-n under bias?

p-n junction under "forward" bias





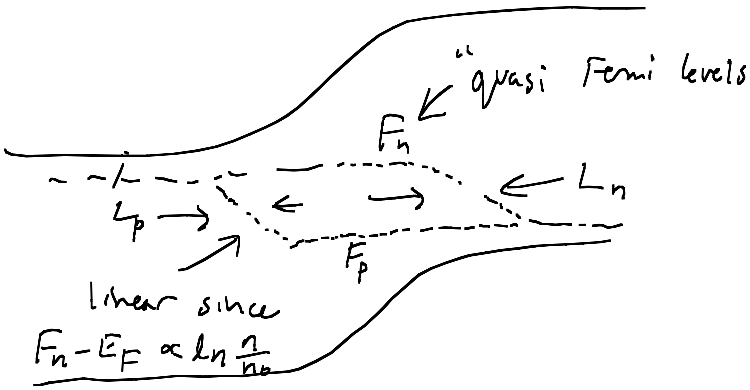
Lowering barrier by amount eU allows high concentration of carriers closer to E_F to be capable of diffusion across depletion region.

Determines B.C. since excess electrons $\Delta n = n_p e^{eU/kT} - n_p$ @ start of p depletion.

Our solution is then

$$n(x) = n_p\left(e^{eU/kT} - 1\right) e^{-x/L}$$ "minority carrier injection"

(Similarly for holes moving in opposite direction)



Ideal diode equation

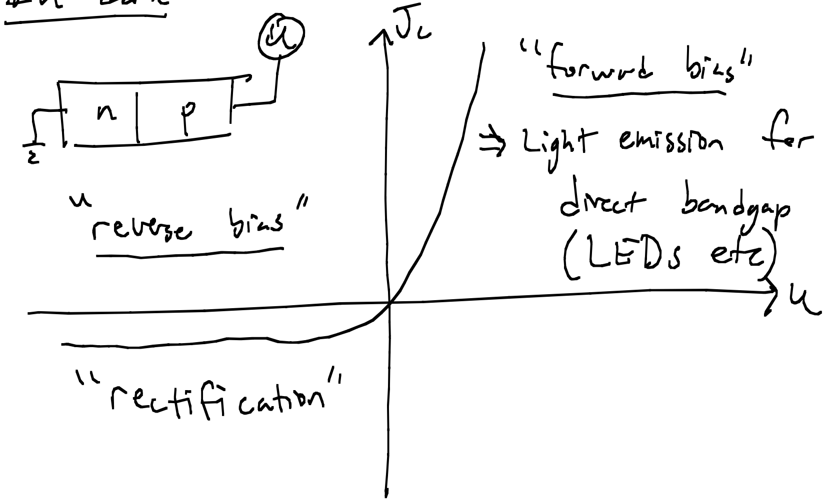
Diffusion current from n → p is $J_D = -D\frac{dn}{dx} = \frac{D}{L} n_p \left(e^{eV/kT}-1\right)$

Same analysis for holes gives total charge current

$$J_c = e\left(\frac{D_n}{L_n} n_p + \frac{D_p}{L_p} p_n\right)\left(e^{eV/kT}-1\right)$$

"ideal diode equation"

In dark



lower barrier: "forward bias":

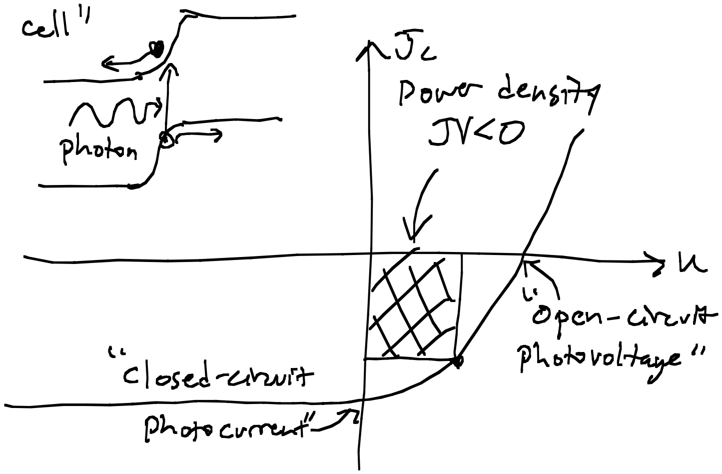
exponential, dominated by diffusion current

higher barrier: "reverse bias"

saturated, dominated by drift current and limited by thermal generation

under illumination (w/ photons $\hbar\omega > E_g$)

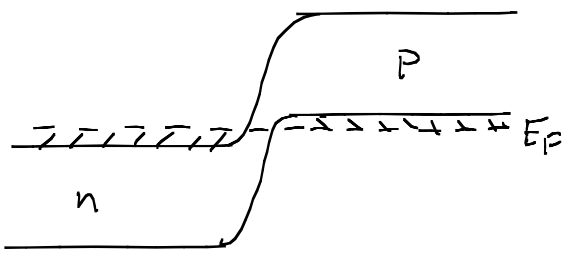
"Solar cell"

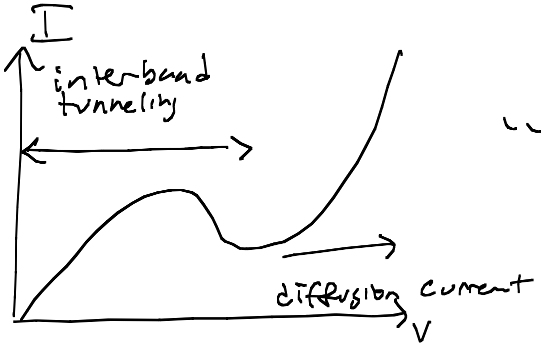


Power generation, not dissipation!

Quick tour of semiconductor devices based on p-n junction

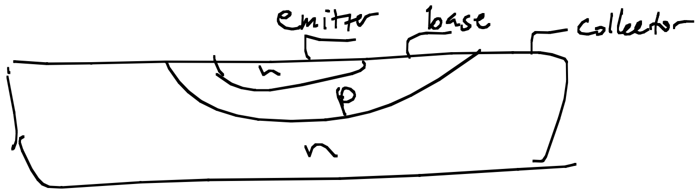
- Esaki diode: (Nobel prize, 1973)



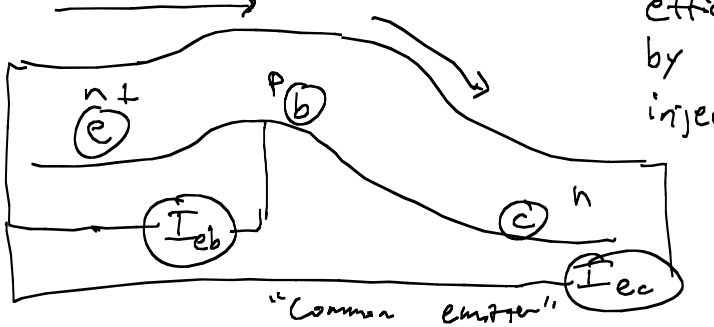


"Negative differential resistance"

- Bipolar junction transistor (Nobel prize, 1956)



minority carrier injection

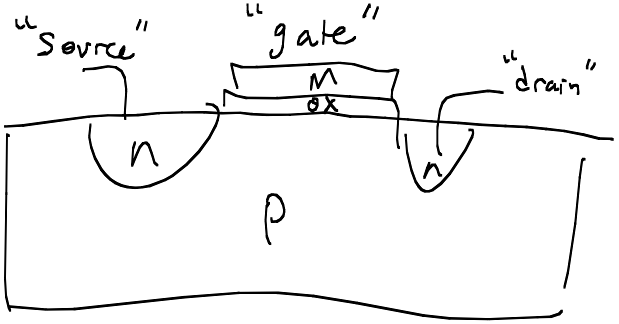


"Common emitter"

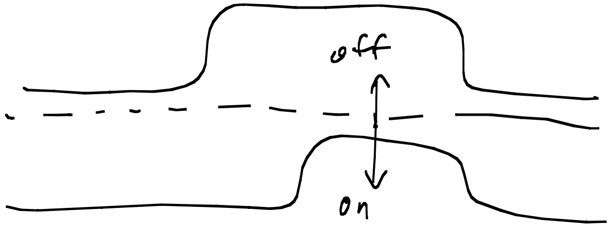
Current amplification

efficiency limited by base recombination, injection from base into emitter, base-collector leakage, etc.

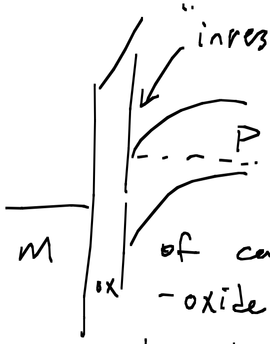
- MOSFET (Nobel prize (for CCD), 2009)



back-to-back p-n junctions! rectifying both ways!



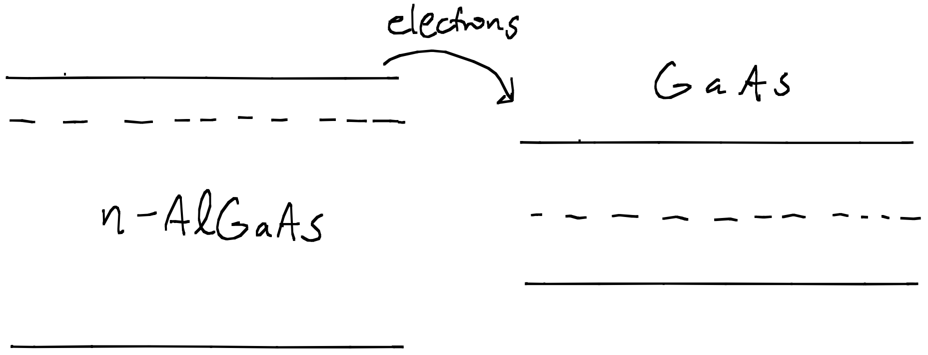
Control barrier w/ gate



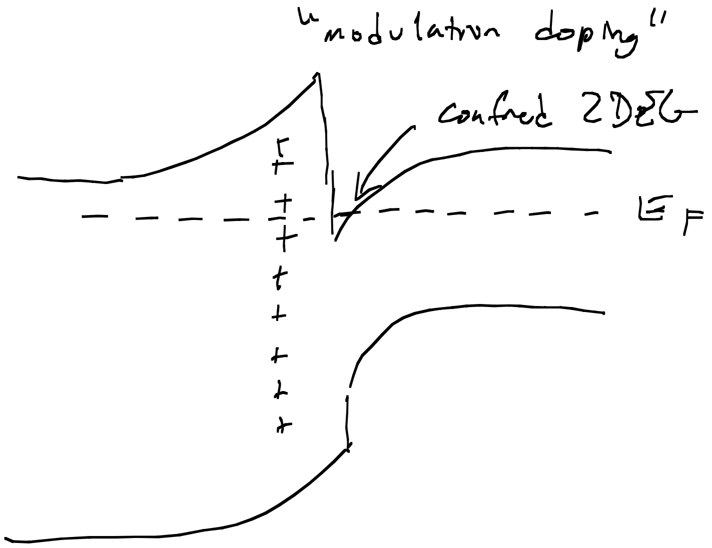
electrostatic control of carriers at semiconductor-oxide interface: used to discover IQHE!

Heterostructures

2DEG band diagram:



$\Rightarrow$



Confinement energy can be substantially larger than k_BT, allowing population solely of ground-state "sub-band".

By providing carriers to the well without putting ionized impurities there, one can obtain 2DEG mobilities $\mu > 50 \times 10^6 \frac{cm^2}{Vs}$!

$\Rightarrow$ used to discover FQHE, and to observe QPC, etc via electrostatic top-gate depletion