

(EE)
Elementary excitations in Fermi-Liquid

EEs are created wrt the ground state of a system. Consider non-interacting electrons in a box $L_x L_y L_z$

In this model we have a quasiparticle with $q/2g = -e$ $s = m_0 m$ p and $E = p^2/2m_0$

$\psi^0 = A e^{i\mathbf{k}\cdot\mathbf{r}}$ where $\mathbf{k} = \mathbf{p}/\hbar$

To avoid the presence of surface $= \psi^0 \psi^0(\mathbf{r} + \mathbf{L}) \Rightarrow e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot(\mathbf{r} + \mathbf{L})} = 1$

$\Rightarrow \mathbf{k} = \frac{2\pi\mathbf{h}}{L}$ $k_x, k_y, k_z = 0, \pm 1, \pm 2, \pm \dots$

So limiting the motion results in discrete \mathbf{k} and hence \mathbf{p} . But the values are almost continuous since $2\pi\hbar/L$ is very small and $\sim \Delta p$ as follows from $\Delta p \Delta x \sim \hbar$

- in \mathbf{k} -space the # of allowed states $\frac{(2\pi)^3}{L^3} = \frac{(2\pi)^3}{V}$ in momentum space $\frac{(2\pi\hbar)^3}{V}$

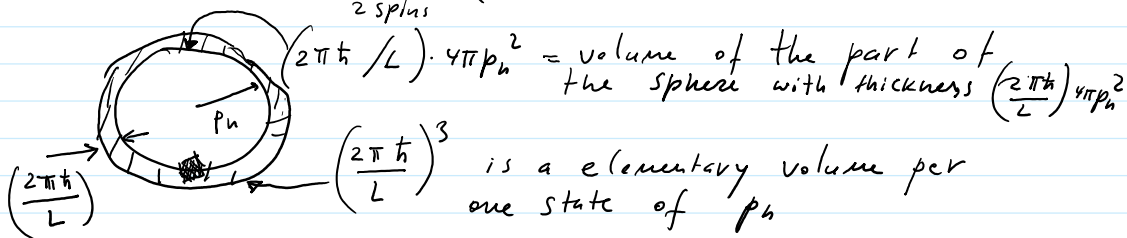
- The dispersion relation: We have 2 electrons per state in \mathbf{k} -space: $E = p^2/2m_0$


$p^2 = \frac{(2\pi\hbar)^2}{L_x^2} h_x^2 + \dots$ and assume all L_s and are the same L_s

$E(h_x, h_y, h_z) = \frac{\hbar^2}{2m_0} \left(\frac{2\pi^2}{L}\right) (h_x^2 + h_y^2 + h_z^2)$
 $= \frac{(2\pi\hbar)^2}{2m_0} \frac{h^2}{3/2 V} = \frac{(2\pi\hbar)^2}{2m_0} \frac{h^2}{3/2 V}$ so in the state

$E_n = \frac{p_n^2}{2m_0}$ Can be only

$N_{E_n} \sim 2 \frac{(2\pi\hbar/L)^3 4\pi p_n^2}{(2\pi\hbar/L)^3} = \frac{16\pi m_0 E_n V}{(2\pi\hbar)^2}$
↑
2 spins



$\left(\frac{2\pi\hbar}{L}\right)$  $\left(\frac{2\pi\hbar}{L}\right)$ is an elementary volume per one state of $p\hbar$

- Energy and Fermi surface

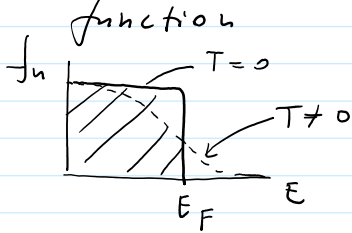
if in crystal we have NZ electrons total then at $T=0$ K they fill in a sphere of \vec{p} up to p_F

$$V \cdot \frac{4/3 \pi p_F^3}{(2\pi\hbar)^3} = NZ \Rightarrow p_F = 2\pi\hbar \left(\frac{3NZ}{8\pi V} \right)^{1/3} = \hbar (3\pi^2 n)^{1/3}$$

$$p_F = \hbar (3\pi^2)^{1/3} \cdot n^{1/3}$$

$$n = \frac{Z \cdot N}{V}$$

- The distribution of electrons is governed by Fermi-Dirac function



$$E_F = \frac{p_F^2}{2m} = \left(\frac{\hbar^2}{2m_0} \right) \left(\frac{3\pi^2 NZ}{V} \right)^{2/3} = \left(\frac{\hbar^2}{2m_0} \right) (3\pi^2 n)^{2/3}$$

$$E_F \sim n^{2/3}$$

$$\text{or } E_F = \hbar \left[\frac{2m_0 E_F(0)}{3\pi^2 \hbar^3} \right]^{3/2}$$

- In this model no $e-e$ interaction

However in a solid we have Coulomb interaction $\sim \frac{e^2}{r}$ and $r \sim \frac{1}{n^{1/3}}$ we have $\sim e^2 \cdot n^{1/3}$ which

is close to $\frac{p_F^2}{2m_0} \sim n^{2/3}$. So what is the effect of interaction in?

- 3 facts:
- metals exist
 - they conduct electricity
 - no electron localization crisis found (except for 2DEG GaAs/GaAs(Al))

So Landau assumed it's liquid. (FL)

* Strong interaction in a FL means that addition of or removal of a particle changes the state of ALL other electrons of the system.

The liquid changes its state when we add electrons so the electrons in it are not free and called quasiparticles. without definitive E and p .

So the electrons in it are not free and called quasiparticles. without definitive E and p .

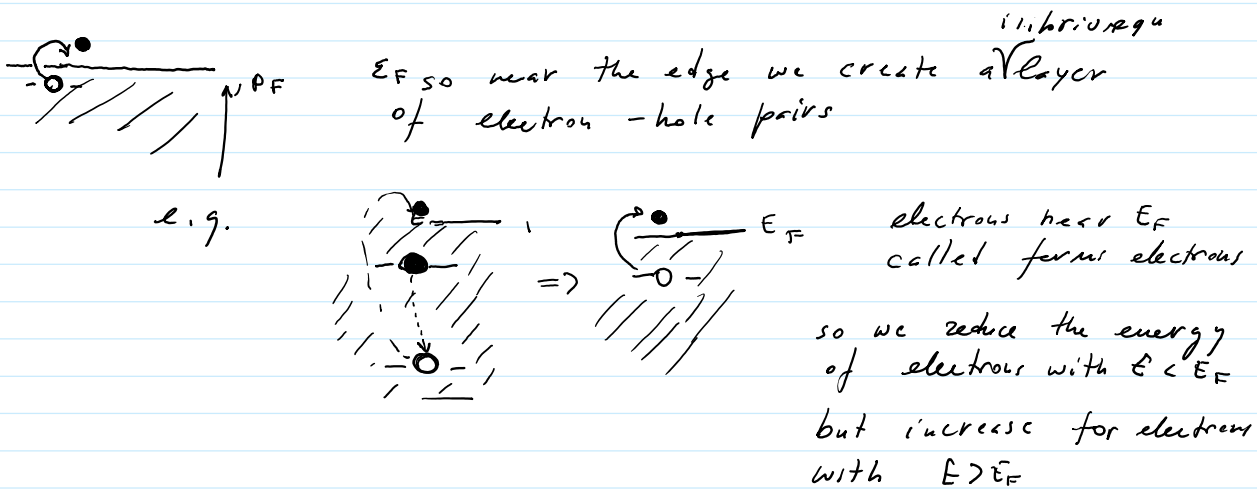
Landau theory.

1. Landau assumed if we turn on interaction between electrons the electronic states don't change

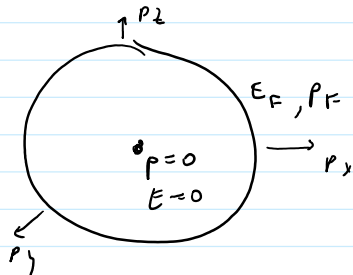
So for $T=0$ the behaviour is like in gas

2. Excited states are described by almost ideal gas of excitations.

How to introduce excitations?



in the momentum space



$$E_p^* = \frac{p^2}{2m_0} \Rightarrow \text{at } T=0 \text{ all electrons inside the sphere}$$

lets move an electron from $p_F - \Delta p$ into $p_F + \Delta p \Rightarrow$

$$\Rightarrow \Delta E_p = \frac{(p_F + \Delta p)^2 - (p_F - \Delta p)^2}{2m} \approx \frac{p_F \Delta p}{m_0} = v_F \Delta p$$

The total energy of the metal: $W_0 = \sum_p E_p^* f(E_p^*)$

$$= \sum_{p < p_F} E_p^* f(E_p^*) = \int_0^{p_F} \frac{v}{c} f = \begin{cases} 0 & p > p_F \\ 1 & p < p_F \end{cases}$$

At finite T : $W_T = \sum_p E_p^* f(E_p^*) = \sum_{p < p_F} + \sum_{p > p_F}$

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$$\sum_{p < p_F} E_p^* - \sum_{p < p_F} E_p^* f = \sum_{p < p_F} E_p^* (1-f)$$

So this energy is reduced from W_0 by the energy of free states below E_F .

For the 2nd term: since # of states with $p < p_F = p > p_F$

$$\sum_p E_p^* f - \sum_{p < p_F} E_p^* f = \sum_{p > p_F} E_p^* f - \sum_{p < p_F} E_p^* (1-f)$$

* Now lets count energy from the fermi edge:

$$E_p = \frac{p^2}{2m_0} - \frac{p_F^2}{2m_0} \quad E_p < 0 \text{ for } p < p_F$$

$$> 0 \quad p > p_F$$

two issues: • the # of electrons for small E_F is quasi-linear

• electrons moving across the edge the energy of electrons with $p < p_F$ is increasing

since now the energy of electron with $E < E_F$

is negative.

in this case we can still have the electron-hole pair

$$\text{for } (p') = E_p \frac{(p')^2}{2m_0} - \frac{p_F^2}{2m_0} \quad \text{and for } p' - p_F < p_F$$

$$(p') \approx E_p p' \frac{p' - p_F}{m_0} = v_p (p' - p_F)$$

- Now for $T=0$ each electron with \bar{p} has

ther analogue with $-\bar{p}$, so the total momentum

of the ground state has $\bar{p} = 0$

But if we move electron ^{with \bar{p} , and charge $-e$} outside the sphere then the system will get $-\bar{p}$ and charge $+e$.

So the whole system gets $-\bar{p}$, $+e$ and $s = -\frac{\hbar}{2}$

which is equivalent to say we have created an hole antiparin the ground state with

$$+e, -\bar{p}, -\frac{\hbar}{2}$$

an ideal anti-fermion the ground state with
 $+e, -p, -\hbar/2$

The total sum momentum of the e-h pair = 0.

For holes $E_h = \frac{p_F^2}{2m_0} - \frac{p^2}{2m_0}$ for $p_F - p \ll p_F$

$$E_h(p) \approx p \frac{p_F - p}{m_0} = v_h (p_F - p)$$

The energy of creation of hole growth with how deep its from E_F .

For holes their velocity is smaller and $\propto \bar{p}$.

Q: Why can we think of e-h as an ideal electron gas?
 with $\sim E_F \sim p_F$

The main reason is that any changes in the external perturbations are very small compared to E_F .

For example, electric field E will change energy of electron $\rightarrow eE \cdot l \approx 10^{-4} - 10^{-6} \text{ eV}$
 \uparrow free mean path

But $E_F \sim \text{few eV}!$

In magnetic field due to quantization:

$$\hbar \omega_c = \hbar e B / m_0 \quad \text{and for } 10^2 \text{ T}$$

$\leftarrow \text{huge! } 10^{-2} \approx \frac{3}{E_F}$

Phonon interaction scatter electrons by $\sim k_B T = 0.03 \text{ eV}$
 so even for 1000 K $\frac{k_B T}{E_F} = 0.02$

So the number of interactions per electron is very small and we consider them as gas.

Q: How long quasiparticle can live?

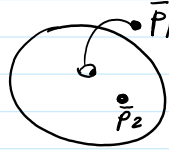
quasiparticles decay! they are not stationary states.

$$e^{i(\omega t - kx)} e^{-t/\tau} = e^{i \left(\frac{E(p)t}{\hbar} - \frac{p x}{\hbar} \right)} e^{-t/\tau}$$

How to estimate τ .

lets estimate $\equiv \tau \frac{1}{\omega}$





electron outside ϵ_F with $p_1 > p_F$
 can interact with electron
 p_2 inside p_F

as the result both electrons will end up outside p_F
 Pauli (principle)

$$\vec{p}_1 + \vec{p}_2 = \vec{p}'_1 + \vec{p}'_2$$

The transition according to Fermi golden rule \sim

$\sim \gamma \cdot$ Density of final states

\uparrow
 interaction strength

both γ and $DOS_{(final)}$ \sim width around fermi edge $p - p_F$

$$\Rightarrow p_F) \omega \sim \gamma^2 (p - p_F)^{-2} \Rightarrow \tau \sim \frac{1}{\omega} \sim \frac{1}{\gamma^2} \frac{1}{(p - p_F)^2} =$$

$$= \frac{1}{\gamma^2} \frac{v_F^2}{E_p^2(p)}$$

$$\text{e.g. } E_p(p) = \frac{p^2}{2m} = \frac{p_F^2}{2m_0} = \frac{1}{2m_0} (p - p_F)(p + p_F)$$

$$= \left(\frac{p_F}{m_0} \right) (p - p_F) \approx 2p_F$$

From this

$$\Delta E \approx \frac{\hbar}{\tau} \sim \frac{\hbar \gamma^2 E_p^2(p)}{E_F} \quad \text{and } < E_p \text{ only}$$

if $p - p_F$ is small

As we move away from E_F the decay increases
 and for large energies there is no meaning to
 talk about quasi particles.

Finally: quasiparticle are excitations of fermi liquid

for which $E(p) \gg \hbar/\tau$ when $|p - p_F| \ll p_F$

$$\text{e.g. for an ideal gas when } \gamma \rightarrow 0 \quad E(p) = \frac{p^2}{2m_0} - E_F(0)$$


for any \hbar moment, for liquid it only works

when $|p - p_F| < p_F$ and then $E(p) \sim v_p (p - p_F)$

For high energies excitation the system needs to be
 described exactly and not as gas.

described exactly and not as gas.

"Electrons" inside solids

Recall we assumed the $\epsilon(p) \sim v_F (p - p_F)$
and as such this also assumes the Fermi surface is 

Now the interaction of electrons with core ions potential changes their dispersion

Adiabatic approximation (AA)

$$1. \quad v_F \sim 10^6 \text{ m/sec} \Rightarrow v_{\text{sound}} = v \cdot \lambda$$

for $\nu \sim 10^{12} \text{ Hz}$ $v_{\text{sound}} \sim 10^3 \text{ m/sec}$ $\hookrightarrow 10^{-9} \text{ m} \approx 2a =$

The AA means that motion of electrons is defined by the instantaneous position of ions, but electrons can influence ions only via their average distribution in space.

Distribution of electrons adiabatically follows the slow changes in ions. So we can think of ions as fixed charge centers.

Bloch orcrthe

$$V(r) \text{ is periodic} \Rightarrow |\psi(r)|^2 = |\psi(r+a)|^2$$

Note: the crystal log e is avoided by the periodic b. condition.

$$\psi \text{ and } \psi(r+a) \text{ governed by } \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) = \epsilon \psi(r)$$

$$V = V_{ie}(r) + V_{e-e}(r)$$

← effective potential of interaction between e and all other electrons

$$\Rightarrow |\psi(r+a)| = |c(a)| |\psi(r)| \text{ if } |c(a)|^2 = 1$$

What can we say about $c(a)$, lets move from $r \rightarrow r+a$

$$\left. \begin{array}{l} \psi(r+a) = c(a) \psi(r) \\ \text{or } \psi(r+a) = c(a') c(a'') \psi(r) \\ \text{where } a = +a' a'' \end{array} \right\} \Rightarrow$$

two way to do this

$$c(a) = c(a') c(a'') \Rightarrow$$

$$\boxed{c(a) = e^{i k a}}$$

$$C(a) = C(a') C(a'') \Rightarrow$$

$$C(a) = e^{ika}$$

So if we move from r to $r+a$
 the w.f. ψ gains phase e^{ika} or $\psi(r+a) = e^{ika} \psi(r)$
 in general

$$\psi_k(r) = u_k(r) e^{ikr} \quad \text{with } u_k(r) = u_k(r+a)$$

Bloch theorem: the wave function of electron in crystal
 is a plane wave with amplitude modulated by
 the period of lattice.

Quasimomentum.

- 1) Momentum only discrete $n \cdot 2\pi\hbar/c$
- 2) Momentum is not well defined.

B/c of station translucence, consider direction \bar{b}
 with the period $|\bar{b}| = b$. Lets introduce a vector

$$k' = \bar{k} + \bar{g} \quad \text{where } \bar{g} = \left(\frac{2\pi n}{b^2} \right) \bar{b}$$

$$\begin{aligned} \psi_{k'}(\bar{r} + n\bar{b}) &= \left[e^{i(k' - 2\pi n \frac{\bar{b}}{b^2}) \cdot n\bar{b}} \right] \psi_{k'}(\bar{r}) \\ &= e^{i k' \cdot n\bar{b}} e^{(-2\pi n^2 \frac{\bar{b}^2}{b^2} \cdot i)} \psi_{k'}(\bar{r}) \end{aligned}$$

↙ also integer

$$e^{-2\pi i n^2 \frac{\bar{b}^2}{b^2}} = e^{-2\pi i n^2} = 1$$

$$\text{So } \psi_{k'}(\bar{r} + n\bar{b}) = e^{i k' \cdot n\bar{b}} \psi_{k'}(\bar{r})$$

this means that by changing $k \rightarrow k + g$
 and $p = \hbar k$ to $p + \frac{2\pi\hbar b h}{b^2}$ doesn't change

$$\psi_k(r+a) = e^{ika} \psi_k(r)$$

this means that k and $k + g$ are the same
 and give the same state and the same energy.

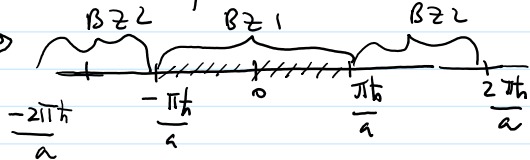
That is why k is quasimomentum
 and

That is why k is quasi momentum
 and g is crystal momentum

Few words about BZ.

Remember we already talked about BZ in the phonon section.

here is few notes:

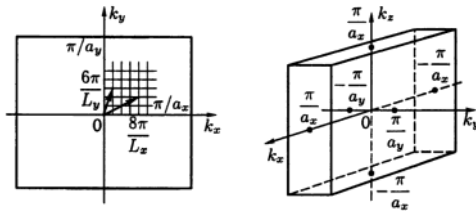


All possible projections of quasi-momentum on the translation vector \vec{a} are in the interval $\frac{2\pi\hbar}{a}$

if I shift it by $\frac{2\pi\hbar}{a}$ the situation remains the same

Since quasi-momentum \vec{p} and $-\vec{p}$ are the same all projections of momentum are symmetric around "0".

In 2D and 3D they would look like this



What happens when we approach the edge of BZ?

Let me assume that interaction with ionic core is small so the amplitude of the scattered wave \ll transmitted one. But because we have many many ions the phase relations matters a lot!

1) if wave length of a particle $q \gg 2a$ then the phase difference is small and electron is almost free

2) But if $n_i \lambda = 2a$ $n = \text{whole number} \Rightarrow$ phase difference = 2π and the reflected waves phases will add up constructively! This means that

even though the amplitude of the ^{reflected} wave is small but b/c of the phase = 2π it dominates \Rightarrow no transmitted wave in the crystal

at 1. 1.1. , 0 ...

no transmitted wave in the crystal

Note this is the same as diffraction: Bragg condition

$$ka = \pm \pi n \quad \text{since } |k| = \frac{2\pi}{\lambda}$$
$$\frac{2\pi}{\lambda} a = \pm \pi n \Rightarrow \lambda n = 2a$$

In short at the BZ the wave group velocity goes down

$$\text{and } |v_g|_{\perp \text{ to BZ}} = \left(\frac{\partial \epsilon}{\partial p} \right)_{\perp \text{ to BZ}} = 0$$

CAN WE LATE CALCULATE ELECTRONIC STRUCTURE OF A SOLID?

Exactly we cannot do this, as after 10 electrons we hit the exponential wall.

DFT fails at about 10^4 electrons and we have to use empirical semi methods.

Enter LCAO method = Linear combination of atomic orbitals

1) We start with

$$H = H_{\text{single atom}} + \Delta U$$

all differences between "real" crystal potential and isolated atom

at the atom position $\Delta U \rightarrow 0$

2) Single particle states are given

$$H \psi_{nk}(r) = E_{nk} \psi_{nk}(r)$$

Band index is n and k is the vector wave in the 1st BZ

- Atomic w.f. $\phi_i(r)$

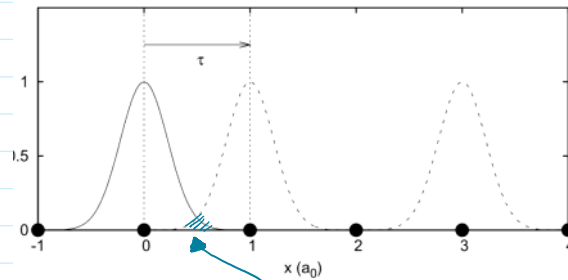
they are eigenstates of

$$H_{\text{at}} \phi_i(r) = \epsilon_i \phi_i(r)$$

$$\text{where } \langle \phi_i | \phi_j(r+R) \rangle = \begin{cases} 1 & i=j \\ & \text{and } R=0 \\ 0 & \text{otherwise} \end{cases}$$

ϵ_i i th energy of an isolated atom, they decay rapidly away from 0

ϵ_i ith energy of an isolated atom, they decay rapidly away from 0



So the overlap integral: $\gamma(R) = \int \phi_i^* H \phi_i(r+R) dr$ is small

Now recall the Bloch theorem

$$\Psi_{nk}(r+R) = e^{i\mathbf{k}\cdot\mathbf{R}} \Psi_{nk}(r)$$

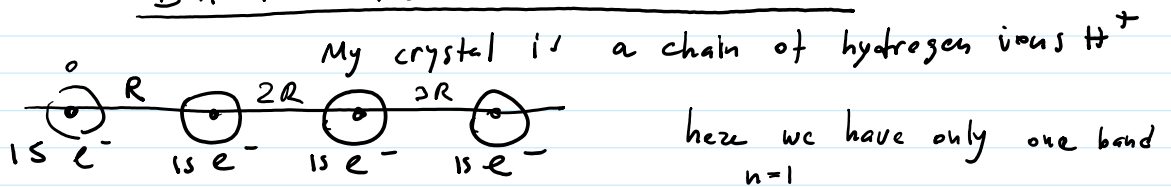
clearly ϕ_i are not good but what about

$$\Psi_{nk}(r) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(r-\mathbf{R})?$$

here we assume N atoms in the crystal.

Proof that $\Psi_{n,\mathbf{k}}(r)$ is Bloch w.f.!

BAND STRUCTURE CALCULATION.



$$|\Psi_k\rangle = \Psi_k(r) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_s(r-\mathbf{R})$$

lets calculate $E(k) = \langle \Psi_k | H | \Psi_k \rangle$ the dispersion relation

$$= \int \Psi_k^* H \Psi_k dr$$

$$E(k) = \frac{1}{\sqrt{N}} \frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} \int \phi_s(r-\mathbf{R}) H \phi_s(r-\mathbf{R}') dr =$$

$$= \sum_{\mathbf{R}} \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} \int dx \phi_s(x) H \phi_s(x-\underbrace{(\mathbf{R}'-\mathbf{R})}_{\mathbf{R}''})$$

since $H(r-\mathbf{R}) = H(r)$

for each specific \mathbf{R} $\mathbf{R}'-\mathbf{R} = \mathbf{R}''$ is another translation vector

$$\sum_{\mathbf{R}'} = \sum_{\mathbf{R}''}$$

$$\sum_{R'} = \sum_{R''}$$

$$E(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}} \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \int dx \phi_s^*(x) \psi_s(x - \mathbf{R}'')$$

↑ since each term is the same = $\sum_{\mathbf{R}} N$

$$E(\mathbf{k}) = \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \int \phi_s^*(x) \psi_s(x - \mathbf{R}'') dx$$

Now the w.f. rapidly decays $\int \phi_s^*(x) \psi_s(x) dx = \epsilon_s$

if $|\mathbf{R}''|$ large $\int \phi_s^* \psi_s(x - \mathbf{R}'') dx \approx 0$ if $\mathbf{R}'' = 0$

So we need to include only terms where \mathbf{R}'' is small τ

thus we have

$$E(\mathbf{k}) = e^{i(\mathbf{k}=0)\cdot\mathbf{R}} \epsilon_s + \sum_{\tau} e^{i\mathbf{k}\cdot\tau} \gamma(\tau)$$

$$E(\mathbf{k}) = \epsilon_s + \sum_{\tau} e^{i\mathbf{k}\cdot\tau} \gamma(|\tau|)$$

e.g. $\gamma(|\tau|) = A e^{-\alpha|\tau|^2} / |\tau|^2$ in Silicon

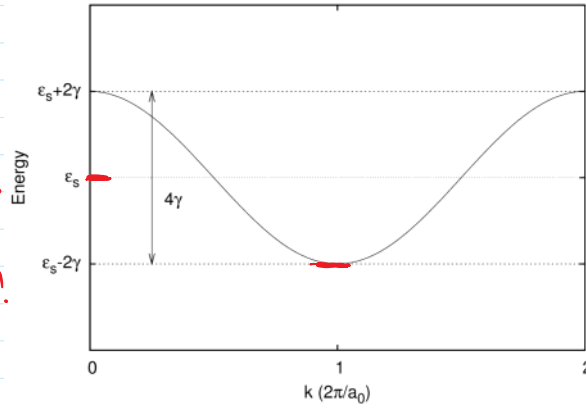
EXAMPLE 1: 1D crystal

$+1a_0\hat{i}$ 1D crystal $\pm a_0\hat{i}$ $\vec{\tau} = \tau_1 = \tau_2 = -a_0\hat{i}$

$$\begin{aligned} E(\mathbf{k}) &= \epsilon_s + \sum_{\tau_1, \tau_2} e^{i\mathbf{k}\cdot\tau} \gamma(|\tau|) = \\ &= \epsilon_s + e^{i\mathbf{k}\cdot\tau_1} \gamma(|\tau_1|) + e^{i\mathbf{k}\cdot\tau_2} \gamma(|\tau_2|) = \\ &= \epsilon_s + e^{i\mathbf{k}\cdot a_0\hat{i}} \gamma(a_0) + e^{-i\mathbf{k}\cdot a_0\hat{i}} \gamma(a_0) = \\ &= \epsilon_s + \gamma(a_0) \left(\frac{e^{i\mathbf{k}\cdot a_0\hat{i}} + e^{-i\mathbf{k}\cdot a_0\hat{i}}}{2} \right) = \\ &= \epsilon_s + \gamma(a_0) 2 \cos(\mathbf{k}\cdot a_0\hat{i}) \end{aligned}$$

METAL →

So we lowered energy compared to isolated atoms!!!



etc: Calcul Dispersion $E(k)$ for 2D

This is how a part of HW3

Plot 2D case:

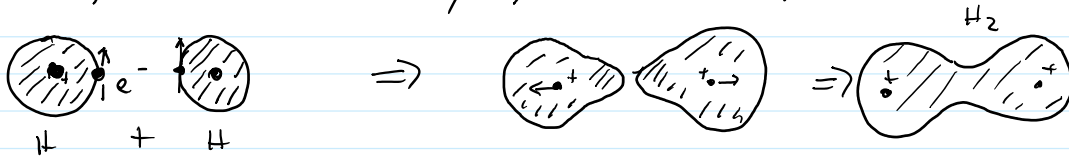
for $a = \text{\AA}$ 30 meV

1. eV
10 eV

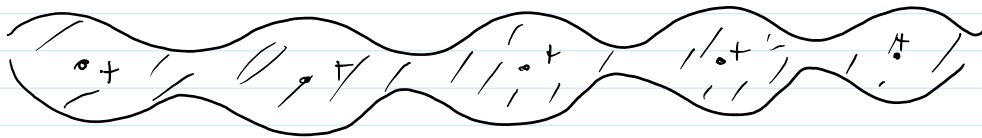
THE same for 3D face centered cubic xlat of size a . with 12 nn.

ORIGIN OF THE BANDS

Before we explain why atoms condense in solids let's try to understand why molecule exists?



Once we understand this we can think of a solid line one giant molecule.



Here we closely follow W. A. HARRISON "Electronic structure and the properties of solids" pp. 16 - 22 Ch. 1

For a hydrogen molecule we have 2 orbitals
 ATOM1 ATOM2
 |1> |2>
 1s 1s

To determine the energy and eigenstates of the molecule we must solve the secular eqn.

Variational principle

$$\sum_{\alpha} \langle \beta | H | \alpha \rangle U_{\alpha} - E U_{\beta} = 0 \quad \text{where} \quad \langle \alpha | \beta \rangle = 0$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$$

So $E_s = \langle 1 | H | 1 \rangle = \langle 2 | H | 2 \rangle$ $\langle 1 | H | 2 \rangle = \langle 2 | H | 1 \rangle = -V_2$

$$\begin{pmatrix} \langle 1 | H | 1 \rangle & \langle 1 | H | 2 \rangle \\ \langle 2 | H | 1 \rangle & \langle 2 | H | 2 \rangle \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} - E \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = 0$$

$$\begin{cases} (E_s - E)U_1 - V_2 U_2 = 0 \\ -V_2 U_1 + (E_s - E)U_2 = 0 \end{cases}$$

We can easily solve these and find

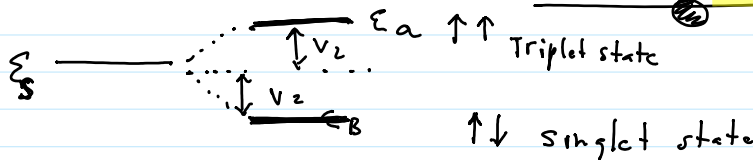
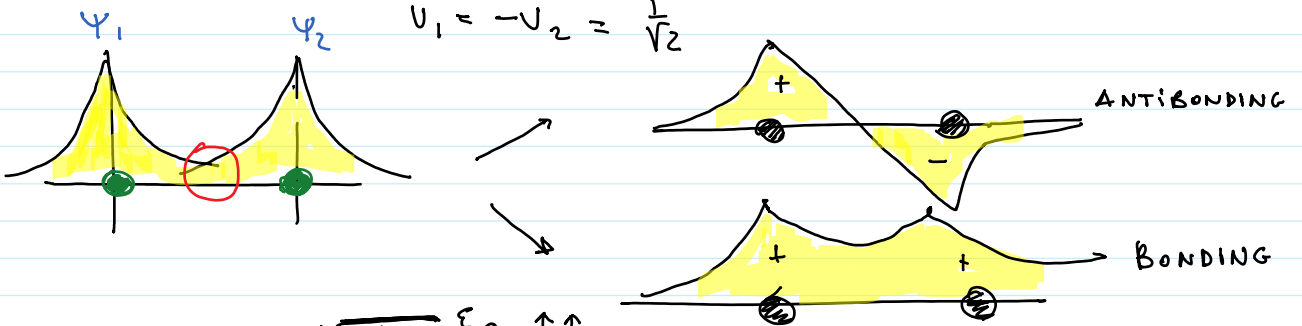
bonding state $\rightarrow E_b = E_s - V_2$ V_2 is called covalent energy and is positive

antibonding state $\rightarrow E_a = E_s + V_2$

Subs. those solutions into we determine the eigenvectors:

bonding: $U_1 = U_2 = \frac{1}{\sqrt{2}}$

$U_1 = -U_2 = \frac{1}{\sqrt{2}}$



Next we describe the case of a POLAR BOND e.g. $\text{Li}^+ \text{H}^-$ or $\text{Na}^+ \text{Cl}^-$ etc.

Now we have to modify our matrix to account for the difference in the energy of the ground state

of $\epsilon_s^1 \rightarrow$ anion
 $\epsilon_s^2 \rightarrow$ cation so we end up

$$\begin{pmatrix} \epsilon_s^1 & -V_2 \\ -V_2 & \epsilon_s^2 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} - E \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$$

Let introduce a new important parameter

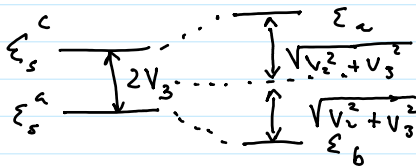
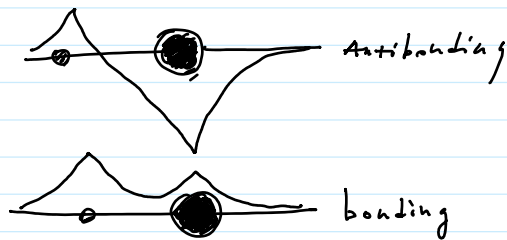
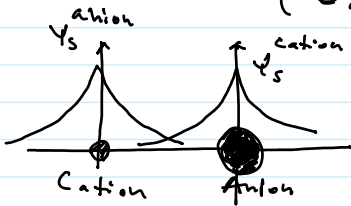
$$V_3 = \frac{\epsilon_s^2 - \epsilon_s^1}{2} \Rightarrow \text{POLAR ENERGY}$$

and also define the average of the cation-anion energy $\bar{\epsilon} = \frac{\epsilon_s^1 + \epsilon_s^2}{2}$

then our equation becomes

$$\begin{pmatrix} \bar{\epsilon} - V_3 & -V_2 \\ -V_2 & \bar{\epsilon} + V_3 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} - E \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$$

$$\begin{cases} \epsilon_b = \bar{\epsilon} - (V_2^2 + V_3^2)^{1/2} \\ \epsilon_a = \bar{\epsilon} + (V_2^2 + V_3^2)^{1/2} \end{cases}$$



Notice how electronic charge distributes in the bonds!

THIS MEANS THE MOLECULE IS POLAR!

To describe the polarity mathematically we find v_1 and v_2 , e.g. first put ϵ_b into

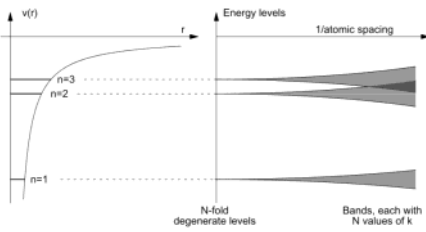
$$v_1 = \frac{V_2}{\sqrt{V_2^2 + V_3^2} - V_3} v_2 \equiv \alpha_p v_2 \quad v_1^2 - v_2^2 = 1$$

$\equiv \alpha_p \leftarrow \text{POLARITY}$

Another useful concept is covalency

$$\alpha_c = \frac{V_2}{\sqrt{V_2^2 + V_3^2}}$$

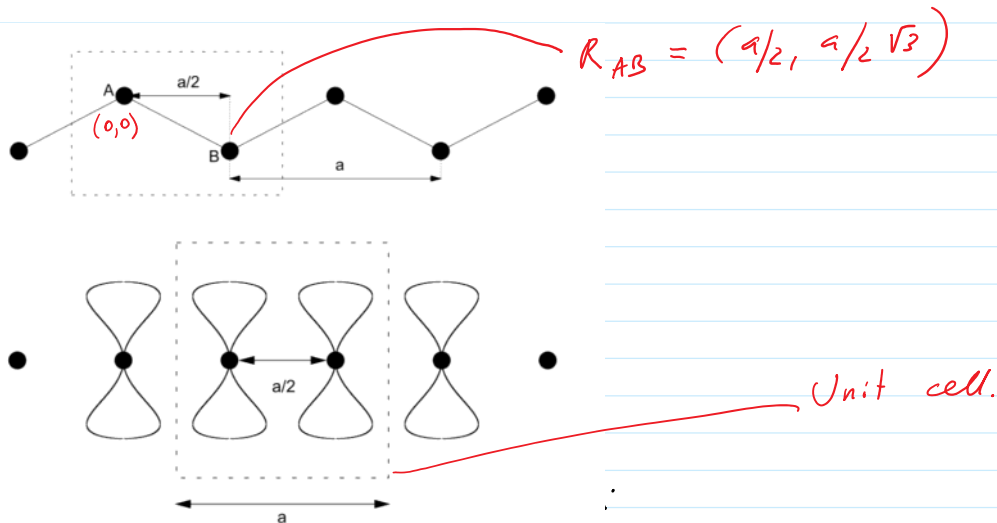
Back to our solids.



As overlap integral γ (or V_2 for the molecule) increases, the N atoms which form N degenerate states overlap, and create bonding and anti-bonding states which called occupied and unoccupied states or valency bands or conduction bands

Each band contains N allowed values of \vec{k} .

Lets describe our first real solid (though soft) trans - polyacetylene.



In the crystal with N_b atoms basis and assuming that each atom contributes only 1 orbital for bonding, we can make N_b linear combinations of atomic orbitals that satisfy Bloch theorem:

$$\Psi_{i,\kappa}(r) = \frac{1}{\sqrt{N}} \sum_{R_i} e^{i\kappa \cdot R_i} \phi(r - R_i)$$

$i = 1, 2, \dots, N_b$ label different atoms in basis

and R_i are the translation vectors that connect different atoms i .

e.g. for our polymer: $\bar{R}_0 = \bar{R}_{AB} \pm a\bar{i}$,
 $\bar{R}_{AB} \pm 2a\bar{i}$ etc

where \bar{R}_{AB} is the vector
 between
 A and B

Then the crystal is defined as:

$$\Psi_{n,\kappa} = \sum_i c_{i,\kappa} \Psi_{i,\kappa}(r) = \frac{1}{\sqrt{N}} \sum_i c_{i,\kappa} \sum_{R_i} e^{i\kappa \cdot R_i} \phi(r - R_i)$$

As for the molecule we use the variational theorem to find a set of $\Psi_{n,\kappa}$ which are determined by minimizing the expectation of H w.r.t. $c_{i,\kappa}$

$$\sum_i (H_{ij} - \delta_{ij} E(\kappa)) c_{j,\kappa} = 0$$

where $H_{ij} = \langle \Psi_{i,\kappa} | H | \Psi_{j,\kappa} \rangle$

Back to our polymer:

2-atom basis

$$N_b = 2 \quad \begin{vmatrix} H_{AA} - \bar{E} & H_{AB} \\ H_{BA} & H_{BB} - \bar{E} \end{vmatrix} = 0$$

where $H_{AB} = H_{BA}^* \Rightarrow$

$$\bar{E}(\kappa) = -\frac{1}{2} (H_{AA} + H_{BB}) \pm \sqrt{\frac{1}{4} (H_{AA} - H_{BB})^2 + H_{AB}^2}$$

2 branches for each κ . \rightarrow 2 BANDS

(NOTE 2 ATOM PER BASIS
 $=$ 2 BANDS)

Let's calculate H_{AA} and H_{BB} for $1p$ -orbital contribution

Let's calculate H_{AA} and H_{BB} for $1p$ -orbital contribution ^{= 2 BANDS)}
atom

$$\begin{aligned}
 H_{AA} &= \frac{1}{N} \sum_{\substack{R_A \\ = N}} \sum_{R'_A} e^{i(R'_A - R_A) \cdot k} \int \psi_s^*(r - R_A) H \psi_s(r - R'_A) dr \\
 &= \sum_{R''_A} e^{i k \cdot R''_A} \int \psi_s^*(x) H \psi_s(x - R''_A) dx = \\
 &= \epsilon_p + \sum_{m \neq 0} e^{i m k a} \gamma(|m a|) \quad m \text{ is } > 0 \text{ integer}
 \end{aligned}$$

The same for H_{BB} .

Next we restrict our overlap integral only to n - n meaning $\gamma(|m a|) = 0$ if $|m| > 1$

thus we end up with:

$$H_{AA} = H_{BB} = \epsilon_p + 2\gamma(a) \cos(ka)$$

Following the same logic for H_{AB}

$$\begin{aligned}
 H_{AB} &= \frac{1}{N} \sum_{R_A} \sum_{R_B} e^{i k (R_A - R_B)} \int \psi_s^*(r - R_A) H \psi_s(r - R_B) dr \\
 &= \sum_{R'_A} e^{i k (\bar{R}_{AB} + R'_A)} \int \psi_s^*(x) H \psi_s(x - (\bar{R}_{AB} + R'_A)) dx
 \end{aligned}$$

Again include only n - n or $R_A = 0$ and $R_B = -a i$

$$H_{AB} = \sum_{\tau} e^{i k \tau} \gamma(|\tau|)$$

τ are the n - n vectors $\bar{\tau} = \bar{R}_{AB} = (a/2, \frac{a}{2}\sqrt{3})$

and $\bar{\tau} = \bar{R}_{AB} - a i = (-a/2, \frac{a}{2}\sqrt{3})$

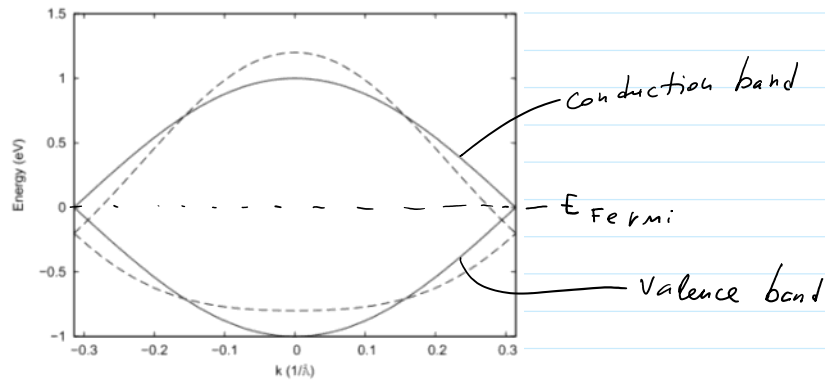
then

$$\begin{aligned}
 H_{AB} &= \left(e^{i k a/2} + e^{-i k a/2} \right) \gamma(|\tau|) = \\
 &= 2 \cos(ka/2) \gamma(|\tau|)
 \end{aligned}$$

Combining all the H_{AA} , H_{BB} and H_{AB} we finally get

$$E(k) = \epsilon_p + 2\gamma(a) \cos(ka) \pm 2 \cos(ka/2) \gamma(|\tau|)$$

$$E(k) = \epsilon_p + 2\gamma(a) \cos(ka) \pm 2 \cos\left(\frac{ka}{2}\right) \gamma(1\tau)l$$



What about more than one orbital?

In graphene the lowest bands are made of $s/p_x/p_y$ orbitals \Rightarrow sp^2 bonding.

So lets generalize the tight binding approach

Imagine we have now $N_b = 2$ s, p_x, p_y, p_z orbitals

We expect 2×4 bands to develop.
 $\uparrow \quad \uparrow$
 2 atoms orbitals
 in basis

Thus we will get (8×8) matrix for each \vec{k} .

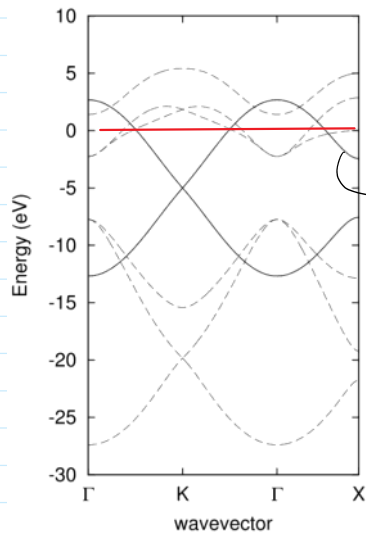
e.g. In this case $i=1$ labels s -orbital on A
 $j=5$ p_x -orb on B

The hamiltonian matrix element will be:

$$H_{ij} = \frac{1}{N} \sum_{R_A} \sum_{R_B} e^{i\vec{k} \cdot (R_A - R_B)} \int \underline{\varphi_s^*(r - R_A)} H \underline{\varphi_p(r - R_B)} dr$$

The rest are similar:

Consider the band structure of graphene
 Graphene



As you can see
there are clearly
8 bands

Mostly p_z orbitals (π -bands)
form the conduction band.