ELECTRONIC STRUCTURE

We know we have to use Schrödinger eqn. with $\{\vec R_i\}$ ← lattice sites. Let's ignore spin.

$$\hat H\, \Phi_n(\bar r_1 \dots \bar r_N) = E_n\, \Phi_n(\bar r_1 \dots \bar r_N)$$

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \sum_i \frac{e^{2}\overset{\#}{Z}}{|\bar r_i - \vec R_i|}\right) + \frac{1}{2}\underbrace{\sum_{i\neq j}^{N}\frac{e^2}{|\bar r_i - \bar r_j|}}_{\text{difficult to solve}}$$

But often: $\mathcal{H} = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 + v_{eff}(\bar r_i)\right)$

↑ effective potential represents interaction of the electron with all other e^-s.

① We can start with v_{eff} = const ⇒ zero approx.

then the single particles are plane waves

$$\psi_k(r) = \frac{1}{\sqrt{L^3}}\, e^{i\bar k\cdot\bar r} \quad \text{with} \quad \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

and are eigenstates for velocity:

$$\hat{\bar v} = \frac{d\bar r}{dt} = \frac{i}{\hbar}[H, r] = \frac{i}{2m\hbar}[\underset{H = \frac{p^2}{2m}}{p\cdot p}, r] =$$

$$= \frac{i}{m\hbar}\, p\,(-i\hbar) = \frac{p}{m_e} = \frac{-i\hbar\nabla}{m}$$

with eigen value $\frac{\hbar \bar k}{m_e}$

b/c velocity is a constant of motion, the electrical resistance = 0 and current doesn't decay in this model.

Next approx: $v_{eff}(\bar{r}) = V(\bar{r})$ where $\boxed{V(\bar{r}) = V(\bar{r} + R_i)}$

lattice vectors

Real, analytical function of r

BLOCH'S THEOREM

is very important to describe the motion of independent electrons in a periodic potential.

Recall from X-ray $\Delta \bar{k} = \bar{G}$ ≡ Bragg scattering

we cannot apply Born approx. to e^- scattering b/c ionic core potentials are very strong:

For a single particle in the periodic potential:

$$H = \frac{\bar{p}^2}{2m} + V(r) , \quad V(r) = V(r + R_i)$$

if we have atomic potentials:

$$V(r) = \sum_{R_j} v(r - R_j) ,$$ b/c of chemical bonding they are not atomic potentials.

Ψ e^- inside a solid ?

Symmetry consideration:

Let's start with $V(\bar{r})$ = Const ⇒ H is translation invariant $[\hat{H},\hat{T}_{\bar{c}}]=0$ for any vector $\bar{c}$

The lattice translation satisfy $[T_e, T_{e'}]=0$ and with $[H\,T_e]=0$, i.e.

$$T_e\,H(r)\psi(r) = H(r+R_e)\,\psi(r+R_e) = H(r)\,T_e\,\psi(r) \Rightarrow$$
$$\Rightarrow [H,T_e]=0$$

This also imply that T_e and H share the same eigenstates:

$$H\,\psi(r) = \epsilon\,\psi(r)$$
$$T_e\,\psi(r) = C(R_e)\,\psi(r)$$

Since charge density is periodic

$$|\psi(r)|^2 = |T_e\,\psi(r)|^2 = C(R_e)^2\,|\psi(r)|^2$$
$$\Rightarrow C(R_e)^2 = 1 \Rightarrow C(R_e) = e^{ik\cdot R_e}$$

k is REAL

Thus :

$$\boxed{T_e\,\psi(r) = \psi(r+R_e) = e^{ik\cdot R_e}\,\psi(r)}$$

This equation expresses the Bloch theorem

The phase accumulated by the w.f after translation by R_e is just $\bar{k}\cdot\bar{R}_e$!

However! from $T_e \Psi(r) = \Psi(r+R_e)$ we can conclude $T_e \cdot T_{e'} \Psi(r) = \Psi(r + R_e + R_{e'}) = T_{e+e'} \Psi$

hence for this case $C(R_{e+e'}) = e^{ik\cdot(R_e+R_{e'})}$

now what if k is imaginary ⇒
charge density ~ $|\Psi(r)|^2$ would exponentially iNCREASE! while moving from site to site.
or DECREASE

But this is not possible b/c of the translational invariance!

In other words: if translational inv. is broken (defects) ∃ complex k is allowed. which represent the localized wave-function otherwise in a perfect xtal <u>**k is real**</u>.

In practice this means we need to determine the w.f. behaviour only inside the <u>primitive</u> <u>u.c.</u>

$$e^{-ik(r+R_e)} \times \Big| \quad \Psi(r+R_e) = e^{ik\cdot R_e}\Psi(r) \Rightarrow$$

$$e^{-i(r+R_e)}\Psi(r+R_e) = e^{ikr}\Psi(r) = U_k(r)$$

with $U_k(r) = U_k(r+R_e)$

Hence the w.f. of an e^- inside xtal is

$$\boxed{\psi_k(r) = u_k(r)\, e^{ik\cdot r}} \qquad \boxed{\text{where } u_k(r) = u_k(r+R)}$$

It states that it's just plane wave with periodically modulated amplitude $U_k(r)$

For computations: we started with

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

$$e^{ikr}\,u_k(r) \Big\downarrow \quad \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{i\hbar^2}{m}\bar{k}\cdot\nabla + \frac{\hbar^2k^2}{2m}\right)u_k(r) + V(r)\,u_k(r) = E\,u_k(r)$$

to be solved inside a p. u. cell, independent on the # of unit cells, with the periodic boundary condition $\psi(r) = \psi(r + N\cdot a)$.

Reminder: Recall we discussed that k is not conserved but $k \pm nG$ is conserved quantity.

Note: $\hbar\bar{k}$ is not electron momentum, but we can make a wave packet out of B. waves, and their group velocity is: $\bar{v}_k = \frac{1}{\hbar}\nabla_k \epsilon(\bar{k})$

This packet travels coherently through the xtal, and m.f.p. $\to\infty$. But in Drude m.f.p. is very short.

Lets restric our self to 1 BZ: $\Rightarrow$

$$\psi_k(r) = \sum_G \underset{\overset{\uparrow}{=a_{G+G'}(k)}}{b_G(k)}\, e^{i(k+G+G')}$$

We can always use G' which bring $k' = \bar{k} + G'$ back to B.Z. ⇒

$$\psi_{nk'}(\bar{r}) = e^{i\bar{k}'\cdot\bar{r}}\, u_{nk'}(r)$$

when $k' \in 1BZ$

$n \equiv$ Band index to make up for this restriction

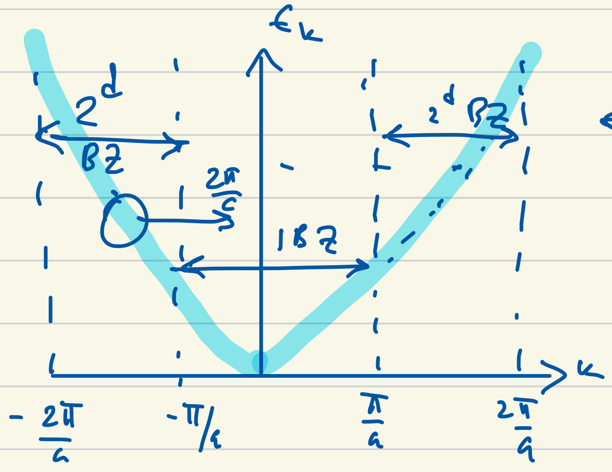
This is similar to Hydrogen atom

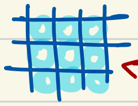
atom	Solid
$n, \underbrace{l, m}_{\text{rotational symmetry}}$	$\underset{\substack{\uparrow \\ \text{lattice translation}}}{k}, n$ ← means the same symmetry but different energy

EMPTY LATTICE MODEL

1D with lattice constan a; $V(r) = 0$ ⇒

$$\psi_k(x) = e^{ikx} \quad \text{and} \quad \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

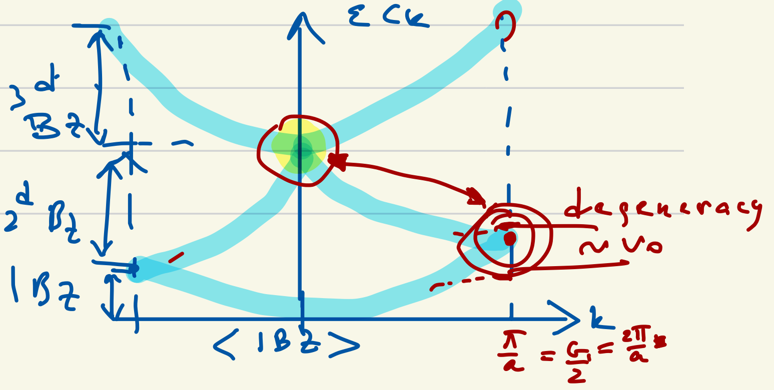




Extended zone scheme

But we can map all wave vectors back to 1BZ by shifting them by $G_1 = \frac{2\pi}{a}$

Reduced zone scheme →



The band energies are:

$$\begin{cases} \underline{\epsilon_0}{}_{k} = \frac{\hbar^2}{2m} k^2 \\ \epsilon_{1k} = \frac{\hbar^2}{2m}\left(k - \underline{G_1}\right)^2 \quad \leftarrow \frac{2\pi}{a} \equiv G_1 \\ \dots\dots \\ \epsilon_{nk} = \frac{\hbar^2}{2m}\left(k - n\underline{G_1}\right)^2 \end{cases}$$

- Looks like phonons But no ending for n.
- Also there is band degeneracy at k=0 But for phonons if mass is different or springs are diff. this degeneracy removed. What about for electrons? <u>in a periodic potential</u> ?

From <u>B.</u> theorem, the S. eqn:

$$\checkmark \quad \hat{h}_{\bar{k}}\, u_{n k}(\bar{r}) = \epsilon_{n\bar{k}}\, \underline{u_{n\bar{k}}(\bar{r})} \qquad u_{nk}(r) = u_{nk}(r + R_e)$$

$$\hat{h}_{\bar{k}} = \frac{(p + \hbar \bar{k})^2}{2m} + \underbrace{\mathcal{V}(r)}, \qquad \mathcal{V}(r) = \mathcal{V}(r + R_e)$$

Because of the periodicity of $u_{n\bar{k}}(r)$ we need to solve the eqn. only for 1st BZ.

⇒ Think of a particle in a box now!

e.g. <u>1D empty lattice:</u> $\mathcal{V}(x) = 0$

$$\frac{1}{2m}(p + \hbar k)^2\, u_{nk}(x) = \epsilon_{nk}\, u_{nk}(x)$$

with the bound. cond:

$$\boxed{u_{nk}(-a/2) = u_{nk}\left(+\frac{a}{2}\right)}$$

$\psi_{n=0}$

$\psi_{n=1}$

we can choose :

From periodic b.c.

$$u_{nk}(x) = \frac{1}{\sqrt{a}} e^{-inG_1 \cdot x} = \frac{1}{\sqrt{a}} e^{-i\underbrace{\overset{\overset{K_n}{\|}}{n}\frac{2\pi}{a}}_{\equiv G_1} \cdot x}$$

$n=0$, $n=1$

From periodic B. cond.

Now we turn on a weak potential $V(r)$:

$$V(x) = \underline{v_0 \cos(G_1 x)} = \frac{v_0}{2}\left(e^{iG_1 x} + e^{-iG_1 x}\right)$$

$\uparrow \frac{2\pi n}{a}$ n = lattice site

$$\boxed{\begin{array}{l}\text{This potential scatters electrons from } \bar{k} \text{ to } \bar{k} \pm \bar{G}_1. \\ \text{At the zone boundary } \bar{k}_\pm = \pm\frac{1}{2}\bar{G}_1 \text{ the states}\end{array}}$$

ψ_{k^+} and ψ_{k^-} are degenerate but mixed by $V(r)$

SHOW THIS

$$\langle \psi_{k^+} | \overset{\neq 0}{V} | \psi_{k^-} \rangle \neq 0 \; ! \; = \boxed{\frac{v_0}{2}} \; \checkmark$$

If you look at the reduced zone you see that

$$\underline{\psi_{k^+}} = \psi_{n=0,\, k = +\frac{G_1}{2}} \quad \text{= at ZB}$$

$$\psi_{k^-} = \psi_{n=1,\, k = +\frac{G}{2}}$$

$\Rightarrow$ Mixing happens at the same k BUT for different Band, n - is diff.

< for n=2 it's too high in energy: >

From degenerate pert. theory, we need to diagonalize all at $k = \frac{G_1}{2}$

$$\begin{pmatrix} \langle \underset{n=0}{0}\, \underset{k}{\frac{G_1}{2}} | H | 0\, \frac{G_1}{2} \rangle^{\checkmark} & \langle 0\, \frac{G_1}{2} | H | 1\, \frac{G_1}{2} \rangle \\ \langle 1\, \frac{G_1}{2} | H | 0\, \frac{G_1}{2} \rangle & \langle \underset{n=1}{1}\, \frac{G_1}{2} | H | 1\, \frac{G_1}{2} \rangle \end{pmatrix} =$$

$\equiv \psi_{0,\frac{G_1}{2}}$

$\equiv \psi_{1,\frac{G_1}{2}}$

$$= \begin{pmatrix} \hbar^2 G_1^2 / 8m & v_0/2^{\checkmark} \\ \frac{v_0}{2}^{\checkmark} & \hbar^2 G_1^2 / 8m \end{pmatrix}^{\checkmark} \checkmark$$

$\frac{G_1}{2}$

$G_n = \frac{2\pi}{a} n$ but n=1 $G_1 = \frac{2\pi}{a}$

⇒ the eigenstates are: at ZB

$$\boxed{\epsilon_\pm = \frac{\hbar^2}{8m} G_1 \pm \underbrace{\overset{=0}{V_0/2}}}$$ and

$$\epsilon_+ - \epsilon_- = \frac{|V_0|}{2} \text{ at } \left(\frac{G_1}{2} = \frac{\pi}{a}\right)$$

eigen-vectors $\chi_\pm = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \pm 1\end{pmatrix}$ and the states are

$$\underline{|\psi_\pm\rangle} = \frac{1}{\sqrt{2}}\left\{|\overset{n}{0}, \overset{k}{\frac{G_1}{2}}\rangle \pm |1, \frac{G_1}{2}\rangle\right\} \text{ or}$$

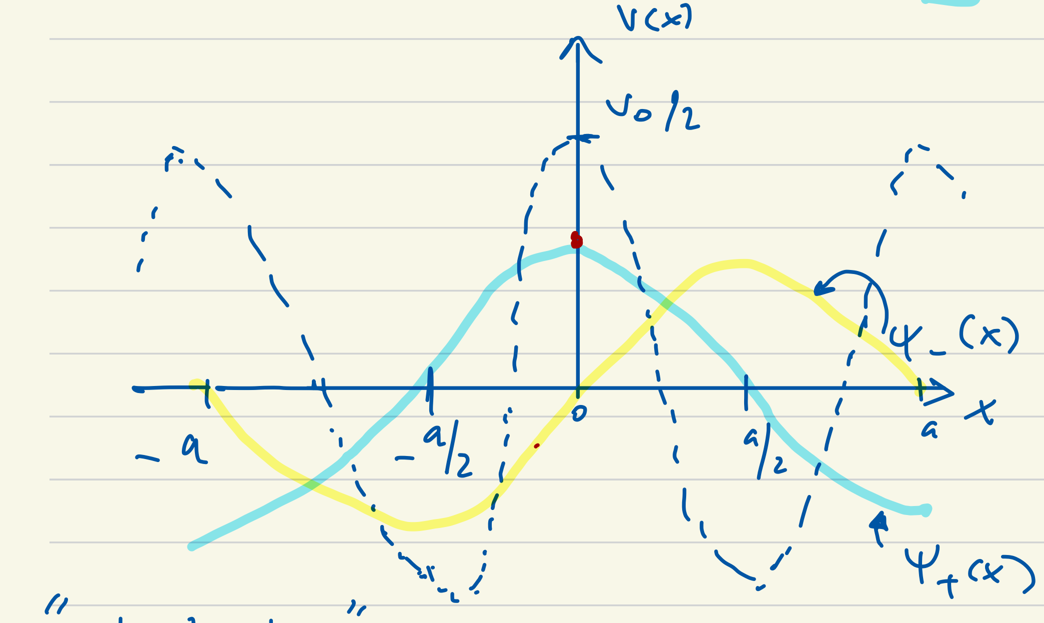
$$\equiv \underbrace{\frac{1}{\sqrt{a}} e^{-inG_1x}}$$

at ZB

$$\left[\begin{aligned}\psi_+(x) &= \sqrt{\frac{2}{a}}\,\underline{\cos}\,\frac{G_1 x}{2}\\ \psi_-(x) &= i\sqrt{\frac{2}{a}}\,\sin\frac{G_1 x}{2}\end{aligned}\right]$$

at the zone boundary

← STANDING WAVES



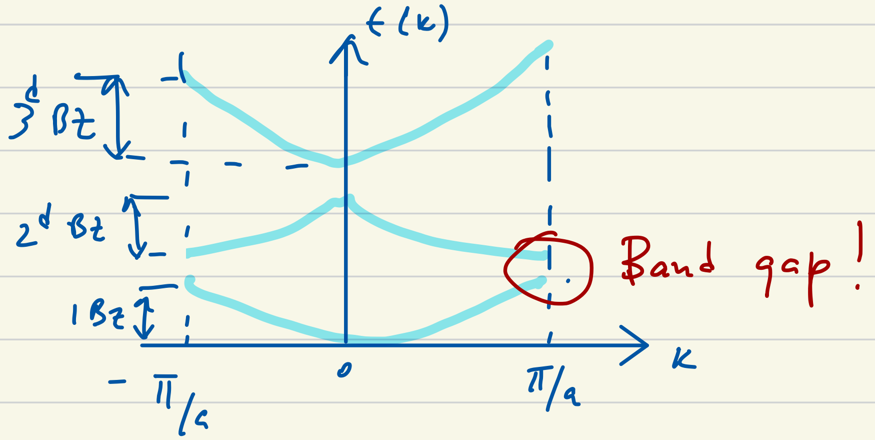
"anti-bonding"

$\underline{\psi_+}$ are at the peaks of V_0 ⇒ higher energy

ψ_- are in the valley of V_0 ⇒ lower energy

"Bonding"

So at the Z.B. the degeneracy is lifted



Let's examin it slightly away from $\pm \pi/a$

e.g. $k = \frac{1}{2} G_1 - \delta k$

The unperturbed states are not degenerate but very close in energy:

$$h = \begin{pmatrix} \hbar^2/2m \, (G_1/2 - \delta k)^2 & U_0/2 \\ U_0/2 & \frac{\hbar^2}{2m}\left(-\frac{G_1}{2} - \delta k\right)^2 \end{pmatrix}$$

$\Rightarrow$ diagonalize and get dispersion near the Z.B.

The band gap has strong impact on transport. e.g. if the chemical potential is inside the gap $\Rightarrow$ INSULATOR and filled band called the VALENZE BANDS and non-filled ones CONDUCTION BANDS.

Band gap & Bragg reflections

! in 1D: scattering between 2 degenerate states by $\bar{V}(r)$ opens a gap.

Consider a general case:

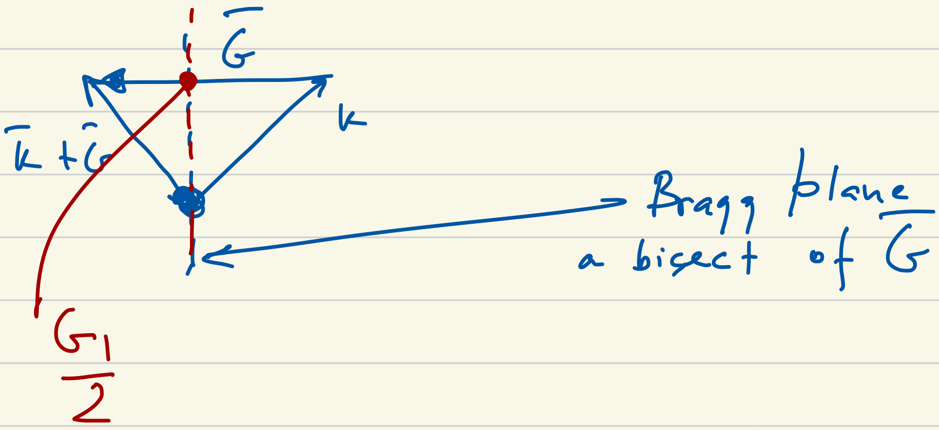
$$V(r) = \sum_{|G|} V_{\bar{G}} \, e^{i\bar{G}\cdot\bar{r}}$$

this potential scatters states from $\bar{k} \rightarrow \bar{k}+\bar{G}$

These 2 unperturbed states are degenerate:

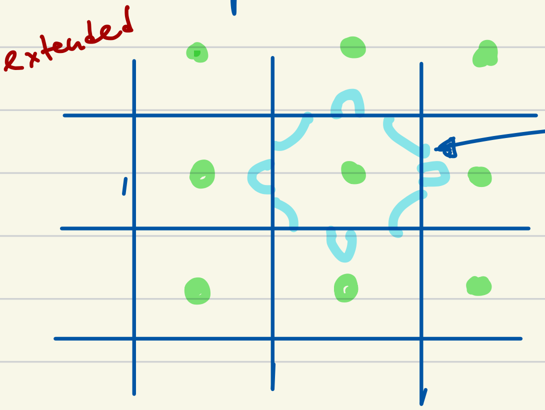
$$\frac{\hbar^2}{2m_e}|k|^2 = \frac{\hbar^2}{2m}|\bar{k}+\bar{G}|^2$$

Consider now the Ewald construction

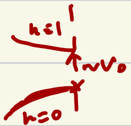


Any point on this dashed line satisfies the Bragg condition.

Thus a countour map of $\epsilon(k)$ in the extended picture looks like this



the line cross the zone boundary at the right angle and discontinious



reduced Zone scheme

[Discontinuity at the Z.B = Bragg plane is the origin of a gap]

In the degenerate perturbation theory

$$\psi_{\bar{k}} = a\, e^{ikr} + b\, e^{i(k+\bar{G})\bar{r}}$$

The 2x2 matrix of the Sch. eqn:

$$h \begin{pmatrix} a \\ b \end{pmatrix} = \epsilon \begin{pmatrix} a \\ b \end{pmatrix}$$ where

$$h \equiv \begin{pmatrix} \epsilon_k & V^*_{\bar{G}} \\ V_{\bar{G}} & \epsilon_{k+G} \end{pmatrix}$$ ⇒ eigenvalues =

$$E_\pm = \epsilon_+ \pm \sqrt{\epsilon_-^2 + |V_G|^2}$$

$$\epsilon_\pm \equiv \frac{1}{2}\left(\epsilon_{\bar{k}} \pm \epsilon_{\bar{k}+\bar{G}}\right)$$

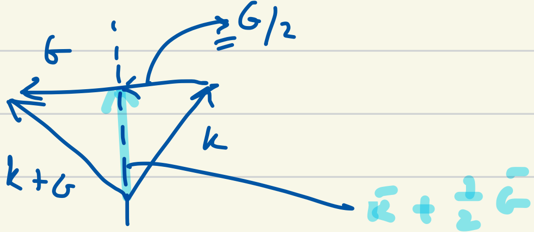
The gradient of energy eigenvalues:

$$\nabla_k E_\pm = \nabla_k \epsilon_+ \pm (\nabla_k \epsilon_-) \frac{\epsilon_-}{\sqrt{\epsilon_-^2 + |V_{\bar{G}}|^2}}$$

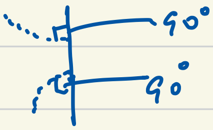
but $\nabla_k \epsilon_+ = \frac{\hbar^2}{m}\left(k + \frac{1}{2}G\right)$ and $\epsilon_- = 0$ at $\frac{G}{2} \leftarrow$ (on the Bragg plane) we obtain

$$\nabla_k E_{\pm} = \frac{\hbar^2}{m}\underbrace{\left(\bar{k} + \frac{1}{2}\bar{G}\right)}$$

but this vector is ⊥ to the Bragg plane ⇒



Thus constant energy lines must enter the Zone boundary at the right angle,



How many e^-s takes to fill up a band?

1D: $$N_{states} = \int_{-\underset{\uparrow \frac{2\pi}{a}}{G_1}/2}^{+G_1/2} \left(\frac{L}{2\pi}\right) dk = \frac{L}{2\pi} G_1 = \frac{L}{a} = N_{cells}$$

d-dimensions: $$N_{states} = \left(\frac{L}{2\pi}\right)^d \int_{BZ} d^d k = N_{cells}$$

⇒ density of states is one per cell/band/spin

Recall from phonons: # of phonons per polarization $= N_{cells}$

but the number of modes: dimensionality × atoms per u.c.

In Bravaös lattice one atom/cell and taking into account spin $2 \times N_{cells} = 2 \times N_{atoms}$ to fill **one** band.

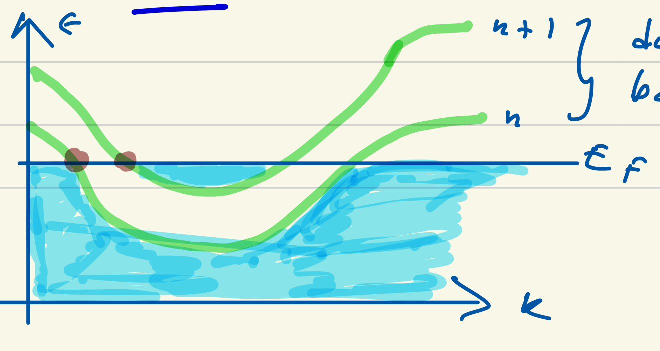
⇒ prediction: even # of $\overset{\boxed{\text{VALENCE}}}{V_{e^-}}$ ⇒ insulator

odd # ⇒ metal

e.g. alcali metals odd valence → metal

Si, C even → insulator

But sometimes,



different bands cross ε_F

sometimes n^{th} is higher than $n{+}1^{th}$ ⇒ charge transfer into n+1, leaving 2 bands partially occupied ⇒ METAL

Spin - Orbit Coupling and band structure

So far we ignored spin; in the spin-independent hamiltonian, spin is conserved:

So the ground state is:

$$\underset{\uparrow}{\psi_{n,k}(r)\begin{pmatrix}1\\0\end{pmatrix}} \quad \text{and} \quad \underset{\downarrow}{\psi_{nk}(r)\begin{pmatrix}0\\1\end{pmatrix}}$$

Two-fold degeneracy for a Bloch states:
We can say that we describe two diffent bands with spin ↑ (majority band)
and ↓ (minority band)

For spin-dependent hamiltonian we have SO Coupling:

$$H_{SO} = \frac{[\nabla V(r) \times p]\cdot S}{2m^2c^2}$$

← spin operator for e^-

Physically = Zeeman coupling between a magnetic moment of the e^- $\vec{\mu} = (-g/\hbar)\,\mu_B \vec{S}$ and the magnetic field in the rest frame of the e^-.

Recall in solid spherical symmetry is broken! and electrons cannot be classified by simple: $\lambda L\cdot S$ or $\vec{J} = \vec{L} + \vec{S}$

Because $[S_z\, H] \neq 0$

$$\psi_{kn}(r, \underset{\uparrow \text{ or } \downarrow}{\sigma}) = e^{ik\cdot r}\begin{pmatrix} u^{\uparrow}_{nk}(r) \\ u^{\downarrow}_{nk}(r)\end{pmatrix}$$

in non-spin dependent case n also carries σ and as such bands always has a degenerate pair

with H_{so} the degeneracy is lifted.

But: degeneracy still preserved for SOC if and only if

⊕ - spatial inversion
- time inversion

} symmetry

are semiltenıosly present

Few symmetry points:

Spin-orbit breaks spin rotation but preserves time-reversal

i.e.
$$r \rightarrow \theta r \theta^{-1} = \bar{r}$$
$$p \rightarrow -p$$
$$s \rightarrow -s$$

$$\Rightarrow \quad H_{so} \rightarrow \theta H \theta^{-1} \quad \text{or} \quad [\theta, H] = 0$$

As the result we have Kramers degeneracy
≡ all energy levels come in pairs.

i.e.
$$\begin{cases} H|\psi\rangle = \epsilon|\psi\rangle \\ H\theta|\psi\rangle = \epsilon|\psi\rangle \end{cases}$$

For $\boxed{\text{spin } 1/2}$ $\boxed{\hat{\theta} = \hat{\sigma}_y \hat{K}}$ ← omplex conjugation operator

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$ purely imaginary

Lets apply Θ to the ψ_{nk}

$$\Theta \psi_{nk}(r,\sigma) = (\sigma_y K)\, e^{ik\cdot r} \begin{pmatrix} u^{\uparrow}_{nk}(r) \\ u^{\downarrow}_{nk}(r) \end{pmatrix}$$

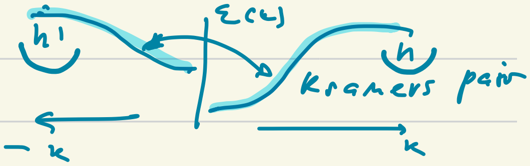
$$= +i\; e^{-ik\cdot r} \begin{pmatrix} -u^{\downarrow *}_{nk}(r) \\ +u^{\uparrow *}_{nk}(r) \end{pmatrix} = \psi_{n-k}(r,\sigma)$$

Thus we have a Kramers pair:

$$\left[\begin{matrix} \psi_{n,k}(r,\sigma) \\ \psi_{n,-k}(r,\sigma) \end{matrix}\right.$$

with $\epsilon_n(k) = \epsilon_{n'}(-k)$

But this does not mean that 2 dispersions are identical



Note in the presence of parity, P or inversion symmetry

$$r \rightarrow PrP = -r$$
$$p \longrightarrow p$$
$$S \longrightarrow S$$

if there a center of inversion such that $V(r) = V(-r)$, parity is a symmetry of hamiltonian H. B/c $k \xrightarrow[P]{} -k$

$$\Rightarrow \epsilon_n(k) = \epsilon_n(-k)$$

and if ΘP: $\epsilon_n(k) = \epsilon_n(-k)$

Lack of any of Θ and P there will no degeneracy.

! {in materials terms: non-centrosymmetric crystals and magnetic long-range ordered}

BAND STRUCTURE METHODS

CAN WE LATE CALCU 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

$$H = H_{\text{single atom}} + \Delta U \leftarrow \text{all differences between "real" crystal potential and isolated atom}$$

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

2) Single particle states are given by

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

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

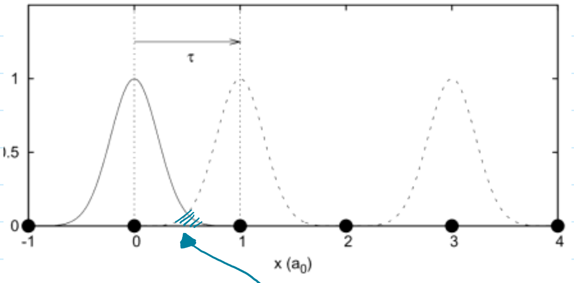
- Atomic w.f. $\phi_i(r)$

they are eigenstates of

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

ϵ_i ith 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 demands that w.f. must be:

$$\psi_{nk}(r+R) = e^{ikR}\psi_{nk}(r)$$

clearly ϕ_i are not good but what about

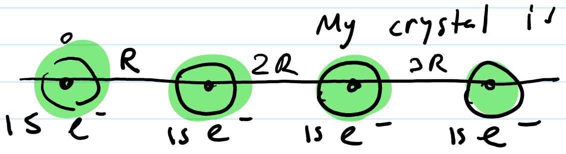
$$\psi_{nk}(\bar{r}) = \frac{1}{\sqrt{N}}\sum_R e^{i\bar{k}\cdot\bar{R}}\phi_n(\bar{r}-\bar{R}) \quad ?$$

here we assume N atoms in the xtal.

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

1st BAND STRUCTURE CALCULATION.

My crystal is a chain of hydrogen ions H^+



here we have only one band $\underline{n=1}$

$$|\psi_k\rangle = \psi_k(r) = \frac{1}{\sqrt{N}}\sum_R e^{ikR}\phi_s(r-R)$$

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

$$= \int \psi_k^* H \psi_k\, dr$$

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

$$= [x \equiv r - R] = \frac{1}{N}\sum_R\sum_{R'} e^{i(k-k')R}\int dx\, \phi_s(x) H \phi_s(x - \underbrace{(R'-R)}_{R''})$$

since $H(r-R) = H(r)$

For each specific R $R' - R \equiv R''$ is another translation vector

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

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

$$E(k) = \frac{1}{N}\sum_{R}\sum_{R''} e^{ikR''}\int dx\, \phi_s^*(x)\, H\, \phi_s(x-R'')$$

↑ since each term is the same $= \sum_R \Rightarrow N$

$$E(k) = \sum_{R''} e^{ikR''}\int \phi_s^*(x)\, H\, \phi_s(x-R'')\,dx$$

Now the w.f. rapidly decays $\int \phi_s^*(x)\, H\, \phi_s(x)\,dx = \epsilon_s$ if $R''=0$

if $|R''|$ large $\int \phi_s^* H\, \phi(x-R'')\,dx \approx 0$

So we need to include only terms where R'' is small $\approx \tau$. For TB we only consider terms where $|R''| = \text{small } \tau$

↑ just a translation vector between n-n atoms

thus we have

$$E(k) = \overset{R''=0}{\epsilon_s} + \sum_{R''\neq 0} e^{ikR''=\tau} \underbrace{\int \varphi_s^* H\, \varphi_s(x-\tau)\,dx}_{=\text{ call this parameter } \gamma}$$

$$\boxed{E(k) = \epsilon_s + \sum_{\tau} e^{ik\tau}\gamma(|\tau|)}$$

e.g. $\gamma(|\tau|) = A e^{-\alpha|\tau|^2}/|\tau|^2$ in Silicon, τ – overlap between n-n so can study strain, pressure

EXAMPLE 1 : 1D crystal

1D xtal $R = \pm a_0\cdot\vec{i}\cdot n$ $\left\{\vec{\tau} = \vec{\tau}_1 = \quad \vec{\tau}_2 = -a_0\vec{i}\right\}$ ← just two n-n translation vectors

$$(k)\,E = \epsilon_s + \sum_{\tau_1,\tau_2} e^{ik\tau}\gamma(|\tau|) =$$

$$= \epsilon_s + e^{ik\tau_1}\gamma(|\tau_1|) + e^{ik\tau_2}\gamma(|\tau_2|) =$$

$$= \epsilon_s + e^{ika_0}\gamma(|\tau|) + e^{-ia_0k}(|\tau|) =$$

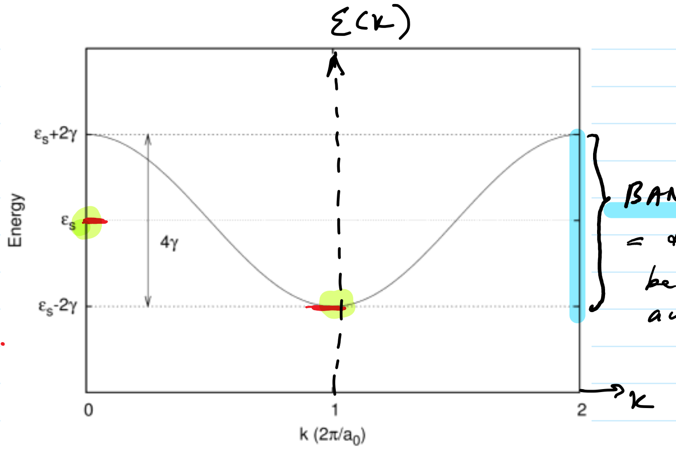
$$= \epsilon_s + \gamma(|\tau|)\left(\frac{e^{ika_0} + e^{a_0ki}}{2}\right) \times 2 =$$

$$= \epsilon_s + \gamma(|\tau|)\, 2\cos(ka_0)$$

Your 1st band structure for 1D solid!

METAL →

So → we lowered energy compared to isolated atoms!!!



BANDWIDTH = difference between min and max allowed values

Exercise: Calculate E(k) for 2D

Plot 2D case:
for a = Å 3 0.1, 5 d eV
1. eV
10 eV
THE same for 3D face centered cubic xtal of size a.
with 12 nn

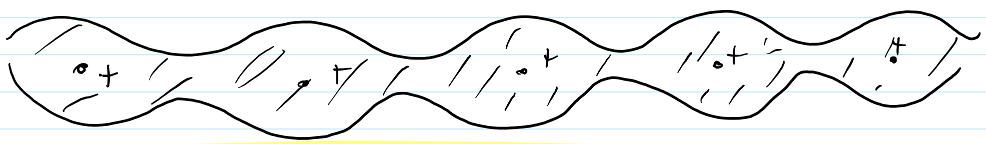
This is now a part of HW.

coming this week!

ORIGIN OF THE BANDS

Before we explain why atom condense in solids lets try to understand why molecule exists?

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



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

Superb electronic structure text!

For a hydrogen molecule we have 2 orbitals

ATOM 1	ATOM 2
$\|1\rangle$	$\|2\rangle$
1s	1s

Homopolar Solids

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

Variational principle

$$\sum_{\alpha} \langle \beta | H | \alpha \rangle v_\alpha - E v_\beta = 0$$

where $\langle \alpha | \beta \rangle = 0$

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

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

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

$$\begin{pmatrix} \overset{=\varepsilon_s}{\langle 1 | H | 1 \rangle} & \overset{=-V_2}{\langle 1 | H | 2 \rangle} \\ \overset{=-V_2}{\langle 2 | H | 1 \rangle} & \overset{=\varepsilon_s}{\langle 2 | H | 2 \rangle} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} - E \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$$

$$\begin{cases} (\varepsilon_s - E) v_1 - V_2 v_2 = 0 \\ -V_2 v_1 + (\varepsilon_s - E) v_2 = 0 \end{cases}$$

we can easily solve these and find

bonding state $\longrightarrow$ $\varepsilon_b = \varepsilon_s - V_2$ $\quad$ V_2 is called covalent energy and is positive

$\varepsilon_a = \varepsilon_s + V_2$

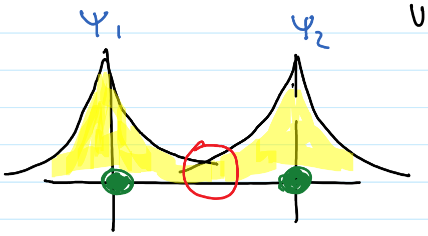
antibonding state

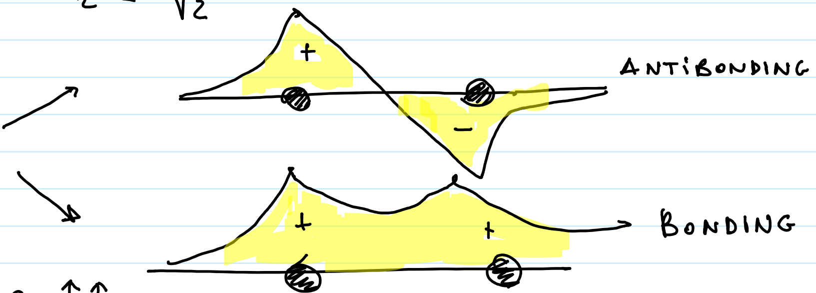
subs. these solutions into

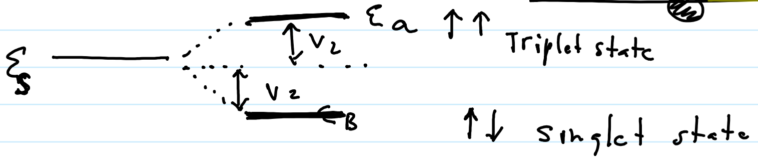
we determine the eigenvectors:

bonding : $v_1 = v_2 = \frac{1}{\sqrt{2}}$

$v_1 = -v_2 = \frac{1}{\sqrt{2}}$







Next we describe the case of a POLAR BOND → heteropolar solids

e.g. $\overset{+}{Li}\overset{-}{H}$ or $\overset{+}{Na}\overset{-}{Cl}$ etc.

Now we have to modify our matrix to account for the difference in the energy of the ground of state of $\varepsilon_s^1 \to$ anion

$\varepsilon_s^2 \to$ 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

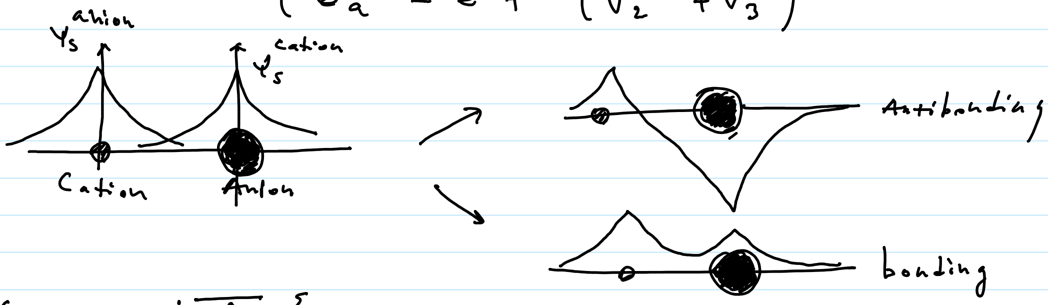
$$V_3 = \frac{\varepsilon_s^2 - \varepsilon_s^1}{2} \Longrightarrow \text{POLAR ENERGY}$$

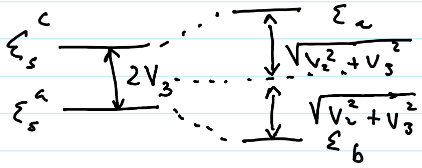
and also define the average of the cation-anion energy $\bar{\varepsilon} = \dfrac{\varepsilon_s^1 + \varepsilon_s^2}{2}$

then our equation becomes

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

$$\begin{cases} \varepsilon_b = \bar{\varepsilon} - (V_2^2 + V_3^2)^{1/2} \\ \varepsilon_a = \bar{\varepsilon} + (V_2^2 + V_3^2)^{1/2} \end{cases}$$





Notice how electronic charge distributes in the bonds!

THIS MEANS THE MOLECULE is POLAR!

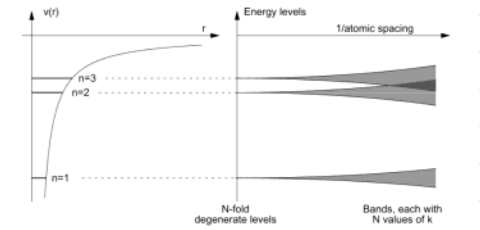
To describe the polarity mathematically we find v_1 and v_2, e.g. first put ε_b into

$$v_1 = \underbrace{\frac{V_2}{\sqrt{V_2^2 + V_3^2} - V_3}}_{\equiv \alpha_p \leftarrow \text{POLARITY}} v_2 \equiv \alpha_p v_2 \qquad v_1^2 - v_2^2 = \alpha_p$$

Another useful concept is covalency of the bond

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

Back to our solids.



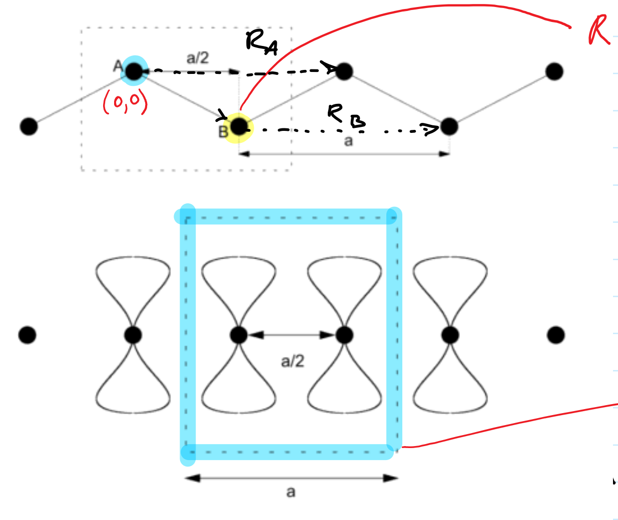
As overlap integral γ (or V_2 for the molecule) increases, the N atoms which form N degenerate states overlap and create bonding and antibonding states which called occupied and unoccupied states or valency bands conduction bands

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

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

this is very topological system, read textbook Ch.7.6

$R_{AB} = (a/2, a/2\sqrt{3})$



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:

25

So here
i = labels A or B,
$R_A = \pm a\hat{i}, \pm 2a\hat{i}$

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

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

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

e.g. for our polymer : $\bar{R}_B = \bar{R}_{AB} \pm a\hat{i}$,
$\bar{R}_{AB} \pm 2a\hat{i}$ etc.
where $\bar{R}_{AB}$ is the vector between A and B

Then the crystal is defined as:

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

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

$$\boxed{\begin{aligned} &\sum_i \left(H_{ij} - \delta_{ij} E(k) \right) c_{j,k} = 0 \\ &\text{where} \quad H_{ij} = \langle \Psi_{i,k} | H | \Psi_{j,k} \rangle \end{aligned}}$$

Back to our polymer:

2 - atom basis

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

where $H_{AB} = H^*_{BA}$ =>

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

2 branches for each K. → 2 BANDS
(Note 2 Atom PER Basis
= 2 BANDS)

Lets calculate H_{AA} and H_{BB} for ~~1~~ p-orbital contribution

Lets calculate H_{AA} and H_{BB} for 1 p-orbital/atom contribution

$$H_{AA} = \frac{1}{N} \underbrace{\sum_{R_A}}_{=N} \sum_{R_A'} \underset{= \bar{R}_A = ma\hat{i}}{e^{i(R_A' - R_A)}} \int \varphi_s^*(r - R_A) H \varphi_s(r - R_A') dr$$

$$= \sum_{R_A''} e^{ik \cdot R_A''} \int \varphi_s^*(x) H \varphi_s(x - R_A'') dx =$$

$$= \epsilon_p + \sum_{m \neq 0} e^{imka} \gamma(|ma|)$$ m is > 0 integer

The same for H_{BB}.

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

thus we end up with:

$$\boxed{H_{AA} = H_{BB} = \epsilon_p + 2\gamma(a) \cdot \mathrm{Cos}(ka)}$$

Following the same logic for H_{AB}

$$H_{AB} = \frac{1}{N} \sum_{R_A} \sum_{R_B} e^{ik(R_A - R_B)} \int \varphi_s^*(r - R_A) H \varphi(r - R_B) dr$$

$$= \sum_{R_A'} e^{ik(\bar{R}_{AB} + R_A')} \int \varphi_s^*(x) H \varphi_s(x - (R_{AB} + R')) dx$$

Again include only n-n: $R_A = 0$ and $R_A = -a\hat{i}$

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

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

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

then

$$H_{AB} = \left(e^{ika/2} + e^{-ika/2}\right) \gamma(|\tau|) =$$

$$= 2\,\mathrm{Cos}(ka/2)\, \gamma(|\tau|)$$

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

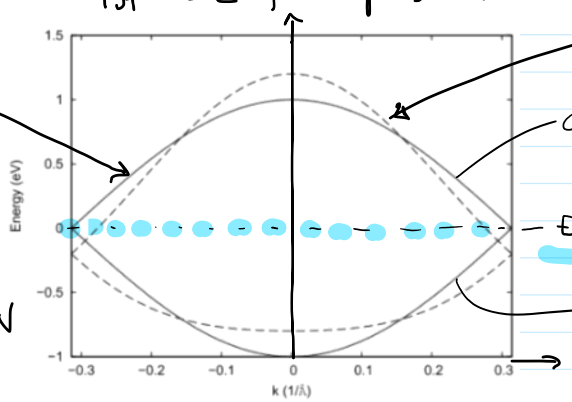
$$\cancel{E(k) = \epsilon_p + 2\gamma(a)\,\mathrm{Cos}(ka) \pm 2\,\mathrm{Cos}(ka/2)\,\gamma(|\tau|)}$$

Finally for:

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

1st BZ of transpolyacetelene

$\gamma(a)=0$ eV
$a = 10$ Å
$\epsilon_p = 0$ eV
$\gamma(|\tilde{\tau}|) = 0.5$ eV
Band with: $4\gamma(\tau) = 2$eV



$\gamma(a) = 0.1$ eV

I want to expand this line in 7.6.1 of the text

What about more than one orbital?

In graphene the lowest bands are made of s/px/py orbitals ⇒ sp2 bonding.

So lets generalize the tight binding approach

Imagine we have now $N_b = 2$ s, px, py, pz orbitals

We expect 2×4 bands to develop.
2 atoms in basis ↗ ↑ orbitals

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

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

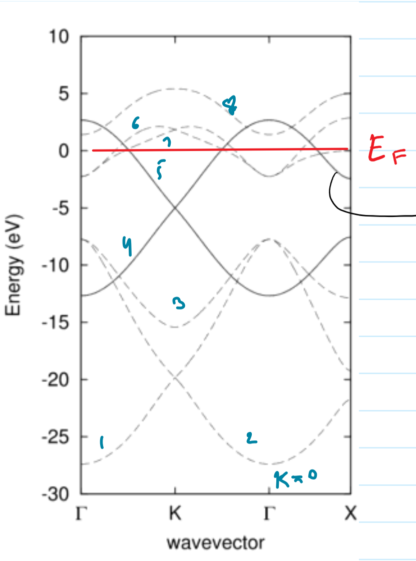
The hamiltoan matrix element will be:

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

The rest are similar:

Consider the bond structure of graphene

Graphene



As you can see there are clearly 8 bands

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

Next we will apply these ideas to tight binding on graphene.

Graphene electronic structure

Friday, October 26, 2018 2:11 PM

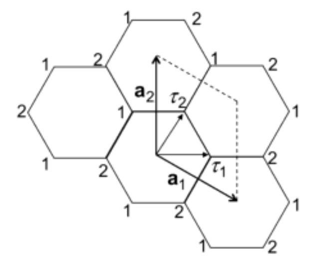
Recal that graphene spans a 2D hexagonal lattice with electrons doing sp_2 hybridization

← valence band state

↑ they make up conduction band

2D hexagonal lattice of graphene is shown below

where $\bar{a}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$ $\bar{a}_2 = a(0,1)$ where a is the lattice constant



The rhombic unit cell contains 2 carbons at the position

$$\bar{\tau}_1 = a\left(\frac{1}{\sqrt{3}}, 0\right) \quad \text{and} \quad \tau_2 = a\left(\frac{1}{2\sqrt{3}}, \frac{1}{2}\right)$$

The position of the rest of atoms can be generated by

$$\bar{\tau}_1 + \bar{R}, \quad \bar{\tau}_2 + \bar{R} \qquad \text{where } \bar{R} = n_1\bar{a}_1 + n_2\bar{a}_2$$

n_1 and $n_2 = 0, \pm 1, \pm 2$ etc.

But as usual you can sellect a different unit cell.

BTW. if you want the unit cell which refects clear hexagonal symmetry use <u>WIGNER - SEITZ cell</u> (see Simon's book)

Few notes:

1. $\bar{a}_1$ and $\bar{a}_2$ are not orthogonal and this is a problem b/c we will need many terms like $e^{ik.R}$

Suppose we write

$$\bar{R} = n_1 \bar{a_1} + n_2 \bar{a_2} \qquad n_1 n_2 = 0, 1, 2, \text{etc}$$

$$\bar{k} = k_1 \bar{b_1} + k_2 \bar{b_2}$$

this can be simple only if

$$k \cdot R = \sum_{i,j=1}^{2} k_i n_i \underbrace{b_i \cdot a_j}$$

Such as $\bar{b_j} \cdot \bar{a_i} = 2\pi \delta_{ji}$

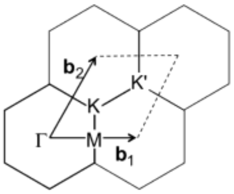
Then the phase factor

$$e^{i\bar{k}\bar{R}} = e^{i2\pi(k_1 n_1 + k_2 n_2)}$$

such inverse lattice vectors $\bar{b_1}$ and $\bar{b_2}$ are of course the reciprocal lattice

such that $K = m_1 b_1 + m_2 b_2$

This reciprocal lattice is shown below



To construct a Bloch wave we can take any k'

but if k' is outside of the cell span by b_1 and b_2

we alwey can $k' = k + K$

$$e^{iK \cdot R} = e^{i2\pi(m_1 n_1 + m_2 n_2)} = 1 \quad \Rightarrow$$

$$e^{ik'R} = e^{ikR}$$ so the ks inside the 1st

BZ cover all the values of k.

So let calculate $\bar{b_i} = (b_{i1}, b_{i2})$ demanding $\bar{b}_i \cdot \bar{a_j} = 2\pi \delta_{ij}$

$$\begin{cases} b_{11} a_{11} + b_{12} a_{12} = \frac{2\pi}{a} = b_{11} \frac{\sqrt{3}}{2} - b_{12} \frac{1}{2} \\ b_{11} a_{21} + b_{12} a_{22} = 0 = b_{12} \end{cases}$$

$$b_{21} a_{11} + b_{22} a_{12} = 0 = b_{21} \frac{\sqrt{3}}{2} - b_{22} \cdot 1/2$$

$$\left\{\begin{array}{l} b_{21}\, a_{11} + b_{22}\, a_{12} = 0 = b_{21}\frac{\sqrt{3}}{2} - b_{22}\cdot 1/2 \\ b_{21}\, a_{21} + b_{22}\, a_{22} = 2\pi/a = b_{22} \end{array}\right.$$

$$\longrightarrow \bar{b}_1 = \frac{2\pi}{a}\left(\frac{2}{\sqrt{3}}, 0\right) \qquad \bar{b}_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 1\right)$$

Labels or specia points in BZ:

$$\Gamma = \frac{2\pi}{a}(0,0) \qquad M = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 0\right) \qquad K = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, \frac{1}{3}\right)$$

$$\Gamma = 0b_1 + 0b_2 \qquad M = \frac{1}{2}b_1 + 0b_2 \qquad K = \frac{1}{3}b_1 + \frac{1}{3}b_2$$

$$K' = \frac{2}{3}b_1 + \frac{2}{3}b_2$$

NN tight Binding model

We need to calculate the matrix elements like

$$H_{11,k} = \sum_R e^{ikR} \langle \chi_1 | H | \chi_{1R} \rangle = \langle \chi_1 | H | \chi_1 \rangle = E_p$$

$$H_{22,k} = \cdots\cdots\cdots = \langle \chi_2 | H | \chi_2 \rangle = E_p$$

since only $R=0$ contributes and both atoms in the sublattice 1 and two are equivalent.

OFF - Diagonal:

$$H_{12,k} = \sum_R e^{ikR} \langle \chi_1 | H | \chi_{2R} \rangle = \overbrace{\langle \chi_1 | H | \chi_2 \rangle}^{\simeq t} \left(1 + e^{ika_1} + e^{-ika_2}\right)$$

$$H_{21,k} = \sum_R e^{ikR} \langle \chi_2 | H | \chi_{1R} \rangle = H^*_{12,k} = \overbrace{\langle \chi_2 | H | \chi_1 \rangle}^{\simeq t} \left(1 + e^{-ika_1} + e^{ika_2}\right)$$

<u>t is a hopping parameter</u>

t is a hopping parameter

thus

$$H_{12,k} = t\left(1 + e^{ika_1} + e^{-ika_2}\right) = t\left(1 + e^{i2\pi k_1} + e^{-i2\pi k_2}\right) =$$

$$= t_k$$

Finally:

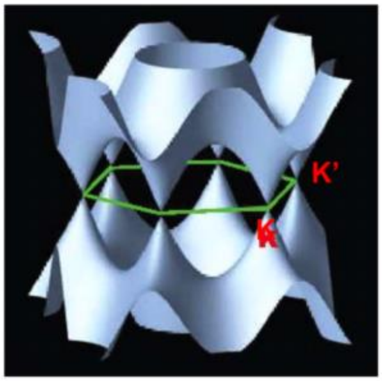
$$\begin{pmatrix} E_p & t_k \\ t_k^* & E_p \end{pmatrix}\begin{pmatrix} c_{1,k} \\ c_{2,k} \end{pmatrix} - E(k)\begin{pmatrix} c_{1,k} \\ c_{2,k} \end{pmatrix} = 0$$

$$E^{\pm}(k) = E_p \pm |t_k| = E_p \pm \sqrt{t_k^* t_k} =$$

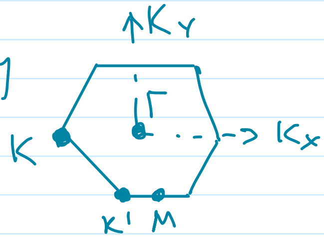
$$= E_p \pm t\sqrt{3 + 2\cos(2\pi k_1) + 2\cos(2\pi k_2) + 2\cos(2\pi(k_1 + k_2))}$$

and $\psi_k^+ = \begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ $\psi^- = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}$

So here is the 2D plot (try this in Mathematica)



High symmetry points:

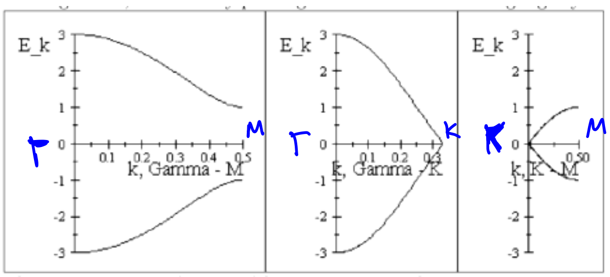


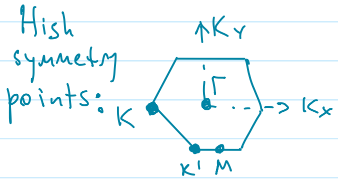
Consider now what happens in high symmetry points? The coordinates in the BZ are given above.

Γ: $E_p \pm 3t$ $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}$

$$\begin{cases} \Gamma: & \varepsilon_p \pm 3t & \frac{1}{\sqrt2}\begin{pmatrix}1\\1\end{pmatrix} \text{ and } \frac{1}{\sqrt2}\begin{pmatrix}1\\1\end{pmatrix} \\ M: & \varepsilon_p \pm t & \frac{1}{\sqrt2}\begin{pmatrix}1\\1\end{pmatrix} \text{ and } \frac{1}{\sqrt2}\begin{pmatrix}-1\\1\end{pmatrix} \\ K: & \varepsilon_p & \begin{pmatrix}1\\0\end{pmatrix} \text{ and } \begin{pmatrix}0\\1\end{pmatrix} \\ K': & \varepsilon_2 & \end{cases}$$

those are doubly degenerate!

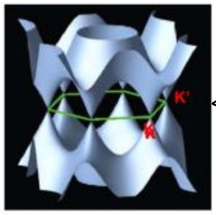




So FAR nothing too exciting, just another exersise in LCAO method 101.

But wait! lets move to the long-wave length.

- Each carbon has one electron in p_z state, assuming spin degeneracy we have the band ½ filled.
- It means the E_F right at K and K' points (also I used the fact that band structure is symmetric)



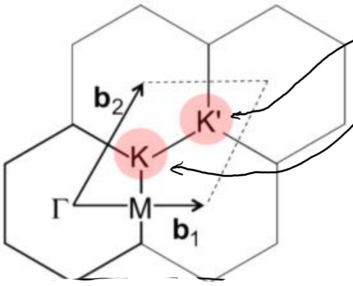
← E_F is here!

- As we know the only interesting states are near the Fermi edge, so lets study those in detail.

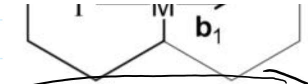
Consider $\bar{k} = \bar{K} + \bar{q}$
$\bar{k}' = \bar{K}' + \bar{q}$

we consider only states with $|q| \ll K$
or $K \sim \frac{1}{a} \Rightarrow qa \ll 1$, or $\lambda \gg a$
and $q'a \ll 1$

Long wave limit



What about Bloch wave phases?



$$\boxed{\begin{aligned} a_1 &= a\left(\tfrac{\sqrt{3}}{2} \quad -\tfrac{1}{2}\right) \\ \boxed{K} &\boxed{= \tfrac{2\pi}{a}\left(\tfrac{1}{\sqrt{3}} \quad \tfrac{1}{3}\right)} \end{aligned}}$$

phases! in the Long wave-length Limit
$K = K + q$; $qa \ll 1$

$$e^{ika_1} = e^{iKa_1} e^{iq a_1} \approx \approx (1 + iq\cdot a_1) \text{ b/c } q\cdot a \ll 1$$

$$\approx \underset{\uparrow}{e^{i\frac{2}{3}\pi}} (1 + i\bar{q}\cdot\bar{a}_1) = e^{i\frac{2}{3}\pi}(1 + iq_x a + iq_y a\sqrt{3})$$

$$a_1 K = 2\pi\left(\tfrac{\sqrt{3}}{2}\tfrac{1}{\sqrt{3}} - \tfrac{1}{2}\tfrac{1}{3}\right) = \tfrac{2}{3}\pi$$

in the same way
$$e^{ika_2} = e^{-iKa_2} e^{-iqa_2} = \approx e^{-i\frac{2\pi}{3}}(1 - iqa_2) = e^{-i\frac{2}{3}\pi}(1 - iq_x a + iq_y a\sqrt{3})$$

Recall $H_{12,k} \equiv t_k = t\,(1 + e^{ika_1} + e^{ika_2}) \cong$
$$\approx \frac{3a}{2} t\,(q_x - iq_y)$$

an similarly for K'
$$t_{K'} \cong \underset{\sim\sim}{\frac{3}{2}at}\,(q_x' + iq_y')$$

Let's define a new parameter = "Fermi velocity"
$$\boxed{\hbar v_F} \equiv -\frac{3}{2}at \qquad \text{and since } t < 0 \quad v_F > 0$$

since $\boxed{\text{for graphene } t = -3\text{ eV} \quad v_F \sim 10^6 \text{ m/sec}}$

– Next if we select our zero at E_p = the atomic values of p-orb.

$$\begin{pmatrix} E_p & t_k \\ t_k^* & E_p \end{pmatrix} \approx \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} \cdot \underline{\left(-\frac{3}{2}at\right)} =$$

$$= \underline{\hbar v_F}\left(\ \cdot\ \right) = \hbar v_F q_x \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\equiv \vec{\sigma}_x\,!} + \hbar v_F q_y \underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\equiv \vec{\sigma}_y\,/}$$

So formaly we have: the Pauli matrixes

$$\hbar v_F q_x \hat{\sigma}_x + \hbar v_F q_y \hat{\sigma}_y = \hbar v_F \bar{q}\cdot\bar{\sigma} = v_F \bar{p}\cdot\bar{\sigma}$$

Since $\hbar q \equiv p$

projection of momentum on spin

The eigenvalue problem now can be written as:

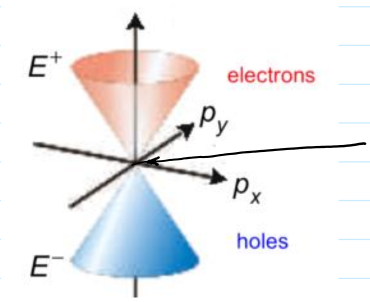
$$\begin{pmatrix} \varepsilon_p & t_k \\ t_k & \varepsilon_p \end{pmatrix}\begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix} = E_k \begin{pmatrix} c_{1k} \\ c_{2k} \end{pmatrix} \Rightarrow \boxed{\left(v_F \bar{p}\cdot\hat{\bar{\sigma}}\right)\psi_p = E\psi_p \quad \text{where } \psi_p = \begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} \text{spinor}}$$

Note: The component of ψ are NOT refering to spin up down but to the amplitudes of ψ on sublattice 1 and 2 of graphene

Lets solve the equation

$$\left(v_F\, p\cdot\sigma\right)\psi_p = E_p \psi \Rightarrow v_F \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix}\begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} = \begin{pmatrix} c_1 p \\ c_2 p \end{pmatrix} E_p$$

$$\boxed{E_p^{\pm} = \pm v_F \sqrt{p_x^2 + p_y^2} = \pm v|p|}$$



In undoped graphene

E_F only one k point is occupied $k \approx 0$

By gating or chemical doping we can fill up states with $p > 0$

or do the same for hole

So this is unique b/c of the complete symmetry of the 2D lattice

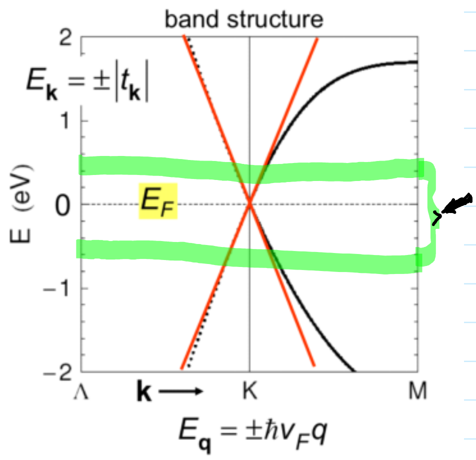
In majority conventional materials electron and holes are very different.

Put back $E_p^{\pm}$ we get the eigenvalues

$$\boxed{\psi_p^{\pm} = \begin{pmatrix} c_{1p} \\ c_{2p} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \pm 1 \\ e^{i\varphi_p} \end{pmatrix}}$$

where φ_p is the phase angle $\underline{p_x + ip_y} = e^{i\varphi_p} \cdot p$

But: If we move away from the long-wave length say > ±0.5eV the dispersion is not linear anylonge



linear only here

We will return to graphene when I will introduce electrons in magnetic field, Topology and quantum hole effect.

THE END OF THE

e-STRUCTURE MODULE.