

$E_n(\vec{k})$ = band structure \Rightarrow continuous, differentiable
 $\vec{p}_{n,m}$ = momentum operator $\equiv \langle \psi_n(\vec{k}) | \frac{\hbar}{i} \vec{\nabla}_r | \psi_m(\vec{k}) \rangle$

$$\vec{p}_{nn} = \frac{m}{\hbar} \vec{\nabla}_k E_n(\vec{k})$$

$\frac{\partial^2}{\partial k_\alpha \partial k_\beta} E_n(\vec{k})$ for free electrons $\equiv \frac{\hbar^2}{m}$

for crystals $E_n(\vec{k})$ is parabolic only at a few points in \vec{k} space. There we can write

$$\frac{\partial^2}{\partial k_\alpha \partial k_\beta} E_n(\vec{k}) = \frac{\hbar^2}{m^*} \equiv \text{tensor which depends on the direction of } \vec{k}.$$

m^* effective mass

$$\hbar^{-1} \epsilon_n(\vec{k}) = \frac{-\hbar^2}{2m} \nabla^2 + v \frac{\hbar}{2m} (\vec{k} \cdot \vec{\sigma}) + \frac{\hbar^2}{2m} k^2 - 2 \frac{\hbar^2}{2m} i \vec{k} \cdot \vec{\sigma}$$

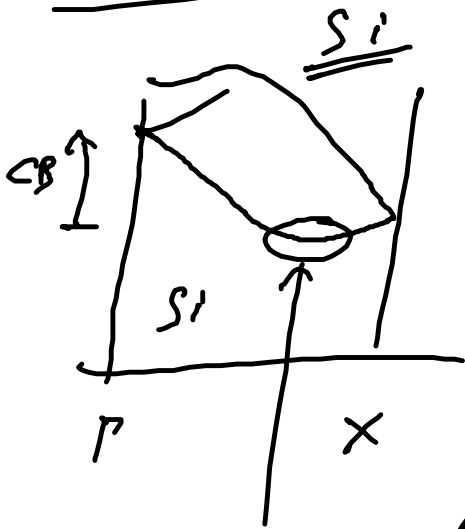
close to max. & min. it can be replaced by $-\frac{\hbar^2}{2m^*} \nabla^2$

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_n(\vec{k})}{\partial k_x \partial k_x}$$

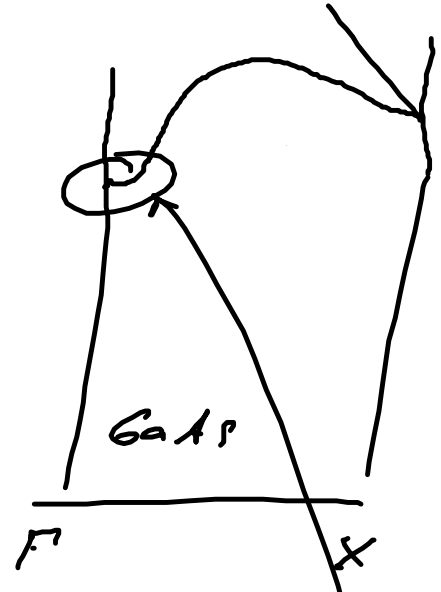
effective mass theory

it is of some - though limited - value still some people are using it.

2 examples



small curvature
small $\frac{1}{m^*}$
large m^*



high curvature
large $\frac{1}{m^*}$
small m^*

\Rightarrow switching is slower in Si than in GaAs

Time reversal reversal

(further properties of $E_n(k)$)

$T_t: t \rightarrow -t$ This operator reverses the state of motion.

time independent Schrödinger equation:

- position operator is invariant
- spin & momentum operators change sign.

Case A: System without spin-orbit coupling

$$\Rightarrow h = h^*$$

$\varphi_n(\vec{k}), \varphi_n^*(\vec{k})$ are they physically different?

$$h \varphi_n(\vec{k}, \vec{r}) = E_n(k) \varphi_n(\vec{k}, \vec{r})$$

$$h^* \varphi_n^*(\vec{k}, \vec{r}) = h \varphi_n^*(\vec{k}, \vec{r}) = E_n(k) \varphi_n^*(\vec{k}, \vec{r})$$

$\varphi_n(\vec{k}, \vec{r})$ and $\varphi_n^*(\vec{k}, \vec{r})$ have the same eigenvalue.

$$T_{\vec{R}_I} \varphi_n(\vec{k}, \vec{r}) = e^{i\vec{k}\vec{R}_I} \varphi_n(\vec{k}, \vec{r}) \quad \parallel \quad \vec{R}_I \in \text{Bravais lattice}$$

$$T_{\vec{R}_I} \varphi_n^*(\vec{k}, \vec{r}) = e^{-i\vec{k}\vec{R}_I} \varphi_n^*(\vec{k}, \vec{r})$$

$$T_{\vec{R}_I} \varphi_n(-\vec{k}, \vec{r}) = e^{-i\vec{k}\vec{R}_I} \varphi_n(\vec{k}, \vec{r})$$

$\varphi_n(\vec{k}, \vec{r})$: quantum numbers: n, \vec{k}
 $\varphi_n^*(\vec{k}, \vec{r})$: " : $n, -\vec{k}$
 $\varphi_n(-\vec{k}, \vec{r})$: " : $n, -\vec{k}$ } the same

$\varphi_n(-\vec{k}, \vec{r})$
 $\varphi_n^*(\vec{k}, \vec{r})$ is different to $\varphi_n(\vec{k}, \vec{r})$
 but have the same eigenvalue

$$\boxed{E_n(\vec{k}) = E_n(-\vec{k})}$$

B) Hamiltonian with spin-orbit
 coupling

$$\Rightarrow \boxed{E_n(\vec{k}, \uparrow) = E_n(-\vec{k}, \downarrow)}$$

see exercise

The Fermi surface

For metals at $T=0K$ all single particle states
 with $E_n(\vec{k}) \leq E_F$ are filled.

$$\boxed{E_n(\vec{k}) = E_F} \equiv \text{surface of constant energy in } \vec{k} \text{ space}$$

example jellium $E(\vec{k}) = \frac{\hbar^2}{2m} k^2$

Fermi surface \equiv sphere

$$|\vec{k}| = k_F = \sqrt{\frac{2m}{\hbar^2} E_F}$$

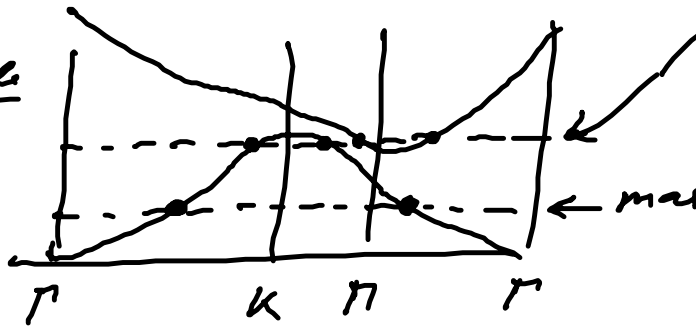
nearly free electrons = periodic potential

$$E_n(\vec{k}) = \frac{\hbar^2}{2m} (\vec{k} + \vec{G}_n)^2 = E_F$$

different bands will contribute

material # 2 = $E_F^{(2)}$

example



material $\in E_F^{(1)}$
Fermi surface
 \approx sphere

some examples

<http://www.phys.ufl.edu/fermisurface/>

The LCAO Method (tight binding)

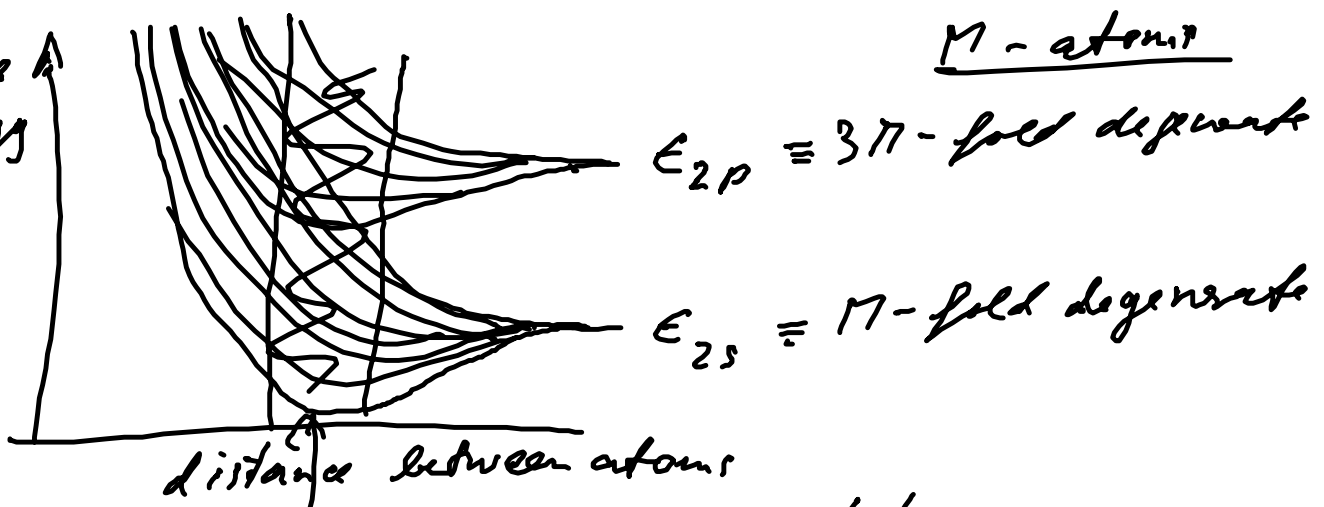
Linear combination of atomic orbitals

A solid may be viewed as matter between two limits

- a) nearly free electrons \leftarrow soft on emphasis
- b) weakly interacting (free) atoms

Case b) may reveal more about physics & chemistry of bonding (cohesion).

single particle energy



M - atoms

$$E_{2p} \equiv 3M\text{-fold degenerate}$$

$$E_{2s} \equiv M\text{-fold degenerate}$$

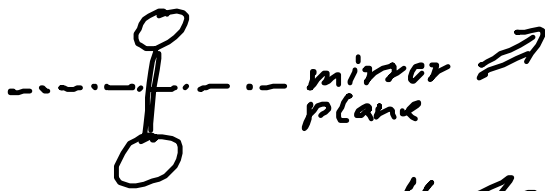
distance between atoms

typical range of equilibrium geometries of crystals.

Modern methods of calculating band structures usually combine concepts from both limits.

- pseudo potential theory
- linear muffin tin orbital method
- (linearized) augmented plane wave method

brief reminder about "chemical bond": H_2 molecule

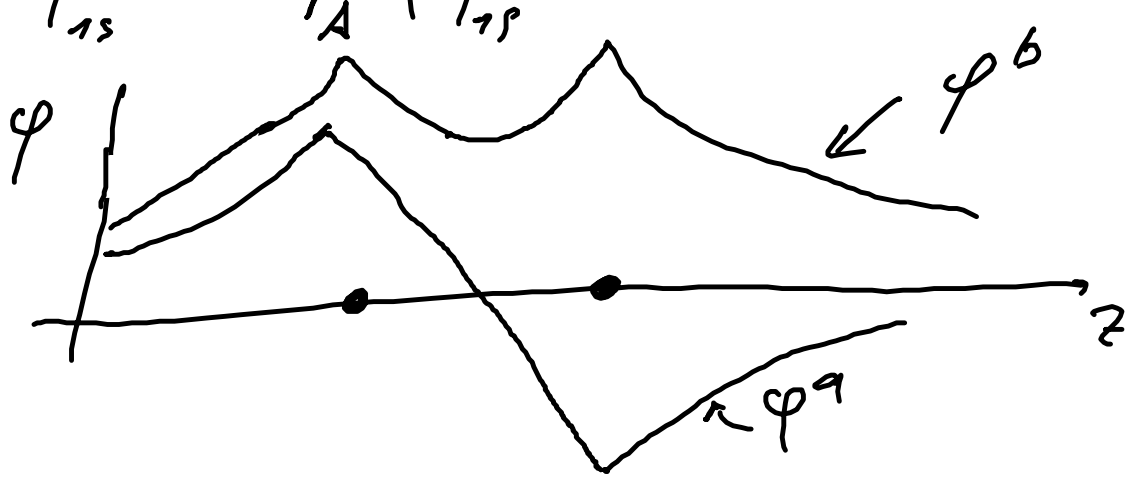


states are either symmetric or antisymmetric with respect to this mirror.

now consider $1s$ function \equiv basis function

$$\psi_{1s}^b(\vec{r}) = \frac{1}{\sqrt{A}} \left(\hat{\psi}_{1s}(\vec{r}-\vec{R}_1) + \hat{\psi}_{1s}(\vec{r}-\vec{R}_2) \right) \text{ bonding}$$

$$\psi_{1s}^a(\vec{r}) = \frac{1}{\sqrt{A}} \left(\hat{\psi}_{1s}(\vec{r}-\vec{R}_1) - \hat{\psi}_{1s}(\vec{r}-\vec{R}_2) \right) \text{ anti-bonding}$$



bonding \equiv lower energy than antibonding

sketch of bonding/antibonding situation

phase factor $+1$ $\left(\begin{array}{c} \oplus \\ \oplus \end{array} \right) \leftarrow s\text{-orbitals}$ phase of orbital
 \equiv bonding \equiv low (favorable) energy

-1 $\left(\begin{array}{c} \oplus \\ \ominus \end{array} \right) \leftarrow$ zero \equiv antibonding \equiv bad energy

now crystal using atomic orbitals as basis set
 sometimes "atomic like" or "atom centered"

Basis set: most faithful Bloch theorem

$$\chi_{\alpha}(\vec{k}, \vec{r}) = \frac{1}{\sqrt{A}} \sum_{\vec{R}_I} \gamma_I(\vec{k}) \hat{\varphi}_{\alpha}(\vec{r} - \vec{R}_I)$$

$N = \text{number of atoms}$

$\hat{\psi} = \text{atom center orbital}$

$$\psi_I(\vec{k}) = e^{i\vec{k}\vec{R}_I} \equiv \text{Bloch}$$

$$\alpha = 1s, 2s, 2p, 3s, \dots$$

For $N \rightarrow \infty$ # \vec{k} vectors also goes to ∞
and phase between neighboring atoms

goes from $+1 \dots -1$.

\mathbb{C} complex number

The $+1$ value for ψ_I is found for $\Gamma \in \vec{k} = (0, 0, 0)$

-1 " " " at edge of BZ
 $\vec{k} = \frac{1}{2}\vec{G} \Rightarrow e^{i\frac{1}{2}\vec{G}\vec{R}_I} = e^{i\pi} = -1$

We choose the basis normalisation as follows:

$$\langle \hat{\psi}_\alpha | \hat{\psi}_\beta \rangle = \delta_{\alpha\beta}$$

$\Rightarrow A = N \equiv \text{number of atoms}$

$\Rightarrow \chi_\alpha(\vec{k}, \vec{r})$ are not orthogonal

\Rightarrow KS orbitals:

$$\varphi_n(\vec{k}, \vec{r}) = \sum_{\alpha, \beta} c_{n, \alpha}(\vec{k}) \chi_\beta(\vec{k}, \vec{r})$$

KS equation read

$$\sum_{\beta} \left[h_{\alpha\beta} - \sum_{\alpha} S_{\alpha\beta} E_{\alpha}(\vec{k}) \right] c_{\alpha\beta}(\vec{k}) = 0$$

$$S_{\alpha\beta} \equiv \text{overlap} = \langle \chi_{\alpha}(\vec{k}, \vec{r}) | \chi_{\beta}(\vec{k}, \vec{r}) \rangle$$

and

$$h_{\alpha\beta} = \langle \chi_{\alpha}(\vec{k}, \vec{r}) | h | \chi_{\beta}(\vec{k}, \vec{r}) \rangle$$

$$= \sum_{\vec{R}_I, \vec{R}_J} e^{i\vec{k}\vec{R}_I} e^{-i\vec{k}\vec{R}_J} \langle \hat{\psi}_{\alpha}(\vec{r}-\vec{R}_I) | h | \hat{\psi}_{\beta}(\vec{r}-\vec{R}_J) \rangle$$

$$= \sum_{\vec{R}_I} e^{i\vec{k}\vec{R}_I} \underbrace{\langle \hat{\psi}_{\alpha}(\vec{r}-\vec{R}_I) | h | \hat{\psi}_{\beta}(\vec{r}) \rangle}_{E_{\alpha\beta}}$$

$$S_{\alpha\beta} = \sum_{\vec{R}_I} e^{i\vec{k}\vec{R}_I} \underbrace{\langle \hat{\psi}_{\alpha}(\vec{r}-\vec{R}_I) | \hat{\psi}_{\beta}(\vec{r}) \rangle}_{S_{\alpha\beta}}$$

$\hat{\psi}$ are very localized
 most of the element $h_{\alpha\beta}$ & $S_{\alpha\beta}$ are zero

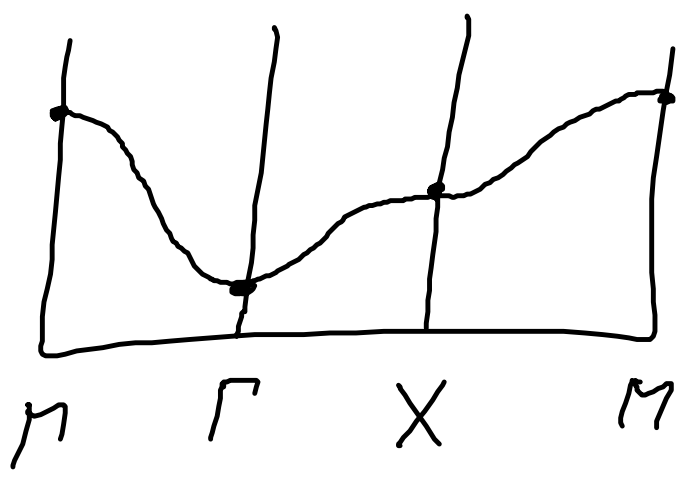
we now only use one orbital per atom (lecture)



qualitatively understand of the band structures even without a calculation - for 1s orbitals

k-point	$\Psi_n(\vec{k}, \vec{r})$	
Γ phase +1		fully bonding \Rightarrow low energy
X $\vec{k} = (\frac{\pi}{a}, 0)$		half bonding half antibonding \Rightarrow some mid energy
M $\vec{k} = (\frac{\pi}{a}, \frac{\pi}{a})$		fully antibonding "bad" energy

\Rightarrow band structure



band structure of s-states

p-states ;
square lattice

$p_z \perp$ to plane
 \hat{z} look very much
like s-states



\leftarrow antibonding

~~Ex~~

∞

The more bonding states are occupied (compared to antibonding states) the more stable is

is the material

e.g. Fe is harder than Cu. (see Cohesion)

The density of states

= number of states per unit volume at energy E

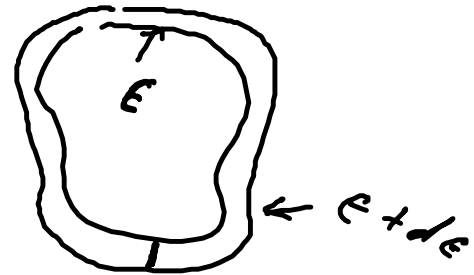
$$N(E) = \sum_n \frac{2}{(2\pi)^3} \int_{\text{BZ}} \delta(E - E_n(\vec{k})) d^3k$$

$N_n(E)$ = density of states of the n -th band

$N_n(E) dE$ = volume in k -space that lies in between $E_n(\vec{k}) = E$ and $E_n(\vec{k}) = E + dE$

$$N_n(E) dE = \frac{2}{(2\pi)^3} \int_{\text{BZ}} d^3k \left. \begin{array}{l} 1 \text{ if } E \leq E_n(\vec{k}) \leq E + dE \\ 0 \text{ otherwise} \end{array} \right\}$$

$$= \frac{2}{(2\pi)^3} \int_{E_n(\vec{k})=E} \delta(E - E_n(\vec{k})) d^3k$$



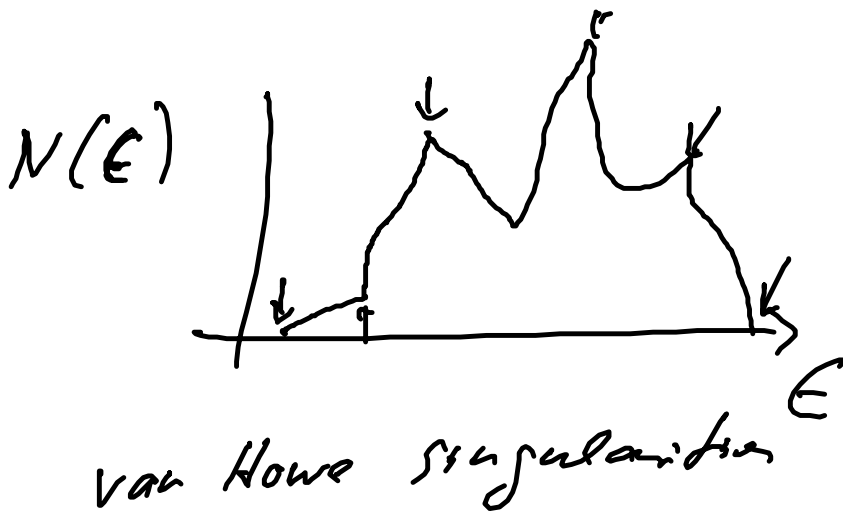
$$N_n(\epsilon) = \frac{2}{(2\pi)^3} \int_{E_n(\vec{k}) = \epsilon} \frac{1}{|\nabla_{\vec{k}} E_n(\vec{k})|} d^3k$$

$S_F(\vec{k})$
distance
between the
surface

$$\frac{d\epsilon}{dk} = \nabla_{\vec{k}} E_n(\vec{k})$$

characteristic structures
in $N_n(\epsilon)$ or $N(\epsilon)$ at points where

$$\nabla_{\vec{k}} E_n(\vec{k}) = 0$$



$$\nabla_{\vec{k}} E_n(\vec{k}) = 0$$