

$E_n(\vec{k}) =$  band structure  $\rightarrow$  continuous, differentiable  
 $\vec{p}_{n\alpha} \equiv$  momentum operator  $\equiv \langle \varphi_n(\vec{k}) | \frac{\hbar}{i} \vec{\nabla}_k | \varphi_n(\vec{k}) \rangle$

$$\vec{p}_{n\alpha} = \frac{\hbar}{i} \vec{\nabla}_k E_n(\vec{k})$$

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

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

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

$m^*$  effective mass

$$\tilde{h}(\vec{k}) = \frac{-\hbar^2}{2m} \nabla^2 + v \frac{\hbar}{v} \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} k^2 - 2 \frac{\hbar^2}{2m} i \vec{k} \cdot \vec{\nabla}$$

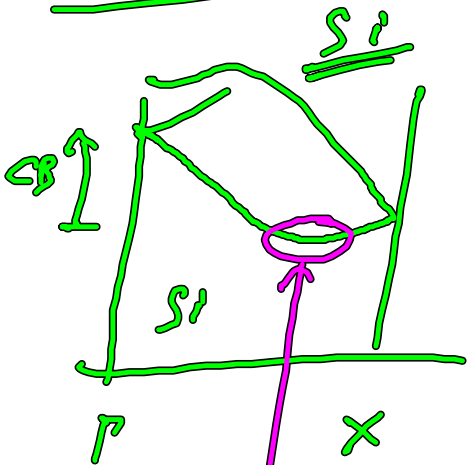
close to mat. & mil. it can be replaced by  $-\frac{\hbar^2}{2m^*} \nabla^2$

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

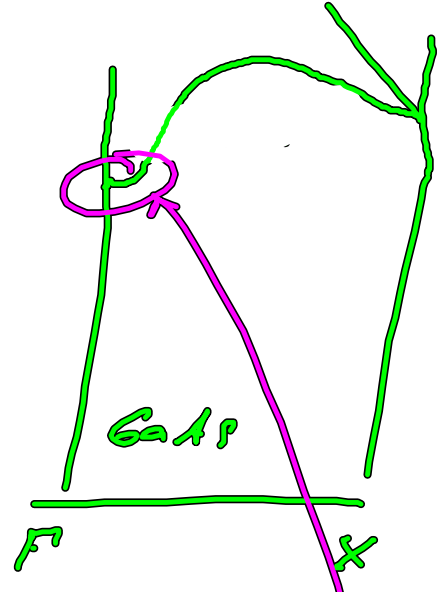
effective mass theory

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  $m^*$

⇒ switching is slower in Si than in GaAs

Time reversal reversal

(further properties of  $\epsilon_n(k)$ )

$T_t$ :  $t \rightarrow -t$  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?

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

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

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

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

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

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

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

$\varphi_n(-\vec{k}, \uparrow)$   
 $\varphi_n^*(\vec{k}, \uparrow)$  is different to  $\varphi_n(\vec{k}, \uparrow)$   
 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.

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

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

Fermi surface is sphere

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

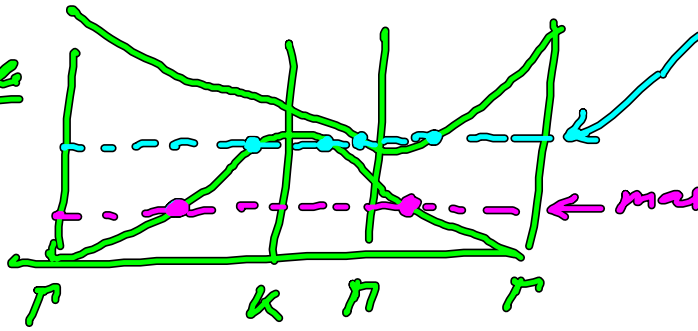
nearly free electrons & periodic potential

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

different bands will contribute

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

example



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

some examples

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

The LCAO Method (tight binding)

linear combination of atomic orbitals

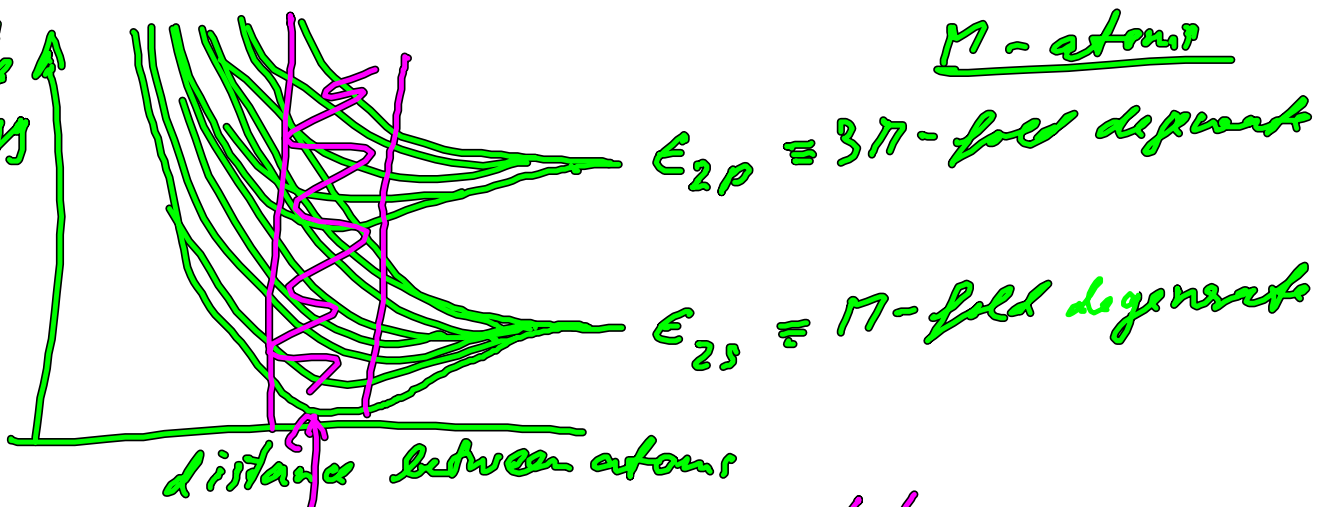
A solid may be viewed as matter between two limits

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

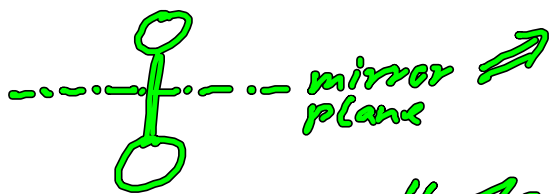


typical range of equilibrium geometries of crystals.

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

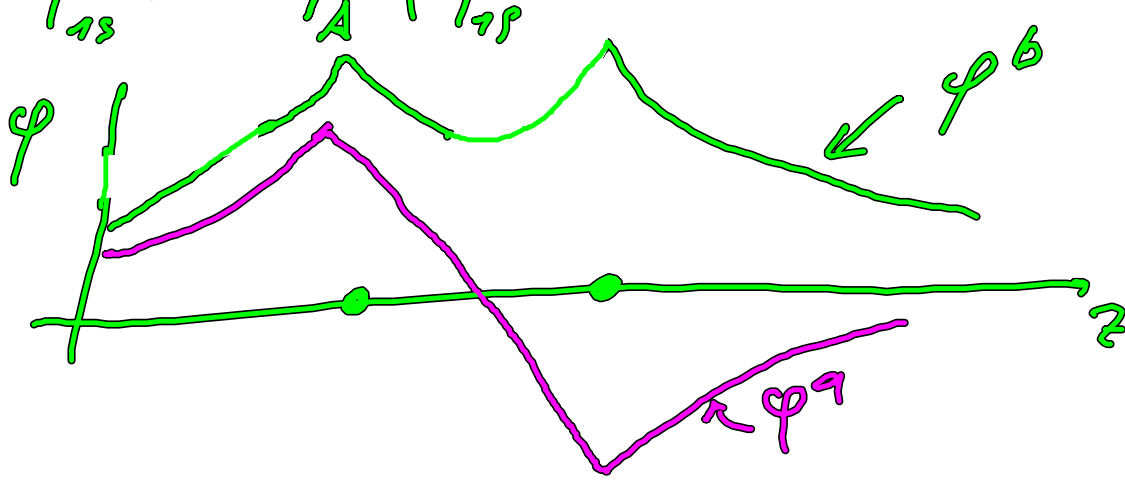


states are either symmetric or antisymmetric with respect to this mirror.

now consider  $1s$  function  $\equiv$  basis function

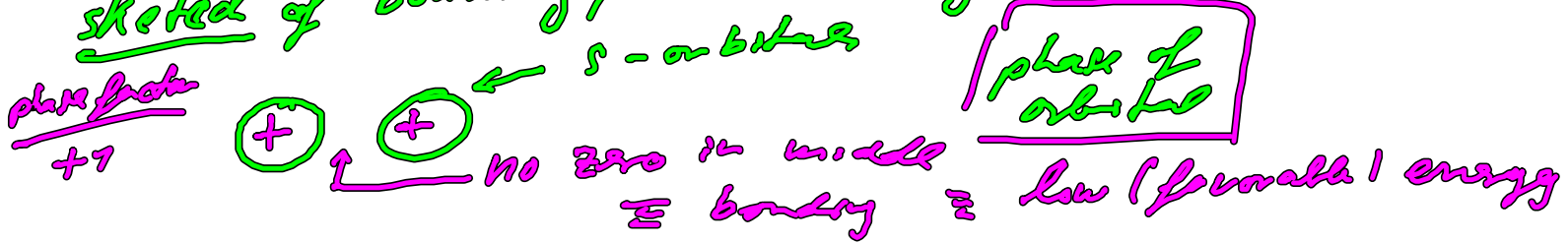
$$\psi_{1s}^b(\vec{r}) = \frac{1}{\sqrt{2}} \left( \hat{\psi}_{1s}(\vec{r}-\vec{R}_1) + \hat{\psi}_{1s}(\vec{r}-\vec{R}_2) \right) \text{ bonding}$$

$$\psi_{1s}^a(\vec{r}) = \frac{1}{\sqrt{2}} \left( \hat{\psi}_{1s}(\vec{r}-\vec{R}_1) - \hat{\psi}_{1s}(\vec{r}-\vec{R}_2) \right) \text{ anti-bonding}$$



bonding = lower energy than antibonding

sketch of bonding/antibonding situation



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

Basis set: most useful Bloch theorem

$$\chi_{\alpha}(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_I} \psi_I(\vec{k}) \hat{\psi}_{\alpha}(\vec{r} - \vec{R}_I)$$

$n =$  number of atoms

$\hat{\psi} =$  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  $\infty$   
and phase between neighboring atoms

goes from  $+1 \dots -1$ .

$\mathbb{C}$  complex number

The  $+1$  value for  $\psi_I$  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:

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

$\Rightarrow A = n =$  number of atoms

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

$\Rightarrow$  KS orbitals:

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



k s equation  $\vec{r} \text{ and } \vec{r}'$

$$\sum_{\beta} [h_{\alpha\beta} - S_{\alpha\beta} E_n(\vec{k})] c_{n,\beta}(\vec{k}) = 0$$

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

and

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

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

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

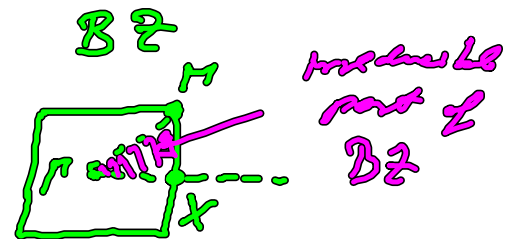
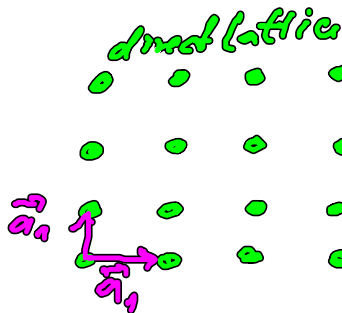
$$S_{\alpha\beta} = \sum_{\vec{R}_I} e^{i\vec{k}\vec{R}_I} \underbrace{\langle \hat{\psi}_{\alpha}(\vec{r}-\vec{R}_I) | \hat{\psi}_{\beta}(\vec{r}) \rangle}_{S_{\alpha\beta}}$$

$\hat{\psi}$  are very localized

most of the elements  $h_{\alpha\beta}$  &  $S_{\alpha\beta}$  are zero

we now only use one orbital per atom (lecture)

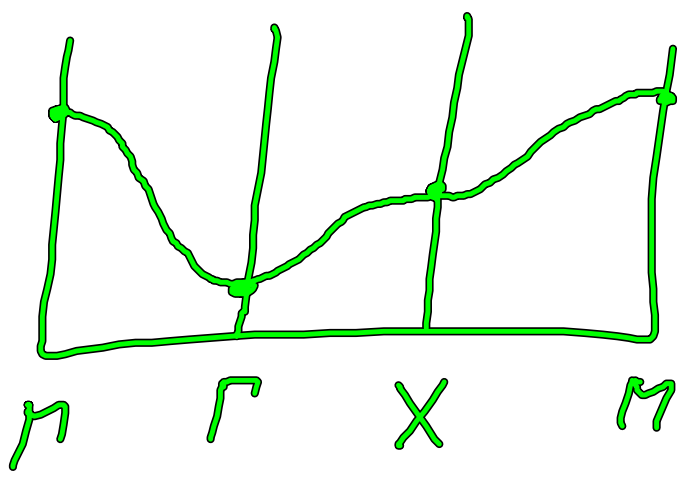
square lattice



quantum understand of the band structure even without a calculation - for 1s orbitals

k-point	$\psi_n(\vec{k}, \vec{r})$	
$\Gamma$ phase +1		<u>fully bonding</u> $\Rightarrow$ low energy
X $\vec{k}(\frac{\pi}{a}, 0)$		half bonding half antibonding $\Rightarrow$ same <u>mid</u> 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  
 $\vec{r}$  look very much like s-states

$p_x$



~~Ex~~



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

is the material

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

### The density of states

= number of states per unit volume at energy  $E$

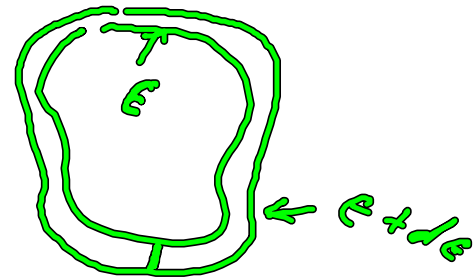
$$N(E) = \sum_n \frac{2}{(2\pi)^3} \int_{\text{BZ}} \delta(E - E_n(\vec{k})) d^3k$$

$N_n(E)$  = 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  $E_n(\vec{k}) = E + dE$

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

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

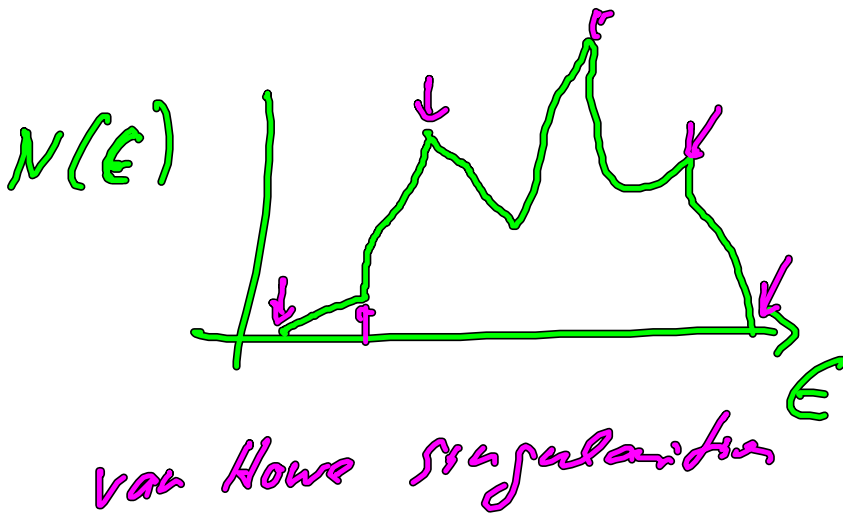


$$N_n(E) = \frac{2}{(2\pi)^3} \int_{E_n(\vec{k})=E} \frac{1}{|\nabla_{\vec{k}} E_n(\vec{k})|} d\vec{k}$$

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

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

characteristic structures  
in  $N_n(E)$  or  $N(E)$  at points where  
 $\nabla_{\vec{k}} E_n(\vec{k}) = 0$



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