

The approximations:

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The Hamiltonian of a piece of matter is

$$(T_e + T_N + V_{ee} + V_{eN} + V_{NN}) \Phi(\{\bar{r}\}, \{\bar{R}\}) = E \Phi(\{\bar{r}\}, \{\bar{R}\})$$

$T_e$  = kinetic energy operator of all the electrons

$T_N$  = " " " " " " " nuclei

$V_{ee}$  = Coulombian electron-electron repulsion

$V_{NN}$  = " " nucleus-nucleus "

$V_{eN}$  = " " electron-nucleus attraction

$\Phi$  is the wavefunction of  $\approx 10^{23}$  nuclei, electrons

$\{r\}$  is the set of the electron coordinates

$\{R\}$  is the set of the coordinates of the nuclei

Born-Oppenheimer approximation (Adiabatic approx.)

Let us assume  $\Phi(\{\bar{r}\}, \{\bar{R}\}) = \Psi_{\{\bar{R}\}}(\{\bar{r}\}) \chi(\{\bar{R}\})$

then  $(T_e + V_{ee} + V_{eN}) \Psi_{\{\bar{R}\}}(\{\bar{r}\}) = E_e \Psi_{\{\bar{R}\}}(\{\bar{r}\})$

$(T_N + V_{NN} + E_e) \chi(\{\bar{R}\}) = E \chi(\{\bar{R}\})$  if we neglect

terms such as  $\nabla_R \chi \nabla_R \Psi$  .....

this is valid if  $M \gg m$  ( $M$  mass of the nucleus  
 $m$  electron mass)

$$(T_e + V_{ee} + V_{eN}) \Psi_{\{R\}}(\{r\}) = E_{e\{R\}} \Psi_{\{R\}}(\{r\})$$

gives the wavefunction of the electrons for fixed Nuclei coordinates  $\{R\}$ . It is a wavefunction of  $\approx 10^{23}$  variables  $\{r\}$ .

Independent electron approx (or single electron approximation)

$V_{ee}$  couples the electron coordinates. Let us replace this term with the average potential ~~seen~~ seen by one electron in  $\vec{r}$  caused by all the other electrons.

Let us use the mean field instead of the actual field (mean field approximation).

In this way the problem of  $\approx 10^{23}$  electrons interacting with themselves reduces to the problem of single electrons in a mean field

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

where  $\phi(r)$  is the single electron wave function and

$V(r)$  is the potential of the Nuclei + the average potential of the other electrons

(Approx: Independent electron approx)

(each electron in the mean field of the other electrons and of the ions)

$$\underbrace{-\frac{\hbar^2 \nabla^2}{2m} \Phi + V_c \Phi}_{H_{\text{cryst}} \Phi} = E \Phi$$

$V_c(\vec{r})$  is the potential of the perfect crystal  
 $\Phi$  are Bloch wavefunct.

Let us add a potential that is not periodic  $U(\vec{r})$   
(e.g. an external electric field, an impurity, the "end" of the crystal ---)  
(boundary)

$$\underbrace{-\frac{\hbar^2 \nabla^2}{2m} \Psi + V_c \Psi + U \Psi}_{H_{\text{cryst}} \Psi} = E \Psi$$

$\Psi$  are the new wavefunctions of the new system (crystal with a field, or an impurity, or a boundary ---)

They are not Bloch functions.

Because the Bloch functions are an orthonormal complete set

$$\phi_{\vec{k},n} = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k},n}(\vec{r})$$

$$\Psi = \sum_n \int d^3\vec{k} c_{\vec{k},n} \phi_{\vec{k},n}$$

The problem is : how to calculate  $c_{n,\vec{k}}$

It is easier if the potential  $U(\vec{r})$  is a <sup>small</sup> perturbation. We can use first order perturbation theory.

Perturbation theory :

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

$$\Rightarrow (H_0 + \lambda V) |N\rangle = E_N |N\rangle$$

$$|n^{(1)}\rangle = \sum_{k \neq n} \frac{\langle k^0 | V | n^0 \rangle}{E_n^{(0)} - E_k^{(0)}} |k^0\rangle$$

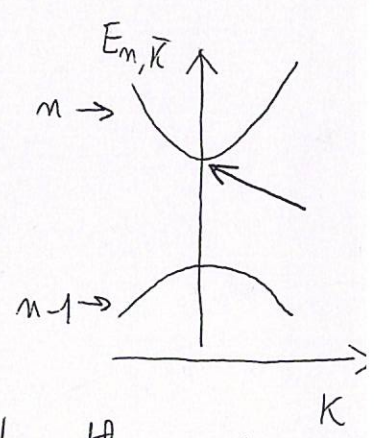
if  $H = H_0 + \lambda V \Rightarrow$

$$E_N = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$|N\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots$$

Perturbation theory tells us that  $c_{n,\vec{k}}$  will be appreciable only if  $E_{n,\vec{k}}$  is very close to the energies of the state we are ~~was~~ taking into account, if  $U(r)$  is "small".

Let us assume this band structure of the unperturbed crystal.



Let us turn on the perturbation  $U(r)$  and see what happens to the state ~~marked~~ pointed by the arrow.

It is a state belonging to the  $n$ th band (when  $U(r)=0$ ),  
it is  $e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(r)$  for  $\vec{k}=0$ ,  
~~is~~ far in energy from the other bands.

When  $U(r)$  is  $\neq 0$  but "small" this state evolves  
from 1.  $u_{n,0}(r)$  to  $\psi \approx \int d^3k e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r}) c_{n,\vec{k}}$

because  
with  $c_{n,\vec{k}}$  not negligible only for small  $\vec{k}$  and no  
summation on  $n$  because other states on other  
bands are far in energy. (remember

$$|n^{(1)}\rangle = \sum_{K \neq n} \frac{\langle K^{(0)} | V | n^{(0)} \rangle}{E_n^{(0)} - E_K^{(0)}} |K\rangle$$

If  $\psi \approx \int d^3k e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(r) c_{n,\vec{k}}$  and  $c_{n,\vec{k}} \neq 0$  for small  $\vec{k}$  only

then  $\psi \approx \int d^3k e^{i\vec{k}\cdot\vec{r}} u_{n,0}(r) c_{n,\vec{k}} \approx u_{n,0} \tilde{c}_n(r)$

$\hat{E}(r) = \int d^3k e^{i\vec{k}\cdot\vec{r}} c_{n,\vec{k}}$ , the Fourier transform of  $c_{n,\vec{k}}$

So the old wave function 1.  $u_{n,0}(r)$  becomes  
 $\tilde{c}_n(r) u_{n,0}(r)$  when  $U(r) \neq 0$ .

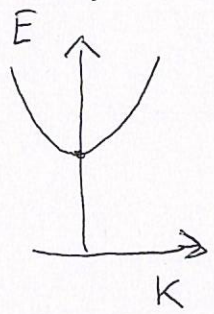
Now we have to find  $\tilde{c}_n(r)$

$$\underbrace{\left( \frac{-\hbar^2 \nabla^2}{2m} + V_{\text{cryst}} + \bar{U} \right)}_{H_{\text{cryst}}} \psi = E \psi \quad \psi = \int d^3k \phi_{\mathbf{k}}^{(r)} c_{\mathbf{k}}$$

$$\int d^3k H_{\text{cryst}} \phi_{\mathbf{k}}^{(r)} c_{\mathbf{k}} + \bar{U}(r) \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)} = E \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)}$$

$$\int d^3k E_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)} c_{\mathbf{k}} + \bar{U}(r) \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)} = E \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)}$$

for  $k \approx 0$   $E_{\mathbf{k}} = E_0 + \frac{\hbar^2 k^2}{2m^*}$



$m^*$  = electron effective mass  
 $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$

⇓

$$\frac{\hbar^2}{2m^*} \int d^3k k^2 c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)} + \bar{U}(r) \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)} = (E - E_0) \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)}$$

let us multiply by  $\phi_{\mathbf{k}'}^{*(r)}$  and integrate in  $d^3r$

$$-\frac{\hbar^2}{2m^*} k'^2 c_{\mathbf{k}'} + \int d^3r \phi_{\mathbf{k}'}^{*(r)} \bar{U}(r) \int d^3k c_{\mathbf{k}} \phi_{\mathbf{k}}^{(r)} = (E - E_0) c_{\mathbf{k}'}$$

this is  $\approx \int d^3r e^{i\mathbf{k}' \cdot \mathbf{r}} u_0^*(r) \bar{U}(r) \int d^3k c_{\mathbf{k}} u_0(r) e^{i\mathbf{k} \cdot \mathbf{r}} =$

$$\int d^3r e^{-i\mathbf{k}' \cdot \mathbf{r}} u_0^*(r) u_0(r) \bar{U}(r) \int d^3k c_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} = \int d^3r e^{i\mathbf{k}' \cdot \mathbf{r}} |u_0(r)|^2 \bar{U}(r) c_{\mathbf{k}'}$$

If  $U(r)$  is a smooth function,  $\left( a \cdot \frac{\partial U}{\partial r} \ll U \right)$  7  
 $\Rightarrow c_k \neq 0$  only for small  $k$ ,  $a =$  lattice parameter

$U(r)$  is nearly constant over a unit cell

$$\int d^3r e^{-i\mathbf{k}' \cdot \mathbf{r}} |u_0(r)|^2 U(r) \tilde{c}(r) \simeq$$

$$\sum_{\mathbf{R}} e^{-i\mathbf{k}' \cdot \mathbf{R}} U(\mathbf{R}) \tilde{c}(\mathbf{R}) \int_{\text{cell}} d^3r |u_0(r)|^2 = \frac{1}{N}$$

$N =$  number of cells

Bravais lattice vectors

$$= \frac{1}{N} \sum_{\mathbf{R}} e^{i\mathbf{k}' \cdot \mathbf{R}} U(\mathbf{R}) \tilde{c}(\mathbf{R})$$

$$\frac{\hbar^2}{2m^*} k'^2 c_{\mathbf{k}'} + \int d^3r e^{-i\mathbf{k}' \cdot \mathbf{r}} U(r) \tilde{c}(r) = (E - E_0) c_{\mathbf{k}'}$$

let us multiply by  $e^{i\mathbf{k}' \cdot \mathbf{r}'}$  and integrate over  $\mathbf{r}'$

$$-\frac{\hbar^2 \nabla^2}{2m^*} \tilde{c}(r) + \int d^3r' U(r') \tilde{c}(r') \delta(r-r') = (E - E_0) \tilde{c}(r)$$

$$\left( -\frac{\hbar^2 \nabla^2}{2m^*} + U(r') \right) \tilde{c}(r') = (E - E_0) \tilde{c}(r')$$