S.E: $H\psi_n = E_n \psi_n$ (using a somewhat simplified notation!)

with

$$H = H_a + \Delta V$$

$$E_n = \varepsilon_n + \Delta\varepsilon_n$$

Multiply SE with $\int d^3r\, \chi_n^*$:

$$\int d^3r\, \chi_n^* \left(H_a + \Delta V \right) \psi_n = E_n \int d^3r\, \chi_n^* \psi_n$$

Here, since H_a is hermitian,

$$\int d^3r\, \chi_n^* H_a \psi_n = \int d^3r\, \psi_n \left(H_a \chi_n\right)^* = \int d^3r\, \psi_n \left(\varepsilon_n \chi_n\right)^*$$

$$= \varepsilon_n \int d^3r\, \chi_n^* \psi_n$$

$$\Rightarrow E_n(\vec{k}) = \varepsilon_n + \frac{\int d^3r\, \chi_n^* \Delta V \psi_n}{\int d^3r\, \chi_n^* \psi_n}$$

$$= \varepsilon_n + \frac{\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \int d^3r\, \chi_n^*(\vec{r})\, \Delta V\, \chi_n(\vec{r}-\vec{R})}{\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \int d^3r\, \chi_n^*(\vec{r})\, \chi_n(\vec{r}-\vec{R})}$$

<u>Overlap integrals</u> are assumed to be negligible for different atoms:

$$\int d^3r\, \chi_n^*(\vec{r})\, \chi_n(\vec{r}-\vec{R}) = \delta_{\vec{R},0}$$

<u>Transfer integrals</u> (or "hopping integrals"):

$$\gamma(\vec{R}) = \int d^3r\, \chi_n^*(\vec{r})\, \Delta V\, \chi_n(\vec{r}-\vec{R}) = \sum_{\vec{R}' \neq 0} \int d^3r\, \chi_n(\vec{r})\, V_a(\vec{r}-\vec{R}')\, \chi_n(\vec{r}-\vec{R})$$

One usually keeps only $\vec{R} = 0$ and $\vec{R} = \vec{R}_{nn}$ = nearest neighbours

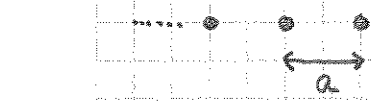
$$\Rightarrow \boxed{E_n(\vec{k}) = \varepsilon_n + \gamma(0) + \sum_{nn} e^{i\vec{k}\cdot\vec{R}}\,\gamma(\vec{R})}$$

$$\gamma(0) = \sum_{\vec{R}'\neq 0} \int d^3r\, |\chi_n(\vec{r})|^2\, V_a(\vec{r}-\vec{R}')$$

= a small (since $\vec{R}' \neq 0$) and constant contribution

$\gamma(\vec{R}_{nn}) = \gamma$ = empirical parameter, has the same value for all $\vec{R}_{nn}$ for a given atomic orbital χ_n, determines band width and/or effective mass

Simplest possible <u>example</u>: 1D lattice, 1 atomic orbital, atomic level ε



$\vec{R}_j = j\cdot a\,\hat{x}$, $\vec{K}_\ell = \ell \cdot \frac{2\pi}{a}\,\hat{x}$

$\Rightarrow$ 1BZ: $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$

$E_0 = \varepsilon + \gamma(0)$

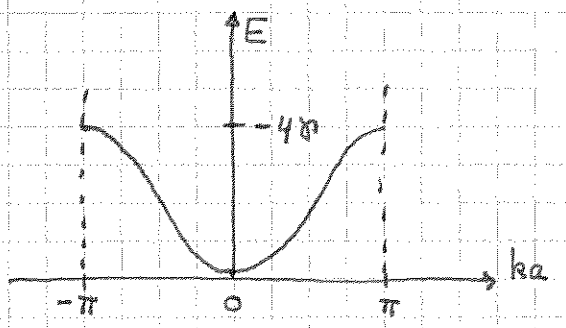
$$\Rightarrow E(k) = E_0 + \gamma \sum_{nn} e^{ikR_{nn}} = E_0 + \gamma\left(e^{ika} + e^{-ika}\right)$$

$$= E_0 + 2\gamma \cos ka$$

$\gamma < 0$ (assume e.g. s-state, and $V_a < 0$)

$E(0) = 0$ if $E_0 = -2\gamma$

$\Rightarrow E(k) = -2\gamma\,(1-\cos ka)$



Small k: $1-\cos ka \approx \frac{1}{2}k^2a^2$

$\Rightarrow E(k) = \hbar^2k^2/2m$ if $\gamma = -\hbar^2/2ma^2$

In general, for symmetric $E(k)$:

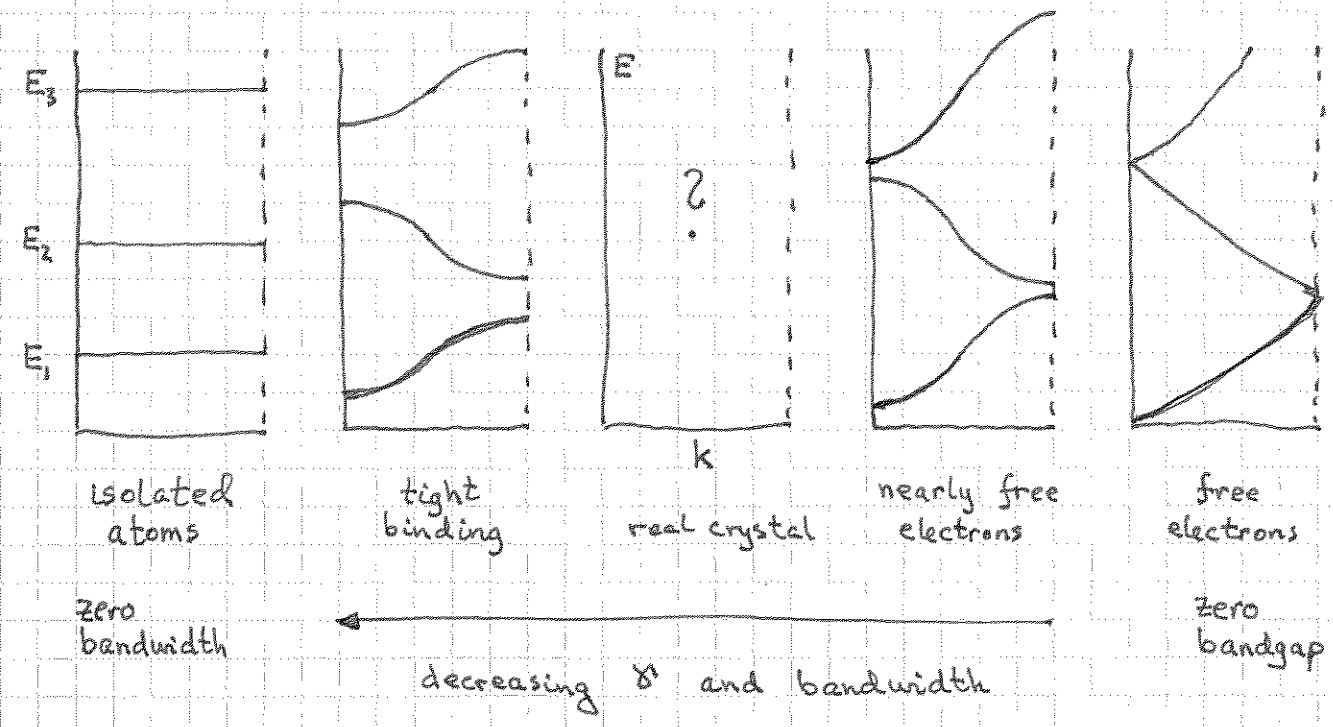
$$E(k) = E(0) + \frac{1}{2} \left(\partial^2 E / \partial k^2 \right)_{k=0} \cdot k^2 + \dots$$

$\Rightarrow$ <u>Effective mass</u>: $m^* = \hbar^2 \left[\left(\partial^2 E / \partial k^2 \right)_{k=0} \right]^{-1}$

Generalizations:

- 1D $\rightarrow$ 2D or 3D
- 1 atomic orbital $\rightarrow$ several atomic orbitals (e.g. s, p_x, p_y, p_z)
- 1 atom in basis $\rightarrow$ several atoms in basis (e.g. graphene, Exercise 2)

Band structure as function of potential strength:



Convenient "bra - ket" notation

assume 1D, 1 orbital pr atom

$|j\rangle$ = orbital centered on atom ("site") j

$|x\rangle$ = eigenstate for position operator: $\hat{x}|x\rangle = x|x\rangle$

Completeness: $\sum_j |j\rangle\langle j| = 1$ ($\int dx\, |x\rangle\langle x| = 1$)

Orthogonality and normalization: $\langle i|j\rangle = \delta_{ij}$ ($\langle x'|x\rangle = \delta(x'-x)$)

$\langle x|j\rangle = \chi(x-x_j)$, $\langle j|x\rangle = \chi^*(x-x_j)$

$$\Rightarrow \int dx\, \chi^*(x-x_i)\chi(x-x_j) = \int dx\, \langle i|x\rangle\langle x|j\rangle = \langle i|j\rangle = \delta_{ij}$$

Bloch functions:

$$|\psi\rangle = \sum_j c_j |j\rangle \quad \text{with } c_j = e^{i\vec{k}\cdot\vec{R}_j} \overset{1D}{=} e^{ikja}$$

$$\Rightarrow \psi(x) = \langle x|\psi\rangle = \sum_j c_j \langle x|j\rangle = \sum_j e^{ikja}\,\chi(x-x_j) \quad \text{(OK!)}$$

$$\langle \ell|\psi\rangle = \sum_j c_j \langle \ell|j\rangle = \sum_j c_j \delta_{\ell j} = c_\ell$$

$$\Rightarrow \quad c_j = \langle j|\psi\rangle$$

Example of generalization: Graphene, 2 carbon atoms in primitive cell, e.g. in positions $(0,0)$ and $(a,0)$ for "site nr 0"

$$\Rightarrow |\psi\rangle = \sum_A c_A |A\rangle + \lambda \sum_B c_B |B\rangle$$

with $c_A = e^{i\vec{k}\cdot\vec{R}_A}$, $c_B = e^{i\vec{k}\cdot\vec{R}_B}$, $|\lambda| = 1$

$\underbrace{\vec{R}_A = n_1\vec{a}_1 + n_2\vec{a}_2}_{\text{triangular sublattice A}}$, $\underbrace{\vec{R}_B = \vec{R}_A + a\hat{x}}_{\text{triangular sublattice B}}$

Dynamics of electrons in crystals

Dispersion relation:

For classical wave packet:

$$\vec{v}_g = \nabla_k \omega = \text{group velocity}$$

$$\nabla_k = \hat{x}\frac{\partial}{\partial k_x} + \hat{y}\frac{\partial}{\partial k_y} + \hat{z}\frac{\partial}{\partial k_z} = \sum_{i=1}^{3} \hat{x}_i \frac{\partial}{\partial k_i}$$

Will derive $\boxed{\langle \vec{v} \rangle = \hbar^{-1} \nabla_k E(\vec{k})}$ for electrons in crystals:

$$\langle v_x \rangle = \frac{1}{m}\langle p_x \rangle = \frac{1}{m}\int \psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi \, d^3r$$

Bloch state: $\psi = e^{i\vec{k}\cdot\vec{r}}\, u \Rightarrow \frac{\partial \psi}{\partial x} = e^{i\vec{k}\cdot\vec{r}}\left(ik_x + \frac{\partial}{\partial x}\right)u$

$$\Rightarrow \langle v_x \rangle = \frac{1}{m}\int u^* \left(\hbar k_x + \frac{\hbar}{i}\frac{\partial}{\partial x}\right) u \, d^3r$$

From p. 10: $\tilde{H}u = Eu$ with $\tilde{H} = -\frac{\hbar^2}{2m}(\nabla + i\vec{k})^2 + V$

$$\Rightarrow \frac{\partial \tilde{H}}{\partial k_x} = -\frac{\hbar^2}{2m}\cdot 2\left(\frac{\partial}{\partial x} + ik_x\right)\cdot i = \frac{\hbar}{m}\left(\hbar k_x + \frac{\hbar}{i}\frac{\partial}{\partial x}\right)$$

$$\Rightarrow \langle v_x \rangle = \frac{1}{\hbar}\int u^* \frac{\partial \tilde{H}}{\partial k_x} u \, d^3r$$

Take $\int d^3r \, u^* \frac{\partial}{\partial k_x}$ of $\tilde{H}u = Eu$:

$$\int d^3r \, u^* \left(\frac{\partial \tilde{H}}{\partial k_x} u + \tilde{H}\frac{\partial u}{\partial k_x}\right) = \int d^3r \, u^* \left(\frac{\partial E}{\partial k_x} u + E\frac{\partial u}{\partial k_x}\right)$$

1. term, LHS: $\hbar \langle v_x \rangle$

2. term, LHS:

$$\int d^3r \, u^* \tilde{H}\frac{\partial u}{\partial k_x} = \int d^3r \underbrace{(\tilde{H}u)^*}_{=Eu^*}\frac{\partial u}{\partial k_x} = \text{2. term, RHS}$$

1. term, RHS: $\int d^3r \, u^* \frac{\partial E}{\partial k_x} u = \frac{\partial E}{\partial k_x}\underbrace{\int d^3r \, u^* u}_{=1} = \frac{\partial E}{\partial k_x}$

$\Rightarrow \langle v_x \rangle = \hbar^{-1}\, \partial E/\partial k_x \Rightarrow \langle \vec{v} \rangle = \hbar^{-1} \nabla_k E(\vec{k})$ (QED)

Dynamics (i.e. effect of external force $\vec{F}$):

$$dE = \vec{F}\cdot d\vec{r} = \vec{F}\cdot\vec{v}\,dt = dt\,\vec{F}\cdot\hbar^{-1}\nabla_k E = \frac{dt}{\hbar}\sum_{j=1}^{3} F_j \frac{\partial E}{\partial k_j}$$

General relation: $\dfrac{dE(\vec{k})}{dt} = \sum_{j=1}^{3}\dfrac{\partial E}{\partial k_j}\dfrac{dk_j}{dt}$

By comparison: $\hbar^{-1}F_j = dk_j/dt \Rightarrow \boxed{\vec{F} = \hbar\, d\vec{k}/dt}$

which is Newton's 2. law, provided we identify $\vec{p} = \hbar\vec{k}$ as the momentum

Effective mass:

$$a_j = \frac{dv_j}{dt} = \frac{1}{\hbar}\frac{d}{dt}\frac{\partial E}{\partial k_j} = \frac{1}{\hbar}\frac{\partial}{\partial k_j}\frac{dE}{dt} = \frac{1}{\hbar}\frac{\partial}{\partial k_j}\sum_{l=1}^{3}\frac{\partial E}{\partial k_l}\underbrace{\frac{dk_l}{dt}}_{=F_l/\hbar}$$

$$= \hbar^{-2}\sum_{l=1}^{3}\frac{\partial^2 E}{\partial k_j\,\partial k_l}F_l$$

By comparison with N2, $\vec{a} = \vec{F}/m^*$, we identify the inverse mass tensor:

$$\boxed{\left(\frac{1}{m^*}\right)_{jl} = \hbar^{-2}\frac{\partial^2 E}{\partial k_j\,\partial k_l}} \qquad j,l = 1,2,3$$

We often have isotropic and parabolic band structure near certain k-points, i.e., $E(\vec{k}) \sim (\vec{k}-\vec{k}_0)^2$. Then,

$m^* = \hbar^2\left(\partial^2 E/\partial k^2\right)^{-1}$ = scalar effective mass

NB: $\vec{F}$ is external force, so $\vec{a} \neq \vec{F}/m_e$, since the periodic potential represents an additional contribution to the total force. Writing $\vec{a} = \vec{F}/m^*$, the effective mass m^* includes the influence of the periodic potential.

Classification of crystals

Empirical def. (at $T=0$):

Metal if small $\vec{E}$ gives nonzero current I

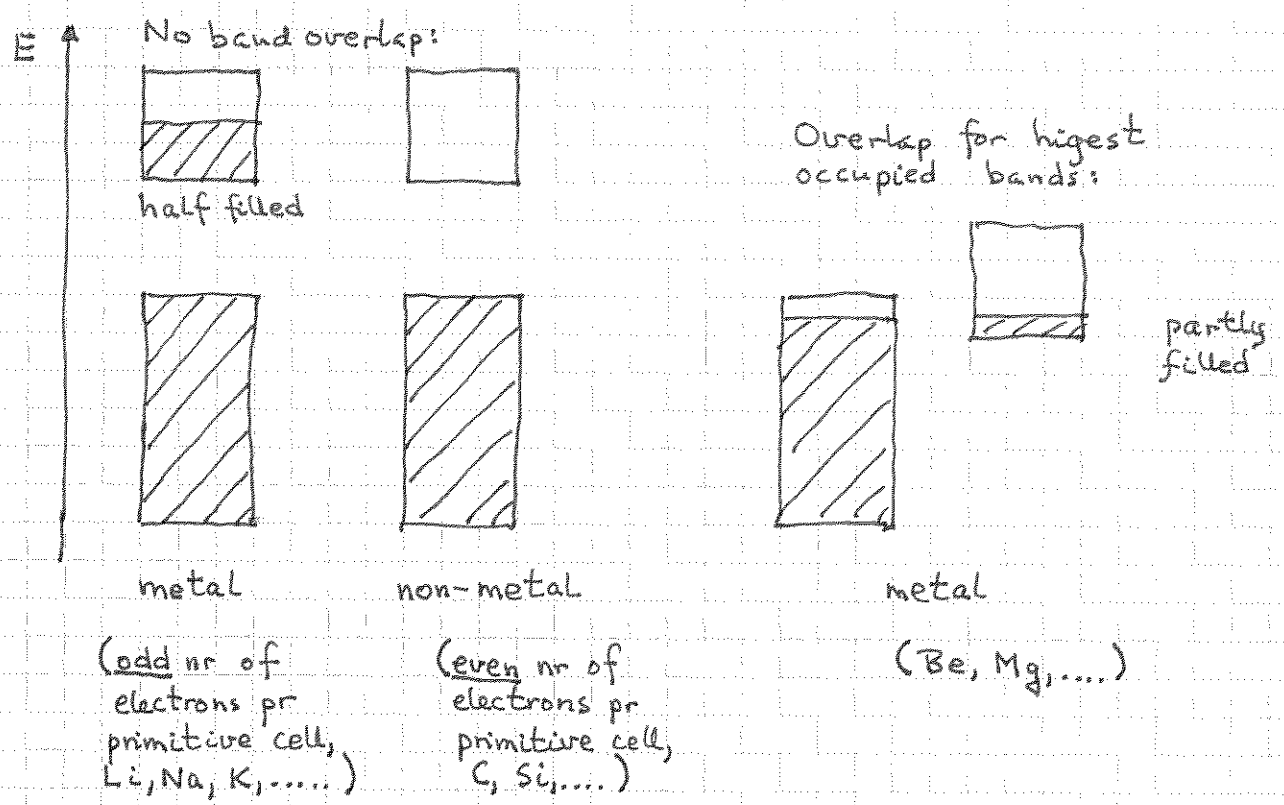
Non-metal ——— " ——— $I=0$

Theoretical def:

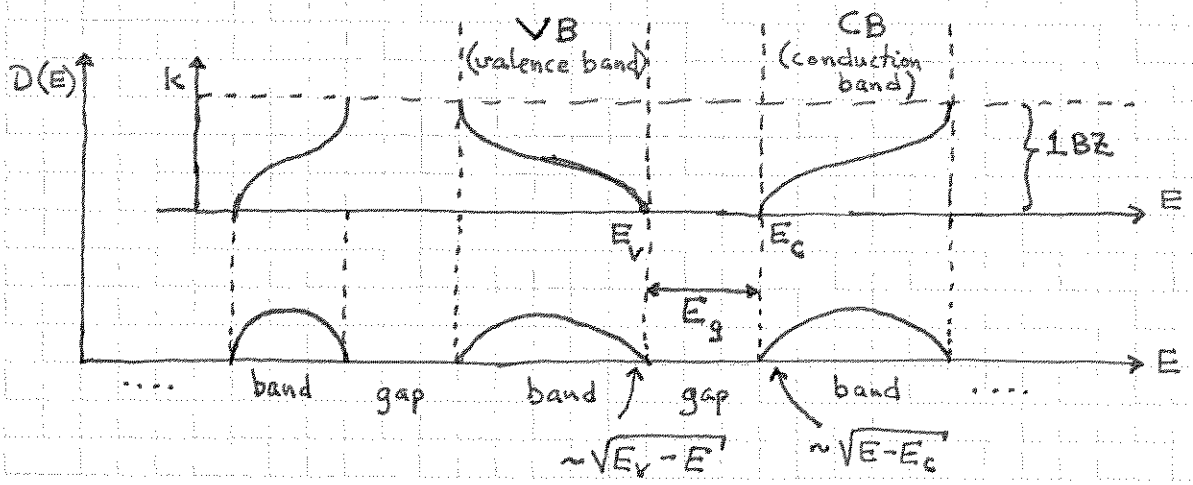
Metal if partly occupied energy band(s)

Non-metal if all bands fully occupied or empty

With N primitive cells and 2N states pr energy band:



"Typical" band structure and DOS (in 3D):



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