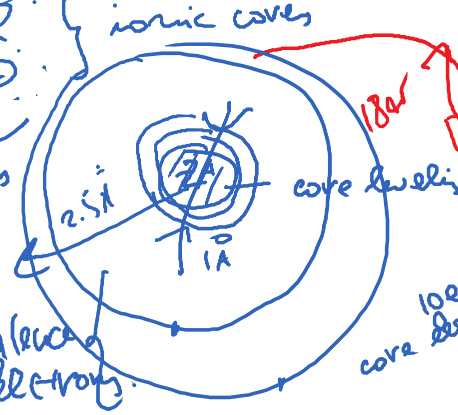
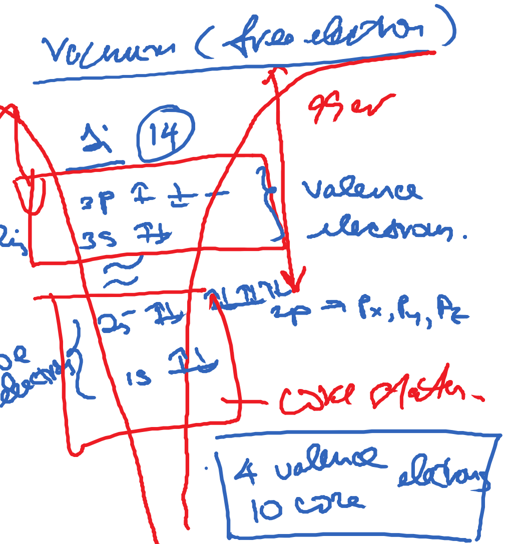
Lecture 20, April 14, 2020

Part IV: Electron in a periodic potential

1. empty lattice
2. Kronig-Penney model
3. Weak periodic potential





$\langle 3s|2p\rangle = 0$

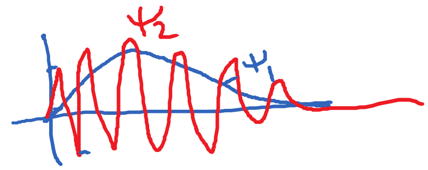
$\langle 3s|2s\rangle = 0$

$\langle 3s|\hat{K}|2p\rangle \neq 0$

$$\frac{\langle 3s|\hat{K}|2p\rangle}{\varepsilon_{3s} - \varepsilon_{2p}}$$

~ 60 eV

How can you be orthogonal?



$\int \psi_2^* \psi_1 \, dx = 0$ (Nature's way).

$$\left[H_{el} + K_{ions}\right] \Psi_{el}(\bar{r}, \bar{R}) \chi(\bar{R}) = E \, \Psi_{el} \chi$$ ← Born-Oppenheimer.

$\hat{H}_{el} \Psi_{el} = \mathcal{E}_{el} \Psi_{el}(\{\vec{r}_i\}\{R\})$ – we claimed to solve it!

$$\left[K_{ions} + \mathcal{E}_{el}(R)\right] \chi(R) = E \, \chi(R)$$

$$\mathcal{E}_{el}(R) = \mathcal{E}_{el}(R_{eq}^{(0)}) + \underbrace{\frac{1}{2!} \sum_{\alpha\beta} \frac{\partial^2 \mathcal{E}}{\partial u_\alpha \partial u_\beta} u_\alpha u_\beta}_{\text{harmonic approximation}} + \underbrace{\ldots}_{\text{ignore the higher order terms.}}$$

anharmonic approximation ⇓ phonons! order terms.

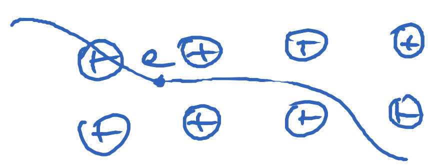
Revisit $\hat{H}_{el}\psi_{el} = \varepsilon_{el}\psi_{el}$.

$\sim 10^{12}$ electrons, they interact, this is hard, I give up!

$$\psi_{el}^{n}(r_1, r_2, \ldots s_1 s_2) = \sum_{\alpha}^{N_\alpha} C_\alpha^n \, |\text{Slater det}|_\alpha \qquad (CI)$$

all electrons are the same, and they are blind to other electrons.

one-electron approximation



$$\boxed{\left(\frac{p^2}{2m} + \underbrace{\sum_{R_e} V(r-R_e)}_{\text{periodic potential}}\right)\psi_{n\vec{k}}(\vec{r}) = \underbrace{\varepsilon_{nk}}_{\text{single-particle energy}}\psi_{nk}(r)}$$

Pauli principle

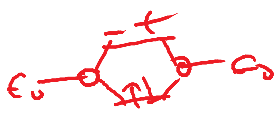
$V(r-R_e)$?

$+$.

$$\frac{\overset{\text{core charge}}{Ze}}{|r-R_e|} + e\underbrace{\int \frac{\rho(r')}{|r-r'|}dr'}_{\text{other electrons}}$$

in Si what is the charge? 4

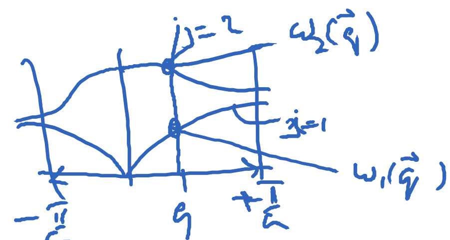
1. Intuition is always right.
2. if not, see 1.



$$\begin{vmatrix} \epsilon_0 & -t \\ -t & \epsilon_0 \end{vmatrix}\psi = \varepsilon\psi$$

$$\varepsilon_{\pm} = \epsilon_0 \pm t$$

We will follow this recipe



remember phonons: $\omega_f \equiv \omega_{j,q} = \omega_j(\vec{q})$

$e\binom{\vec{q}}{j} \to \chi\binom{q}{j}$

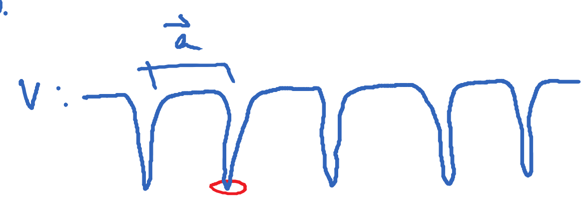
in a periodic system, the eigenvalue and eigenvector are labeled by 2 quantum numbers: $j, \vec{q}$.

$j \to n$ (band index)

$\vec{q} \to \vec{k}$ (quasi momentum) $\hbar k = \vec{p}$

Let's limit our discussion to 1D for now.

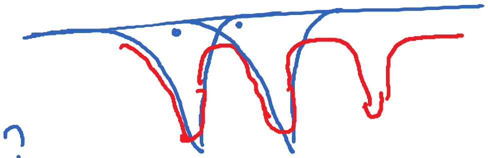
$$\boxed{\left(\frac{p^2}{2m} + V_{periodic}\right)\psi_{n\vec{k}}(V) = \varepsilon_{n}(V)}$$



$$\boxed{\left(\frac{p^2}{2m} + \underline{V_{\text{periodic}}}\right)\psi_{nk}(r) = \ldots}$$

$\left(\frac{\partial^2}{\partial x^2}\right.$

$$\boxed{\underline{V(r+\vec{L}) = V(r)}}$$



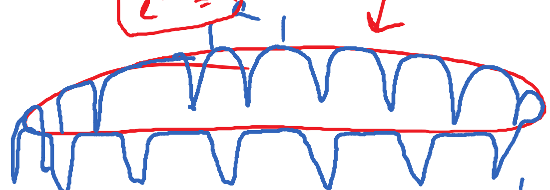
$\vec{L} = n\vec{a}$

periodicity! How can we exploit it?

Bloch Theorem $\qquad \underline{\psi_k}(r+\vec{L}) = e^{i\underline{k}R}\,\psi_k(r)$

$\vec{L} \to n\vec{a}$

$\boxed{e^{ikNL} = 1}$ $\qquad$ PBC.



Not them on the Loop!

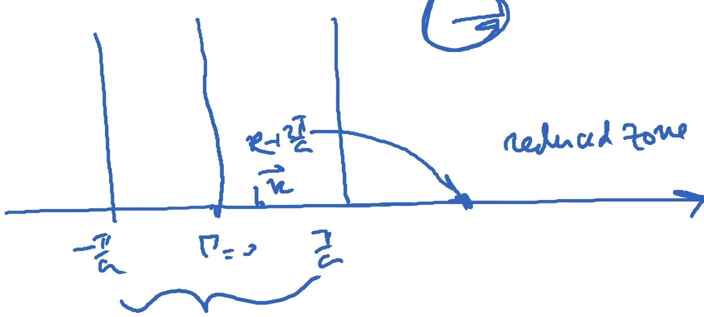
$L = Na$ — the length of the crystal.

$\vec{G} = \frac{2\pi}{a}$ (reciprocal lattice vectors).

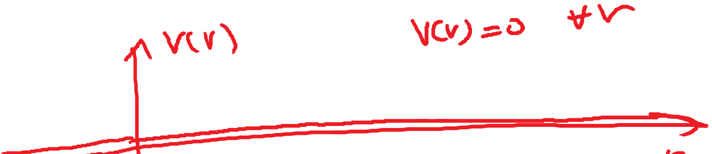
shift $\vec{k}$ by $\vec{G}$ $\qquad$ does nothing!

$(\underline{\vec{G}} + \vec{k})\,na = nak + \underbrace{n2\pi}$

reduced zone picture: $\vec{k}$ is limited to 1^{st} BZ.



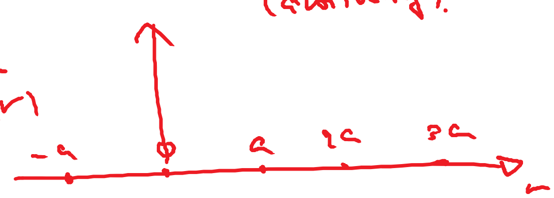
$V(r) = 0 \quad \forall r \qquad V(r+\vec{L}) = V(r)$



↳ a periodic potential $\qquad$ (stupid!)

$$\boxed{\left(\frac{p^2}{2m} + 0\right)\psi_{nk}(\vec{r}) = \mathcal{E}_{nk}\,\psi_{nk}(r)}$$

$\underline{a}$ — the periodicity specify (arbitrary).



free electron.

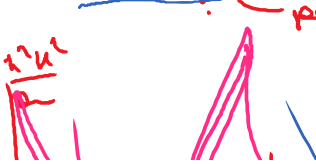
$\psi_k = e^{ikr} = e^{i(k-g)r}\,\underbrace{e^{igr}} =$

$= \boxed{e^{ik'r}\,u(r)} = \psi_{k'g}(r)$ — periodic

$g = 2\pi/a$

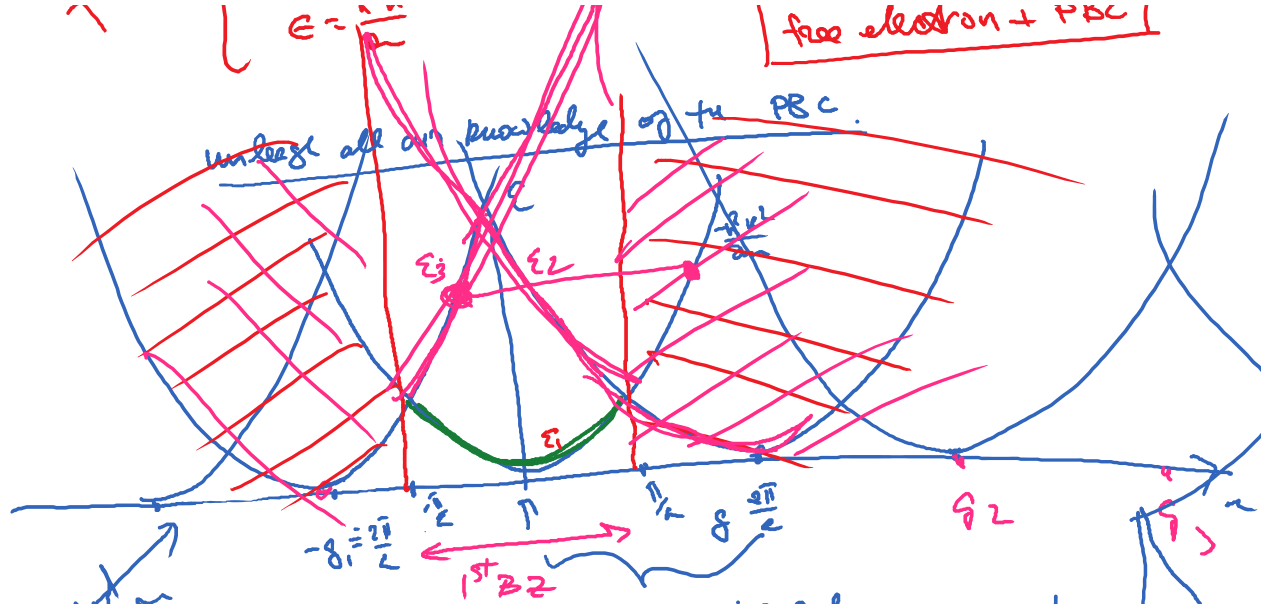
$\epsilon = \frac{\hbar^2 k^2}{2m}$

$\boxed{\text{free electron + PBC}}$

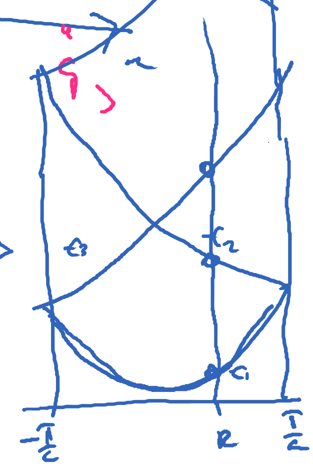


free electron + PBC

unleash all our knowledge of the PBC.



reduced



$\varepsilon_1 = \frac{\hbar^2}{2m}(k+0)^2 \quad k \in [-\frac{\pi}{a}; \frac{\pi}{a}]$

1st BZ

$\varepsilon_3(k+G) = \frac{\hbar^2 (k+G)^2}{2m}, \quad \varepsilon_2 = \frac{\hbar^2(k-G)^2}{2m} \quad k \in [-\frac{\pi}{a}\ \frac{\pi}{a}]$

$\psi(k+G)$ empty lattice approximation

ϵ_{nk}

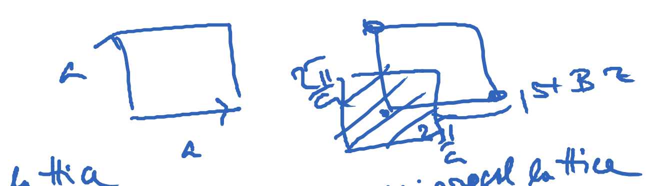
g

in the 1st BZ

limit your $\vec{k}$ to 1st BZ, your n (band index) tells you which $\vec{G}$ to use.

and the wf is $e^{i(\vec{k}+\vec{g})r}$ or $e^{i(k-\vec{g})r}$

2D square lattice in the empty lattice approximation.



$\boxed{\epsilon = \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2}$

$\vec{k} = (k_x, k_y)$

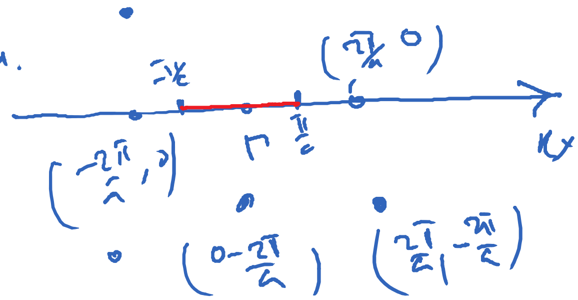
$\vec{G} = (G_x, G_y)$

$(0\ \frac{2\pi}{a})$

$(\frac{2\pi}{a}\ 0)$

$(k_x, 0)$ ← a line in the reciprocal space.

$(k_x, 0)$ ← a line in the reciprocal space.



$\vec{G} = 0$ (the Γ point).

$\frac{2\pi}{a}(\pm 1, 0)$

$\frac{2\pi}{a}(0, \pm 1)$

$\frac{2\pi}{a}(\pm 1, \pm 1)$

① $E_1 = \frac{\hbar^2}{2m}(\vec{k}+0)^2$ $\qquad k^2 = (k_x\ 0)\begin{pmatrix}k_y\\0\end{pmatrix} = k_x^2$

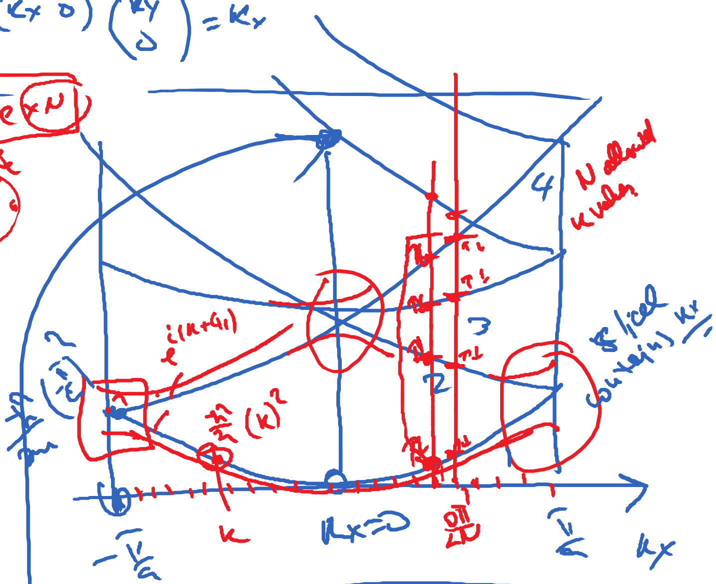
② $\vec{k}+\vec{G} = \left(k_x \pm \frac{2\pi}{a}, 0\right)$

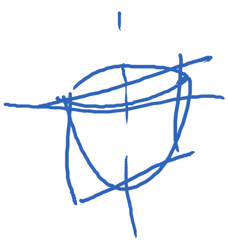
③ $E = \frac{\hbar^2}{2m}\left(k_x \pm \frac{2\pi}{a}\right)^2$

8e $\quad \boxed{8e \times N}$ $\quad$ N

④ $\vec{k}+\vec{G} = \left(k_x \pm \frac{2\pi}{a}; \pm\frac{2\pi}{a}\right)$

$E_4 = \frac{\hbar^2}{2m}\left(\left(k_x \pm \frac{2\pi}{a}\right)^2 + \left(\frac{2\pi}{a}\right)^2\right)$





$E_4 = \frac{\hbar^2}{2m}\left[\left(k_x + \frac{2\pi}{a}\right)^2 + \left(\frac{2\pi}{a}\right)^2\right]$

$\frac{4\pi^2}{a^2} + \frac{4\pi^2}{a^2} = \frac{8\pi^2}{a^2}$

$k_x = 0$

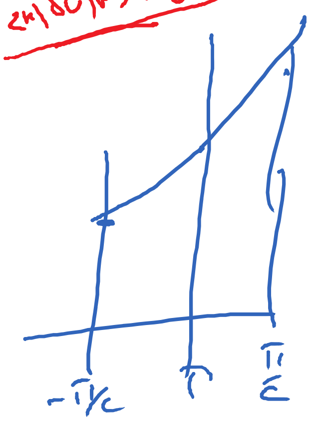
$\delta V(r+a) = \delta V(r)$ weak

$e^{i(k+G)x}$ $\quad \langle k|\delta U|k'\rangle = \int e^{i(k-k')x}\,\delta U\,dx$

$e^{i(k+g)\cdot x}$

$k_x = -\frac{\pi}{a}$ $\qquad E_4\left(-\frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\left(-\frac{\pi}{a}+\frac{2\pi}{a}\right)^2 + \left(\frac{2\pi}{a}\right)^2\right)$

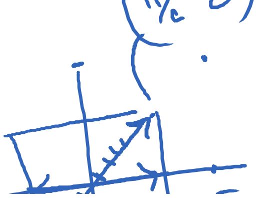
$\frac{\pi^2}{a^2} + \frac{4\pi^2}{a^2} = \frac{5\pi^2}{a^2}$



$k_x = \frac{\pi}{a}$ $\qquad \frac{\hbar^2}{2m}\left[\left[\frac{\pi}{a}+\frac{2\pi}{a}\right]^2 + \left(\frac{2\pi}{a}\right)^2\right] =$

$= \frac{\hbar^2}{2m}\left[\frac{9\pi^2}{a^2} + \frac{4\pi^2}{a^2}\right] = \frac{\hbar^2}{2m}\,\frac{13\pi^2}{a^2}$

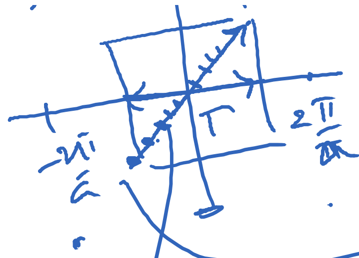
$\left(\pi/a, \frac{\pi}{a}\right)$



$\vec{k} = (k, k)$

$G = 0$, $\quad G = \pm\frac{2\pi}{a}\ \ 0$

$G_1\ \ 0\ \ \pm\frac{2\pi}{a}$



$\vec{k} = (k, k)$

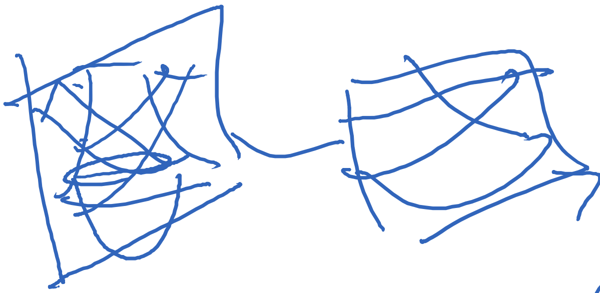
$G_1 \quad 0 \quad \pm\frac{2\pi}{a}$

$G \ldots \left(\pm\frac{2\pi}{a} \pm \frac{2\pi}{a}\right)$

$\left(-\frac{\pi}{a} - \frac{\pi}{a}\right)$ $\qquad \frac{2\pi}{a} / 10$

10 points?

$\left(-\frac{\pi}{a}\ \ -\frac{\pi}{a}\right), \left(-\frac{\pi}{a} + \frac{2\pi/a}{10},\ -\frac{\pi}{a} + \frac{2\pi/a}{10}\right)$

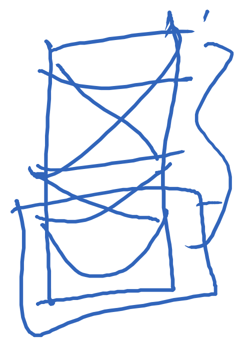


a – is arbitrary

$\epsilon \quad \frac{\hbar^2 k^2}{2m}$

Take home message

$n, \vec{k} \qquad \psi_{n,\vec{k}}(r), \quad \varepsilon_{nk}$



$\psi_{kG}(r) = e^{i(k+G)\cdot r}$

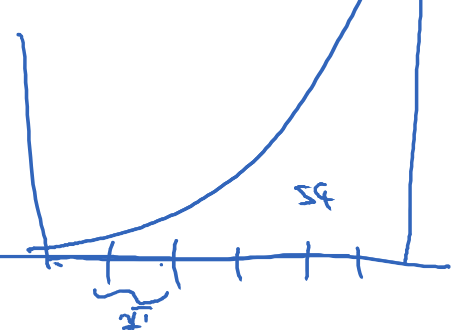
$G \leftarrow n$

little black box $\quad n \leftrightarrow \vec{G}$

In real life

$\psi_{n,\vec{k}}(\vec{r}) = \sum_G C_G^k e^{i(\vec{k}-\vec{G})\cdot\vec{r}}$ — a plane wave basis.

Bloch Th



$\left(\frac{p^2}{2m} + U\right) \sum_G C_G^k e^{i(k-G)\cdot r} = \varepsilon_{nk} \sum_G C_G^k e^{i(k-G)\cdot r}$

$$\begin{bmatrix} \ \ \end{bmatrix} \begin{bmatrix} C_{G_1}^k \\ C_{G_2} \\ C_{G_3} \\ \vdots \end{bmatrix} = \epsilon \begin{bmatrix} \ \ \end{bmatrix}$$

→ 50,000 values of G's

The empty lattice approx. is the 0th order P.T.

$$\begin{bmatrix} \; & \; \\ \; & \; \end{bmatrix}\begin{bmatrix} C^{u}_{g_1} \\ C_{g_2} \\ C_{g_3} \\ \vdots \end{bmatrix} = \epsilon \begin{bmatrix} \; \\ \; \end{bmatrix} \rightarrow 50{,}000 \text{ values of } G's$$

The empty lattice approx. is the 0^{th} order P.T.

N allowed k values

spin

$$2 \sum_{k}^{PBC} \sum_{i}^{occupied} \epsilon_i(k) = E_{el.\,energy}$$

k_1 : $\epsilon_1(k)$, $\epsilon_2(k_1)$ ...