Electrons in a Crystal Lattice

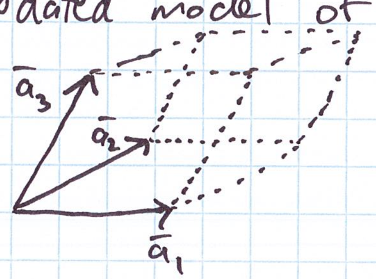
→ return to the quantum free electron model

Periodic Boundary Conditions:

e.g. $\psi(x,y,z) = \psi(x+L, y, z)$ ⇒ L is crystal length.

→ results quantize the system ⇒ k-space!

Updated model of our material:



Primitive cell
(direct lattice)

→ the macroscopic crystal is composed of a large # of primitive unit cells "stacked" in each direction a_i:

N_1 in direction $\bar{a}_1$
N_2 in direction $\bar{a}_2$
N_3 in direction $\bar{a}_3$

} each N_i is very large. $\approx 10^8$

Total # of unit cells in the crystal is:

$$N = N_1 N_2 N_3 \qquad N \approx 10^{22}$$

N is similar to total # of $\bar{e}$'s

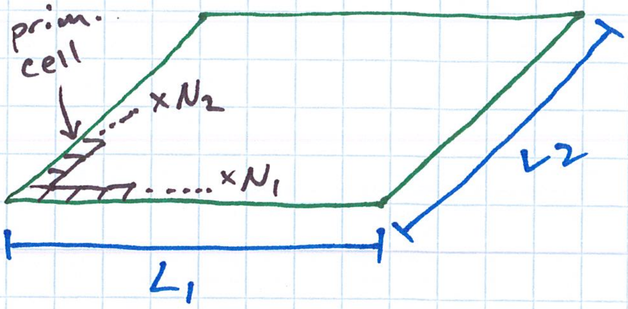
Total crystal volume is

$$\Omega = N\Omega_0 \Rightarrow \Omega_0 = \bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)$$

prim. cell volume

The macroscopic length along each dimension $\bar{a}_i$ is:

$$L_1 = N_1 a_1$$
$$L_2 = N_2 a_2$$
$$L_3 = N_3 a_3$$



Update our PBC: $\psi(x,y,z) \Rightarrow \psi(\bar{r})$

$$\psi(\bar{r}) = \psi(\bar{r} + \bar{L}_1) = \psi(\bar{r} + N_1 \bar{a}_1)$$

$$\& \quad \psi(\bar{r}) = \psi(\bar{r} + N_2 \bar{a}_2)$$

$$\& \quad \psi(\bar{r}) = \psi(\bar{r} + N_3 \bar{a}_3)$$

Plane wave soln's: $\psi(\bar{r}) \propto e^{i\bar{k}\cdot\bar{r}}$

yields: $e^{i\bar{k}\cdot\bar{a}_1 N_1} = 1$

$$\Rightarrow \left.\begin{aligned} N_1\, \bar{k}\cdot\bar{a}_1 &= 2\pi n_1 \\ N_2\, \bar{k}\cdot\bar{a}_2 &= 2\pi n_2 \\ N_3\, \bar{k}\cdot\bar{a}_3 &= 2\pi n_3 \end{aligned}\right\} \quad n_i = 0, \pm 1, \pm 2 \ldots$$

Recall:

$$\bar{k} = k_1 \bar{b}_1 + k_2 \bar{b}_2 + k_3 \bar{b}_3$$

$$\& \quad b_i \cdot a_j = 2\pi \delta_{ij}$$

arb. $\bar{k}$ vector

$$\therefore \quad k_1 = \frac{n_1}{N_1}, \quad k_2 = \frac{n_2}{N_2}, \quad k_3 = \frac{n_3}{N_3}$$

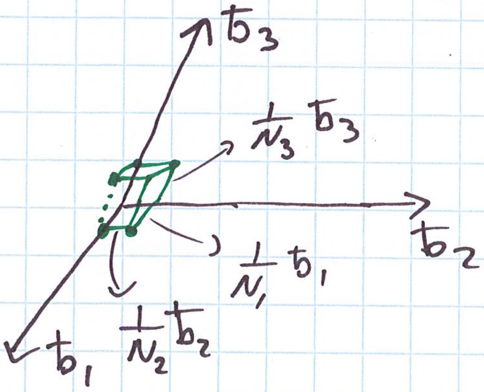
Note ⇒ n_i – small $= 0, \pm 1, \pm 2 \ldots$

N_i – big $\approx \sqrt[3]{10^{22}}$

$\frac{n_i}{N_i}$ can be really small & at most order of 1.

$\therefore$ allowed $\mathbf{k}$'s: $\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3$

⇒ This quantization is very small compared to the ~~the~~ reciprocal lattice cell:



Volume per allowed $\mathbf{k}$?

$$\Delta \mathbf{k} = \frac{1}{N_1}\mathbf{b}_1 \cdot \left(\frac{1}{N_2}\mathbf{b}_2 \times \frac{1}{N_3}\mathbf{b}_3\right)$$

$$= \frac{1}{N}\,\Omega_0 \qquad \Omega_0 = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$$

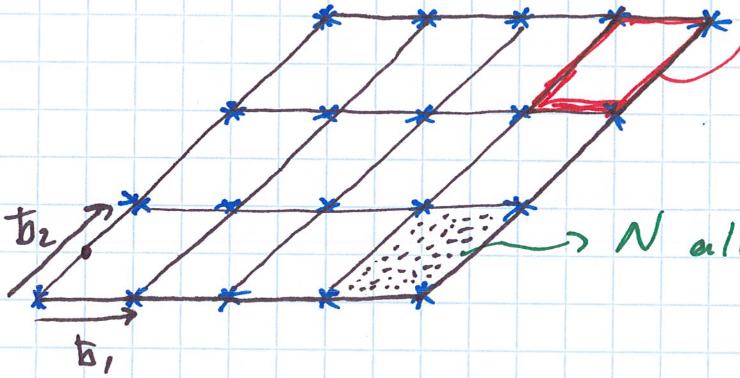
Volume of recip. prim. cell
a.k.a. Brillain Zone.

∴ Each Brillouin Zone contains N allowed $\mathbf{k}$-states!

Density of allowed $\mathbf{k}$'s?

$$\rho_{\mathbf{k}} = \frac{N}{\Omega_0} = N\left(\frac{\Omega_0}{8\pi^3}\right) = \frac{\Omega}{8\pi^3}$$ → total crystal volume

⇒ same result as previously!

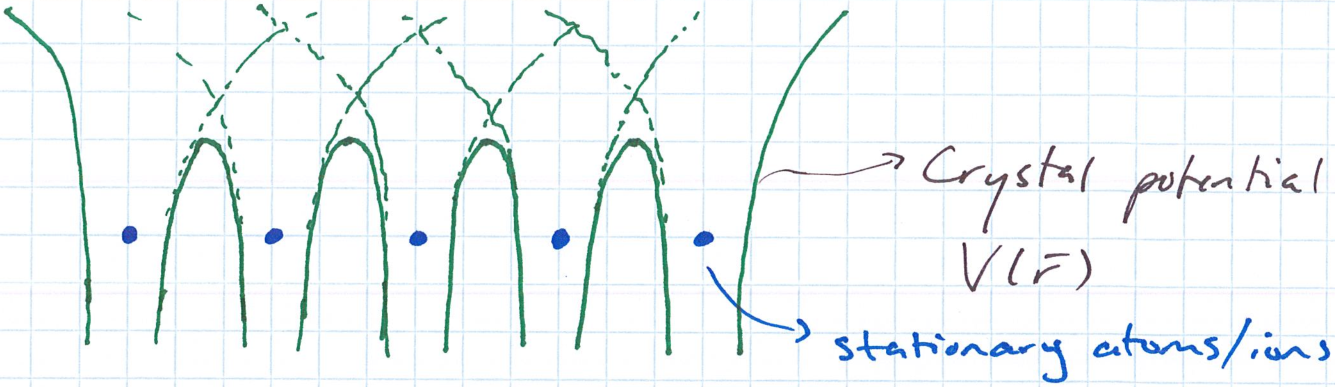


→ Reciprocal Lattice primitive cell

→ N allowed $\mathbf{k}$'s per cell

$$\boxed{\begin{array}{l}\text{Each recip. cell contains } N \text{ states}\\ \text{Each Brillouin Zone contains } N \text{ states}\end{array}}$$

Electrons in a periodic potential



→ previously, we approximated $V(\bar{r})$ as a potential well w̄ $V=0$ (Free electron)

→ We know that the crystal potential must have the same periodicity as the crystal lattice:

$$V(\bar{r}) = V(\bar{r}+\bar{R})$$

$$\bar{R} = n_1\bar{a}_1 + n_2\bar{a}_2 + n_3\bar{a}_3$$

Note: this does not say anything about the functional form of $V(\bar{r})$, just it's periodicity / symmetry.

Hamiltonian for single $\bar{e}$:

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\bar{r})$$

$\hat{H}$ does not have complete translational symmetry, but it is symmetric for translations of $\bar{R}$.

In QM the translation operator $\hat{T}(\bar{r})$ is closely related to the momentum operator $\hat{p} = -i\hbar\bar{\nabla}$

i.e. $\hat{\mathcal{H}}$ does not commute w/ $\hat{p}$ for any translation, but does commute for translations of any $\bar{R}$.

Define translation operator through $\bar{R}$:

$$\hat{T}_{\bar{R}}\, f(\bar{r}) = f(\bar{r}+\bar{R})$$

i.e. $\hat{T}_{\bar{R}}$ shifts $f(\bar{r})$ to $f(\bar{r}+\bar{R})$

Calculate $[\hat{T}_{\bar{R}}, V]$: ⇒ expect to commute $[\hat{T}_{\bar{R}}, V] = 0$.

$$\begin{aligned}\hat{T}_{\bar{R}}\, V(\bar{r})\, \psi(\bar{r}) &= \hat{T}_{\bar{R}}\big(V(\bar{r})\,\psi(\bar{r})\big)\\ &= V(\bar{r}+\bar{R})\,\psi(\bar{r}+\bar{R})\\ &= V(\bar{r})\,\hat{T}_{\bar{R}}\,\psi(\bar{r})\end{aligned}$$

$$\therefore\ \underbrace{\left(\hat{T}_{\bar{R}} V(\bar{r}) - V(\bar{r})\hat{T}_{\bar{R}}\right)}\psi(\bar{r}) = 0$$

$$\equiv [\hat{T}_{\bar{R}}, V] = 0.$$

$\hat{T}_{\bar{R}}$ commutes w/ $V(\bar{r})$

The Hamiltonian is also periodic in $\bar{R}$:

$$\hat{\mathcal{H}} = \frac{-\hbar^2}{2m}\nabla^2 + V(\bar{r})$$

$$\hat{\mathcal{H}}(\bar{r}) = \hat{\mathcal{H}}(\bar{r}+\bar{R})$$

As a result:

$$\hat{T}_{\bar{R}}\mathcal{H}(\bar{r})\psi(\bar{r}) = \underbrace{\mathcal{H}(\bar{r}+\bar{R})}_{=\mathcal{H}(\bar{r})}\underbrace{\psi(\bar{r}+\bar{R})}_{=\hat{T}_{\bar{R}}\psi(\bar{r})}$$

$$= \mathcal{H}(\bar{r})\hat{T}_{\bar{R}}\psi(\bar{r})$$

$$\therefore [\hat{T}_{\bar{R}}, \hat{\mathcal{H}}] = \hat{T}_{\bar{R}}\hat{\mathcal{H}} - \hat{\mathcal{H}}\hat{T}_{\bar{R}} = 0$$

Thus, the Hamitonian $\hat{\mathcal{H}}$ & translation operator $\hat{T}_{\bar{R}}$ commute => share a set of eigenstates!

Aside: This assumes that $[\hat{T}_{R}, \underbrace{\nabla^2}_{\propto K.E.}] = 0$, which is true.

$$\hat{T}_{\bar{R}} f(\bar{r}) = f(\bar{r}+\bar{R}) = \underbrace{\sum_n \frac{1}{n!}(\bar{R}\cdot\nabla)^n}_{\equiv e^{R\cdot\nabla}} f(\bar{r})$$ => Taylor exp. about $R=0$.

Note: $\hat{p} = -i\hbar\nabla$

$$\therefore \hat{T}_{\bar{R}} = e^{i\bar{R}\cdot\hat{p}/\hbar}$$

$\hat{p}$ = momentum operator.

$$K.E. = \frac{-\hbar^2}{2m}\nabla^2 = \frac{\hat{p}^2}{2m}$$

$$\Rightarrow [\hat{p}, \nabla^2] = 0$$

$$\therefore [\hat{T}_{\bar{R}}, \nabla^2] = 0$$

We seek to determine the eigenstates of $\hat{T}_{\bar{R}}$, which are simultaneously eigenstates of $\mathcal{H}$:

⇒ First note: $\hat{T}_{\bar{R}}$ is unitary

$$\hat{T}_{\bar{R}} \hat{T}_{\bar{R}}^{\dagger} = 1$$

$T^{\dagger}$ is Hermitian conj.

and eigenvalues of a unitary operator can always be written in the form:

$$\hat{U} \psi = \lambda \psi$$

$$\lambda = e^{i\theta}$$

⇒ e.v. lie on unit circle

$\theta \Rightarrow$ real

⇒ Second note: $\hat{T}_{\bar{R}}$ commutes $\bar{w}$ $\hat{T}_{\bar{R}'}$

For any $\bar{R}/\bar{R}'$, translations can be applied in any order.

$$\hat{T}_{\bar{R}} \hat{T}_{\bar{R}'} \psi(\bar{r}) = \hat{T}_{\bar{R}} \psi(\bar{r}+\bar{R}') = \psi(\bar{r}+\bar{R}'+\bar{R}) = \hat{T}_{\bar{R}+\bar{R}'} \psi(\bar{r})$$

∴ for any $\bar{R} = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3$

$$\hat{T}_{\bar{R}} \psi = \left(\hat{T}_{\bar{a}_1}\right)^{n_1} \left(\hat{T}_{\bar{a}_2}\right)^{n_2} \left(\hat{T}_{\bar{a}_3}\right)^{n_3} \psi$$

$$= e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)} \psi$$

where θ_i are given by . . .

For each $\bar{a}_i$ we can write:

$$\hat{T}_{\bar{a}_i} \psi = e^{i\theta_i} \psi$$ => θ_i characterizes e.v. of $\hat{T}_{a_i}$.

We must also satisfy our boundary conditions:

$$\psi(\bar{r}) = \psi(\bar{r} + N_i \bar{a}_i)$$

$$\psi(\bar{r} + N_i \bar{a}_i) = \left(\hat{T}_{\bar{a}_i}\right)^{N_i} \psi(\bar{r}) = e^{iN_i\theta_i} \psi(\bar{r})$$

$$\therefore e^{iN_i\theta_i} = 1$$

$$N_i\theta_i = 2\pi m_i \quad , \quad m_i = \text{integer}$$

$$\theta_i = 2\pi \frac{m_i}{N_i}$$

Of course, any reciprocal vector $\bar{k}$ can be written as:

$$\bar{k} = \frac{m_1}{N_1}\bar{b}_1 + \frac{m_2}{N_2}\bar{b}_2 + \frac{m_3}{N_3}\bar{b}_3$$

$$\therefore \bar{k} \cdot \bar{a}_i = 2\pi \frac{m_i}{N_i} \equiv \theta_i$$ Recall: $\bar{b}_i \cdot \bar{a}_j = 2\pi \delta_{ij}$

$\therefore$ Our eigenvalues: $e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)} \equiv e^{i\bar{k}\cdot\bar{R}}$

$$\therefore \hat{T}_{\bar{R}} \psi(\bar{r}) = e^{i\bar{k}\cdot\bar{R}} \psi(\bar{r})$$

$$\hat{T}_{\mathbf{k}} \psi(\bar{r}) = e^{i\mathbf{k}\cdot\bar{R}} \psi(\bar{r}) = \psi(\bar{r}+\bar{R})$$

→ for some allowed (quantized) $\mathbf{k}$ of the system
→ use $\mathbf{k}$ as label to eigenstate $\psi_{\mathbf{k}}(\bar{r})$

Return to Hamiltonian: $\hat{\mathcal{H}}$ has same eigenstates $\psi_{\mathbf{k}}(\bar{r})$

$$\hat{\mathcal{H}} \psi_{\mathbf{k}}(\bar{r}) = E_{\mathbf{k}} \psi_{\mathbf{k}}(\bar{r})$$

The eigenstates of $\hat{\mathcal{H}}$ take the form:

$$\boxed{\psi_{\mathbf{k}}(\bar{r}+\bar{R}) = e^{i\mathbf{k}\cdot\bar{R}} \psi(\bar{r})}$$

Bloch's Theorem

Another way to express Bloch's theorem is to write the Hamiltonian eigenstates as:

$$\psi_{\mathbf{k}}(\bar{r}) = e^{i\mathbf{k}\cdot\bar{r}} u_{\mathbf{k}}(\bar{r})$$

where $u_{\mathbf{k}}(\bar{r})$ is a function w/ the periodicity (symmetry) of the lattice:

$$u_{\mathbf{k}}(\bar{r}) = u_{\mathbf{k}}(\bar{r}+\bar{R})$$

Proof of this result:

take $\psi_{\mathbf{k}}(\bar{r}) = e^{i\mathbf{k}\cdot\bar{r}} u_{\mathbf{k}}(\bar{r})$

& apply $\psi_{\mathbf{k}}(\bar{r}+\bar{R}) = e^{i\mathbf{k}\cdot\bar{R}} \psi(\bar{r})$

$$\hat{T}_{\bar{R}}\,\psi_{\bar{k}}(\bar{r}) = \psi_{\bar{k}}(\bar{r}+\bar{R}) = e^{i\bar{k}\cdot\bar{R}}\,\psi_{\bar{k}}(\bar{r}) = e^{i\bar{k}\cdot(\bar{r}+\bar{R})}\,u_{\bar{k}}(\bar{r})$$

$$\& \quad \psi_{\bar{k}}(\bar{r}+\bar{R}) = e^{i\bar{k}\cdot(\bar{r}+\bar{R})}\,u_{\bar{k}}(\bar{r}+\bar{R})$$

$$\therefore \quad u_{\bar{k}}(\bar{r}) = u_{\bar{k}}(\bar{r}+\bar{R})$$

Bloch's Theorem:

$$\boxed{\psi_{n,\bar{k}}(\bar{r}) = e^{i\bar{k}\cdot\bar{r}}\,u_{n,\bar{k}}(\bar{r})}$$

n = band index
.... later.

For e's in a periodic potential $(V(\bar{r}) = V(\bar{r}+\bar{R}))$ the eigenstates of the Hamiltonian can be written as plane wave solutions multiplied by a function possessing the same as the crystal (potential).

Important notes re: Bloch's theorem:

1. The $\bar{e}$ momentum is no longer $\bar{p} = \hbar\bar{k}$

   $\hat{p}$ does not commute $\bar{c}$ $\hat{H}$ in general (only in translations of $\bar{R}$)

   $\bar{p} = \hbar\bar{k} \Rightarrow$ crystal momentum

   → view $\bar{k}$ as a quantum # to label the $\bar{e}$ state, rather than momentum.

2. $\bar{k}$ can always be confined to the 1st Brillouin Zone (or other recip. prim. cell)

any $\bar{k}'$ outside the 1st BZ can be written as:

$\bar{k}' = \bar{k} + \bar{K}$, where $\bar{k}$ is in 1st BZ.
$\bar{K}$ is recip. lattice vector.

$$\therefore \text{B.T.} \Rightarrow \psi_{\bar{k}'}(\bar{r}+\bar{R}) = e^{i\bar{k}'\cdot\bar{R}}\psi(\bar{r})$$

$$= e^{i(\bar{k}+\bar{K})\cdot\bar{R}}\psi(\bar{r})$$

but $e^{i\bar{K}\cdot\bar{R}} = 1$ by dfn.

$$\therefore \psi_{\bar{k}'}(\bar{r}+\bar{R}) = e^{i\bar{k}\cdot\bar{R}}\psi(\bar{r}) = \psi_{\bar{k}}(\bar{r}+\bar{R})$$

=> this simplifies our view of the recip. lattice.

3. As evidenced by (2) there are ∞ eigenstate solutions for each $\bar{k}$. We use the label n, called the band index, to differentiate.

You can think of each n representing a translation to/from another $\bar{K}$.

4. Note: $$\psi_{n,\bar{k}+\bar{K}}(\bar{r}) = \psi_{n,\bar{k}}(\bar{r})$$

$$\varepsilon_{n,\bar{k}+\bar{K}} = \varepsilon_{n,\bar{k}}$$

=> have periodicity of recip. lattice.

5. An electron in state $\psi_{n,\mathbf{k}}$ has mean velocity:

$$v_n(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathcal{E}_n(\mathbf{k})$$

i.e. the $\bar{e}$ velocity is $\propto$ the gradient of $\mathcal{E}_n(\mathbf{k})$

Band structure

$$\hat{\mathcal{H}} \psi_{n\mathbf{k}}(\bar{r}) = \mathcal{E}_n(\mathbf{k}) \psi_{n\mathbf{k}}(\bar{r})$$

$$\hat{\mathcal{H}} = \frac{-\hbar^2}{2m} \nabla^2 + V(\bar{r})$$

-> in general $V(\bar{r})$ is very complicated (think about atomic/molecular bonding orbitals)

-> but, we can use some simple models to make qualitative explanations & simple predicts for some systems

-> Solving $\mathcal{E}_n(\mathbf{k}) \Rightarrow$ band structure

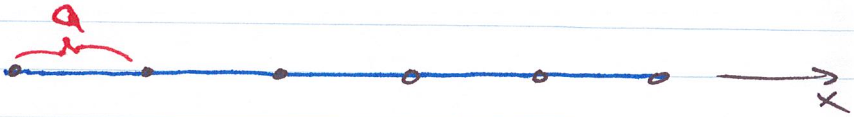
$\hookrightarrow$ dispersion curves / relations.

-> We already know $\mathcal{E}(\mathbf{k})$ for one simple system:

Free electron : $\mathcal{E} = \frac{\hbar^2 k^2}{2m} \Rightarrow \mathcal{E}_n(\mathbf{k}) = \frac{\hbar^2 (\mathbf{k} + \bar{K}_n)^2}{2m}$

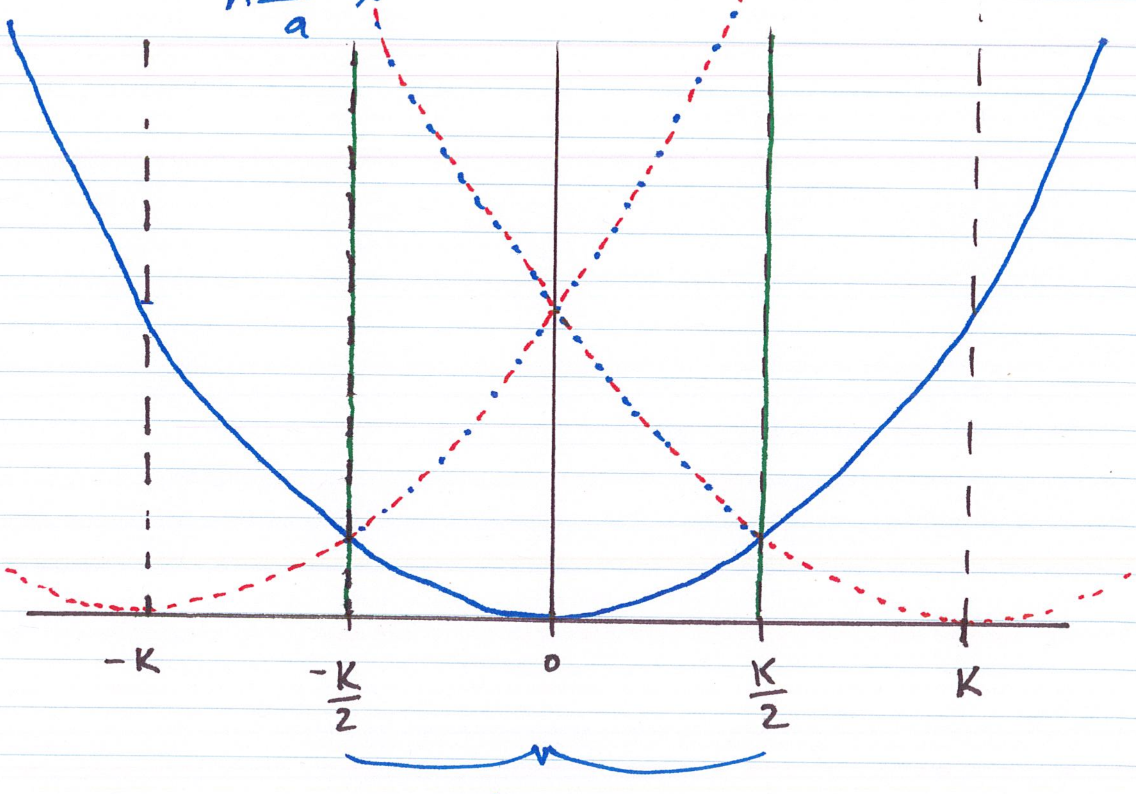
"Empty Lattice Approximation"

Take 1-D case:



$\bar{R} = a\hat{x}$

$\bar{K} = n\frac{2\pi}{a}\hat{x}$



"reduced zone"

—— solid blue shows "extended zone"

- - - - red shows "repeated zone"