Electrons in a periodic potential

→ Crystal potential $V(\bar{r})$

→ stationary atoms/ions
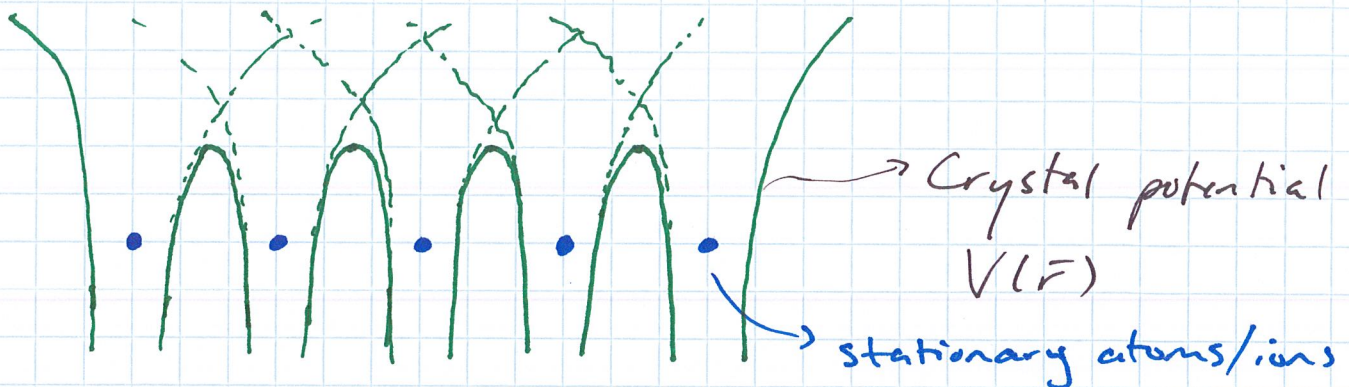
→ previously, we approximated $V(\bar{r})$ as a potential well ≈ $V=0$ (Free electron)

→ 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 <u>complete</u> 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 $\bar{w}$ $\hat{p}$ 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 $[\hat{T}_{\bar{R}}, V]$: $\Rightarrow$ expect to commute $[\hat{T}_{\bar{R}}, V] = 0$.

$$\hat{T}_{\bar{R}} \, V(\bar{r}) \, \psi(\bar{r}) = \hat{T}_{\bar{R}} \left(V(\bar{r}) \, \psi(\bar{r}) \right)$$

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

$$= V(\bar{r}) \, \hat{T}_{\bar{R}} \, \psi(\bar{r})$$

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

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

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

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:

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

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

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

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

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

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

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

$$\therefore \quad \hat{T}_{\bar{R}} = e^{i\bar{R}\cdot\hat{p}/\hbar} \qquad \hat{p} = \text{momentum operator.}$$

$$K.E. = \frac{\hbar^2}{2m}\nabla^2 = \frac{\hat{p}^2}{2m} \quad \Rightarrow [\hat{p},\nabla^2]=0$$

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

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

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

$$\hat{T}_{\bar{R}} \hat{T}_{\bar{R}}^{\dagger} = 1 \qquad\qquad T^{\dagger} \text{ is Hermitian conj.}$$

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

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

$$\lambda = e^{i\theta} \quad\Rightarrow\; \text{e.v. lie on unit circle}$$
$$\theta \Rightarrow \text{real}$$

$\Rightarrow$ Second note: $\hat{T}_{\bar{R}}$ commutes $\bar{\omega}$ $\hat{T}_{\bar{R}'}$

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

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

$\therefore$ 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:

$$\hat{T}_{\bar{a}_i} \psi = e^{i\theta_i} \psi \quad \Rightarrow \quad \theta_i \text{ characterizes e.v. of } \hat{T}_{\bar{a}_i}.$$

We must also satisfy our boundary conditions:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Bloch's Theorem

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

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

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

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

Proof of this result:

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

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

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

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

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

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 $\left(V(\bar{r}) = V(\bar{r}+\bar{R})\right)$ 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 e⁻ momentum is no longer $\bar{p} = \hbar\bar{k}$

$\hat{p}$ does not commute $= \hat{H}$ 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 e⁻ state, rather than momentum.

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

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

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

$$\therefore \text{B.T.} \Rightarrow \mathcal{H}_{\vec{k}'}(\vec{r}+\vec{R}) = e^{i\vec{k}'\cdot\vec{R}} \mathcal{H}(\vec{r})$$

$$= e^{i(\vec{k}+\vec{K})\cdot\vec{R}} \mathcal{H}(\vec{r})$$

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

$$\therefore \mathcal{H}_{\vec{k}'}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \mathcal{H}(\vec{r}) = \mathcal{H}_{\vec{k}}(\vec{r}+\vec{R})$$

$\Rightarrow$ this simplifies our view of the recip. lattice.

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

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

4. Note: $$\mathcal{H}_{n,\vec{k}+\vec{K}}(\vec{r}) = \mathcal{H}_{n,\vec{k}}(\vec{r})$$

$$\mathcal{E}_{n,\vec{k}+\vec{K}} = \mathcal{E}_{n,\vec{k}}$$

$\Rightarrow$ have periodicity of recip. lattice.

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

$$V_n(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} \, \mathcal{E}_n(\vec{k})$$

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

Band structure

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

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

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

$\rightarrow$ but, we can use some simple models to make qualitative explanations & simple predicts for some systems

$\rightarrow$ Solving $\mathcal{E}_n(\vec{k})$ $\Rightarrow$ band structure
$\qquad \hookrightarrow$ dispersion curves/relations.

$\rightarrow$ We already know $\mathcal{E}(\vec{k})$ for one simple system:

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

"Empty Lattice Approximation"

Take 1-D case:

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

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

$-K \qquad \frac{-K}{2} \qquad 0 \qquad \frac{K}{2} \qquad K$
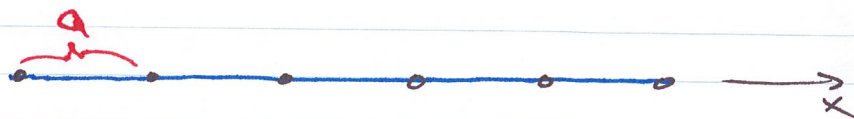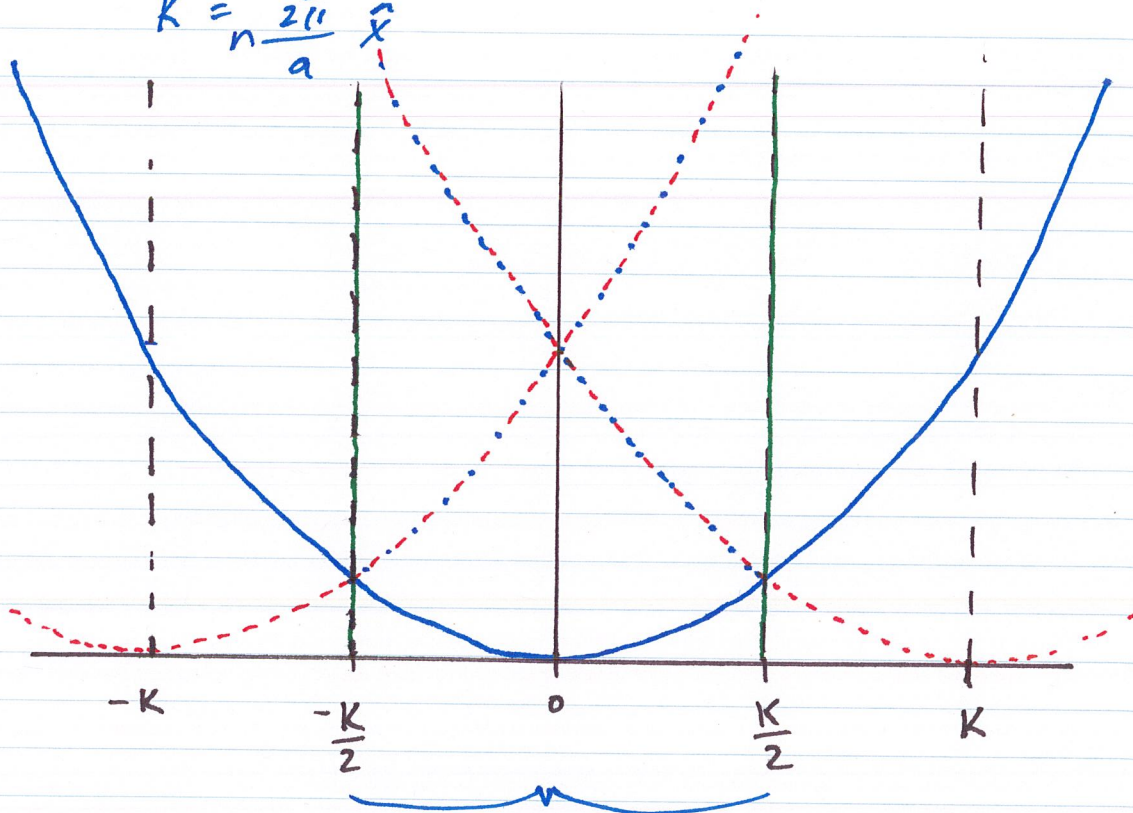
1st Brillouin Zone

"reduced zone"

—— solid blue shows "extended zone"

- - - - red shows "repeated zone"