Electrons in a crystal

When we discussed X-ray scattering we saw that the condition of constructive interference required that an incident wavevector $\vec{k}$ could only scatter into wavevectors $\vec{k}' = \vec{k} - \vec{K}$ where $\vec{K}$ was in the R.L.

For electrons in a crystal we expect similar behavior since our argument depended only on the wave nature of the scattering.

So a free electron plane wave state $e^{i\vec{k}\cdot\vec{r}}$ will get scattered into states $e^{i\vec{k}'\cdot\vec{r}}$ with $\vec{k}' = \vec{k} - \vec{K}$. We therefore expect the eigenstates of an electron in the periodic ionic potential of the crystal will be a mixture of these scattered states

$$\psi_k(\vec{r}) = \sum_K e^{i(\vec{k}-\vec{K})\cdot\vec{r}} c_{k-K}$$

$$= e^{i\vec{k}\cdot\vec{r}} \sum_K e^{-i\vec{K}\cdot\vec{r}} c_{k-K}$$

$$= e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r}) \quad \text{where } u_k(\vec{r}) = \sum_K e^{-i\vec{K}\cdot\vec{r}} c_{k-K}$$

$u_k(\vec{r})$ is periodic on the Bravais lattice:

$$u_k(\vec{r}+\vec{R}) = \sum_K e^{-i\vec{K}\cdot(\vec{r}+\vec{R})} c_{k-K} = \sum_K e^{-i\vec{K}\cdot\vec{R}} e^{-i\vec{K}\cdot\vec{r}} c_{k-K}$$

$$= \sum_K e^{-i\vec{K}\cdot\vec{r}} c_{k-K} = u_k(\vec{r}) \qquad \text{since } e^{-i\vec{K}\cdot\vec{R}} = 1$$

for all $\vec{K}$ in R.L.

This then yields <u>Bloch's Theorem</u> which we prove more rigorously later.

The energy eigenstates of an electron in a potential with the periodicity of a Bravais lattice ~~[illegible]~~ can be written in the form

$$\boxed{\begin{array}{l} \psi_k(\bar{r}) = e^{i\bar{k}\cdot\bar{r}}\, u_k(\bar{r}) \\ \text{where } u_k(\bar{r}+\bar{R}) = u_k(\bar{r}) \text{ is periodic on the B L} \end{array}}$$

An equivalent alternative statement of Bloch's theorem is

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

If the wavevector $\bar{k}$ lies exactly on the Bragg plane bisected by R.L. vector $\bar{K}$, then the two free electron plane wave states $\bar{k}$ and $\bar{k}' = \bar{k} - \bar{K}$ are degenerate in energy and so we expect they must mix equally in forming the new eigenstates in the presence of the periodic potential. Since we start with two states $\bar{k}, \bar{k}'$ we should wind up with two new states. If they mix equally, their relative coefficients should just be a phase factor $e^{i\phi}$. Hence we expect the two eigenstates to have the form

$$\psi_1(\bar{r}) = e^{i\bar{k}\cdot\bar{r}} + e^{i\phi_1} e^{i\bar{k}'\cdot\bar{r}}$$

$$\psi_2(\bar{r}) = e^{i\bar{k}\cdot\bar{r}} + e^{i\phi_2} e^{i\bar{k}'\cdot\bar{r}}$$

The new eigenstates ψ_1 and ψ_2 should be orthogonal

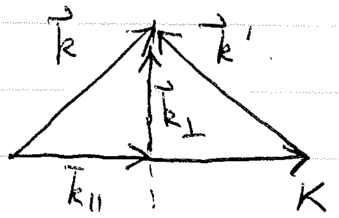
$$0 \overset{?}{=} \langle \psi_1 | \psi_2 \rangle = \int d^3r \; \psi_1^*(\vec r)\, \psi_2(\vec r)$$

$$= \int d^3r \left[e^{-i\vec k\cdot\vec r} + e^{-i\phi_1} e^{-i\vec k'\cdot\vec r} \right]\left[e^{i\vec k\cdot\vec r} + e^{i\phi_2} e^{i\vec k'\cdot\vec r} \right]$$

$$= \int d^3r \left[1 + e^{i(\phi_2-\phi_1)} + \underbrace{e^{-i\phi_1} e^{i(\vec k-\vec k')\cdot\vec r} + e^{i\phi_2} e^{i(\vec k'-\vec k)\cdot\vec r}}_{\text{these two terms integrate to zero - proof later}} \right]$$

$$= V\left[1 + e^{i(\phi_2-\phi_1)} \right]$$

$$= 0 \quad \text{only if} \quad \phi_2 - \phi_1 = \pi$$



$\vec k' = \vec k - \vec K$ write $\vec k = \vec k_\parallel + \vec k_\perp$
then $\vec k' = -\vec k_\parallel + \vec k_\perp$

So

$$\psi_1(\vec r) = e^{i\phi_1/2} e^{i\vec k_\perp\cdot\vec r} \left\{ e^{-i\phi_1/2} e^{i\vec k_\parallel\cdot\vec r} + e^{i\phi_1/2} e^{-i\vec k_\parallel\cdot\vec r} \right\}$$

$$= e^{i\phi_1/2} e^{i\vec k_\perp\cdot\vec r}\, 2\cos(\vec k_\parallel\cdot\vec r - \phi_1/2)$$

Similarly

$$\psi_2(\vec r) = e^{i\phi_2/2} e^{i\vec k_\perp\cdot\vec r}\, 2\cos(\vec k_\parallel\cdot\vec r - \phi_2/2)$$

$$= e^{i\phi_2/2} e^{i\vec k_\perp\cdot\vec r}\, 2\cos\left(\vec k_\parallel\cdot\vec r - \frac{\phi_1}{2} - \frac{\pi}{2}\right)$$

$$= e^{i\phi_2/2} e^{i\vec k_\perp\cdot\vec r}\, 2\sin\left(\vec k_\parallel\cdot\vec r - \frac{\phi_1}{2}\right)$$

so

$$\left.\begin{aligned} |\psi_1(\vec r)|^2 &\sim \cos^2(\vec k_\parallel \cdot \vec r - \phi_1/2) \\ |\psi_2(\vec r)|^2 &\sim \sin^2(\vec k_\parallel \cdot \vec r - \phi_1/2) \end{aligned}\right\} \text{probability density}$$

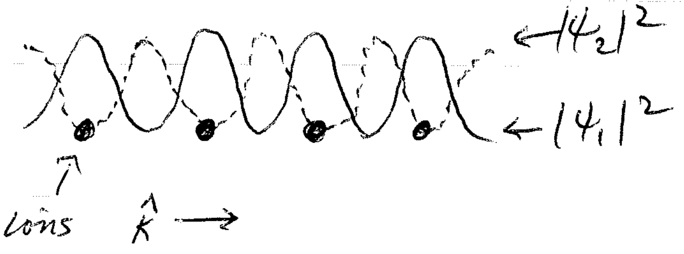
reflection from Bragg plane gives <u>standing</u> waves in direction $\parallel$ to $\vec K$

Since $\vec k_\parallel = \frac{\vec K}{2}$ we have $\vec k_\parallel \cdot \vec R = \frac{\vec K \cdot \vec R}{2} = \pi n$ where n is an integer

$\Rightarrow$ $|\psi_1(\vec r)|^2$ and $|\psi_2(\vec r)|^2$ have the periodicity of the R.L.

ie $|\psi_1(\vec r + \vec R)|^2 = \cos^2(\vec k_\parallel \cdot \vec r + \pi n - \phi_1/2) = \cos^2(\vec k_\parallel \cdot \vec r - \phi_1/2)$
$= |\psi_1(\vec r)|^2$

The only difference between ψ_1 and ψ_2 is their relative phase shift of $\frac{\pi}{2}$, which shifts the location of the peaks of $|\psi_1|^2$ and $|\psi_2|^2$ relative to the positions of the ions. By symmetry we expect one of these, say ψ_1, will have its peaks positioned at the same sites as the ions, while the other, ψ_2, will have its peaks positioned in between the sites of the ions. For example, if $\vec K$ is the smallest non-zero R.L. vector, $|\vec K| = \frac{2\pi}{a}$ with a = separation between ions, we expect,



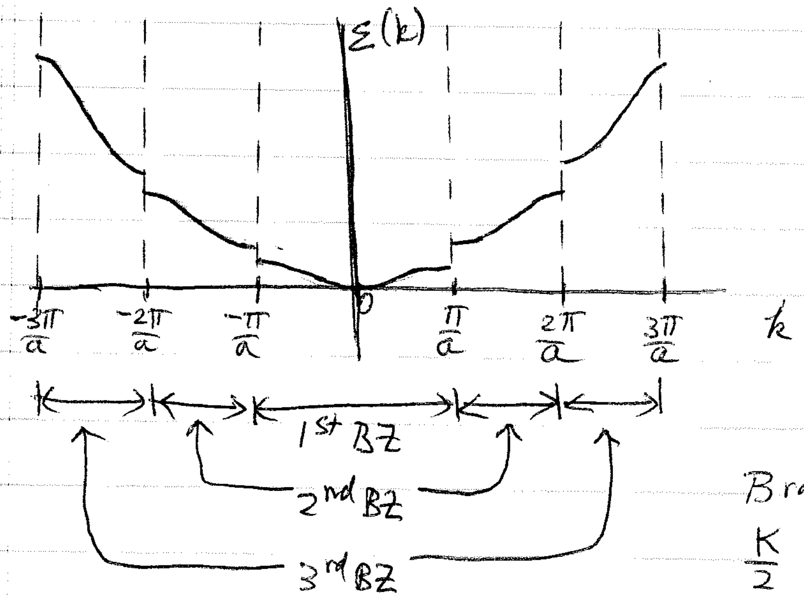
The spatial periodicity of ψ_1 and ψ_2 is $\lambda = \frac{2\pi}{k_{\parallel}} = \frac{2\pi}{(K/2)} = \frac{2\pi}{\pi/a} = 2a$. The spatial periodicity of $|\psi_1|^2$ and $|\psi_2|^2$ is therefore $\frac{1}{2}\lambda = a$. Since ψ_1 and ψ_2 are $\frac{\pi}{2}$ out of phase, then $|\psi_1|^2$ and $|\psi_2|^2$ are π out of phase, hence their relative peaks are separated by $a/2$ as in the diagram above.

Now when one turns on the attractive ionic potential, the state ψ_1 will have a lower energy than the state ψ_2 since ψ_1 has its peaks located at the ions, where the interaction is strongest, while ψ_2 has its peaks inbetween the ions, where the interaction is weakest.

Hence we expect that the two states ψ_1 and ψ_2, which were degenerate in energy before turning on the ionic potential, now split in energy, with a finite energy gap between them, $\varepsilon_1 < \varepsilon_2$.

$\Rightarrow$ Ionic potential cause a gap to appear in the energy dispersion relation $\varepsilon(\vec{k})$ whenever $\vec{k}$ crosses a Bragg plane. Since the Brillouin Zones are formed by the intersections of Bragg planes, gaps in $\varepsilon(\vec{k})$ open as $\vec{k}$ crosses the boundary of any Brillouin Zone.

For a 1-dimension B.L. (of lattice constant a). We expect the dispersion relation to look as in the sketch below:



$R = ma$ m integer,
$K = nb$, $b = \frac{2\pi}{a}$, n integer

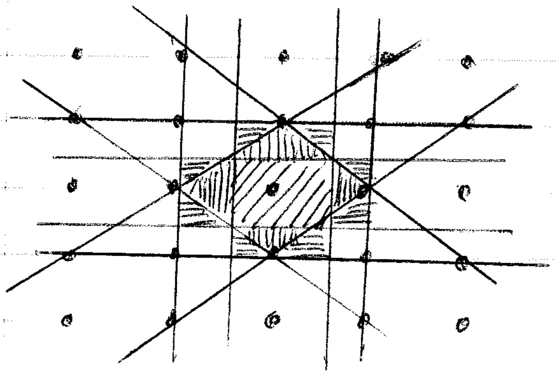
gap open in $\mathcal{E}(k)$ every time k crosses the boundary of a Brillouin Zone

Bragg Planes are at

$$\frac{K}{2} = \left(\frac{2\pi n}{a}\right)\left(\frac{1}{2}\right) = \frac{\pi n}{a}$$

for n integer

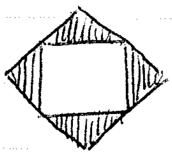
For a 2-dimensional square B.L. of lattice constant a



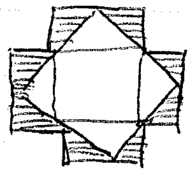
Bragg Planes divide k-space into Brillouin Zones

1st BZ

2nd BZ



3rd BZ



Whenever $\vec{k}$ crosses the surface of a BZ, there then is a discrete jump in the energy $\mathcal{E}(\vec{k})$

Each BZ is a primitive cell of the R.L.

Each $\vec{k}$ in k-space can be written as $\vec{k} = \vec{q} + \vec{K}$ with $\vec{K}$ a R.L. vector and $\vec{q}$ a vector in the 1st B.Z. $\vec{q}$ is unique

$\Rightarrow$ each n^{th} BZ may be mapped onto the 1st BZ by translating its pieces by appropriate R.L. vectors $\vec{K}$

It is customary to label the eigenstates and eigenvalues by this $\vec{q}$ and by discrete index n. $\vec{q}$ is called the "crystal momentum" and n the "band index." The state $(\vec{q}, n)$ corresponds to the free electron state in the n^{th} BZ with wave vector $\vec{k} = \vec{q} + \vec{K}$ ($\vec{K}$ is the RL vector that translates $\vec{q}$ into the n^{th} BZ)

The wavefunctions $\psi_{q,n}$ and energies $\mathcal{E}_n(\vec{q})$ are called the <u>band structure</u>

Born-von Karmen boundary conditions and Fourier transforms for a Bravais Lattice

We generalize the idea of periodic (or Born-von Karman) boundary conditions to electron states on a Bravais lattice.

B.L. vectors $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
n_1, n_2, n_3 integer.

For a BL of finite size we have $0 \le n_i < N_i$
$N = N_1 N_2 N_3$ is total number of points in the BL.
Total volume of this finite BL is

$$V = \underbrace{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}_{\text{volume of primitive cell}} N$$

We want our electron wavefunctions to be periodic on such a finite BL

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

As we saw earlier for free electrons, this imposes a constraint on the wave vectors $\vec{k}$ that can appear in the Fourier transform of $\psi(\vec{r})$.

Write $\psi(\vec{r})$ in terms of its Fourier transform

$$\psi(\vec{r}) = \sum_{k} e^{i\vec{k}\cdot\vec{r}} \, c_{\vec{k}}$$

↑ Fourier coefficients for $\psi(\vec{r})$

Then

$$\psi(\vec{r} + N_i\vec{a}_i) = \sum_k e^{i\vec{k}\cdot(\vec{r}+N_i\vec{a}_i)} c_k$$

$$= e^{iN_i\vec{k}\cdot\vec{a}_i} \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

$$= e^{iN_i\vec{k}\cdot\vec{a}_i} \psi(\vec{r})$$

$\Rightarrow$ must have $e^{iN_i\vec{k}\cdot\vec{a}_i} = 1$ for all $\vec{k}$ that appear in Fourier transform of $\psi(\vec{r})$

Write $\vec{k}$ in terms of the primitive vectors of the RL

$$\vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3$$

x_i are not in general integers

Then $e^{iN_i\vec{k}\cdot\vec{a}_i} = e^{iN_i 2\pi x_i} = 1$

$$\Rightarrow x_i N_i = m_i \text{ integer}$$

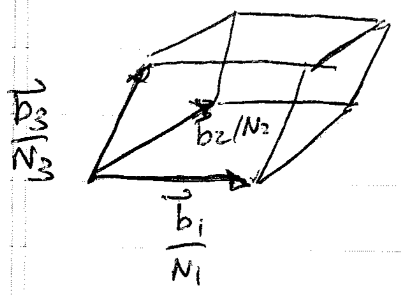
$$x_i = \frac{m_i}{N_i}$$

So the allowed wavevectors are

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

where m_1, m_2, m_3 are integers.

This is the Born - von Karman boundary conditions



volume per allowed wavevector in $\vec{k}$-space is the volume of the parallelpiped formed by the vectors $\frac{\vec{b}_i}{N_i}$

$$= \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3} = \frac{(2\pi)^3}{N\,(\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3))}$$

$$= \frac{(2\pi)^3}{vN} = \frac{(2\pi)^3}{V} \qquad V = vN = \text{total volume BL}$$

where $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the primitive cell of the B.L. and $\frac{(2\pi)^3}{v}$ is the volume of the primitive cell of the R.L.

Note: volume per allowed wavevector $\frac{(2\pi)^3}{V}$ is same as we had for free electrons.

Number of allowed $\vec{k}$ values in any primitive cell of the R.L. is

$$\frac{\left[\frac{(2\pi)^3}{v}\right]}{\left[\frac{(2\pi)^3}{vN}\right]} = N \quad \text{number of ions in BL}$$

Number of allowed $\vec{k}$ values in any primitive cell of the R.L., for exaple the 1st BZ, is N

⇒ # electron states in 1st BZ is $2N$ (2 from spin $= \pm 1$)
⇒ when valence $Z = 1$, ground state occupies half the states of 1st BZ