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

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

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

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

$u_k(\vec{r})$ 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 Bloch's Theorem which we prove more regorously later.

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

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

An equivalent alternative statement of Bloch's theorem is

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

If the wavevector $\vec k$ lies exactly on the Bragg plane bisected by R.L. vector $\vec K$, then the two free electron plane wave states $\vec k$ and $\vec k' = \vec k - \vec K$ 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 $\vec k$, $\vec k'$ 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

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

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

The new eigenstates ψ_1 and ψ_2 should be orthogonal

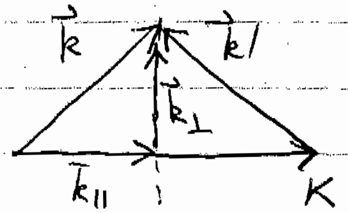
$$0 = \langle \psi_1 | \psi_2 \rangle = \int d^3r \, \psi_1^*(\vec{r}) \psi_2(\vec{r})$$

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

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

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

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



$\vec{k}' = \vec{k} - \vec{K}$ 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

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

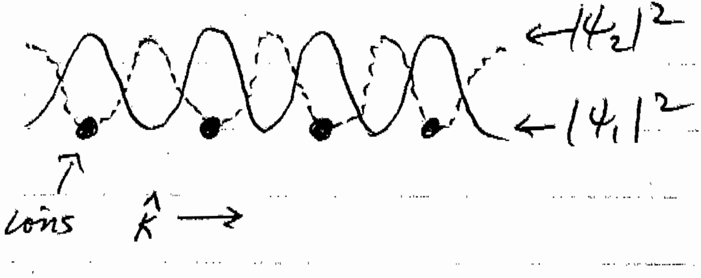
reflection from Bragg plane gives standing waves in direction $\parallel$ to $\vec K$

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 B.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,



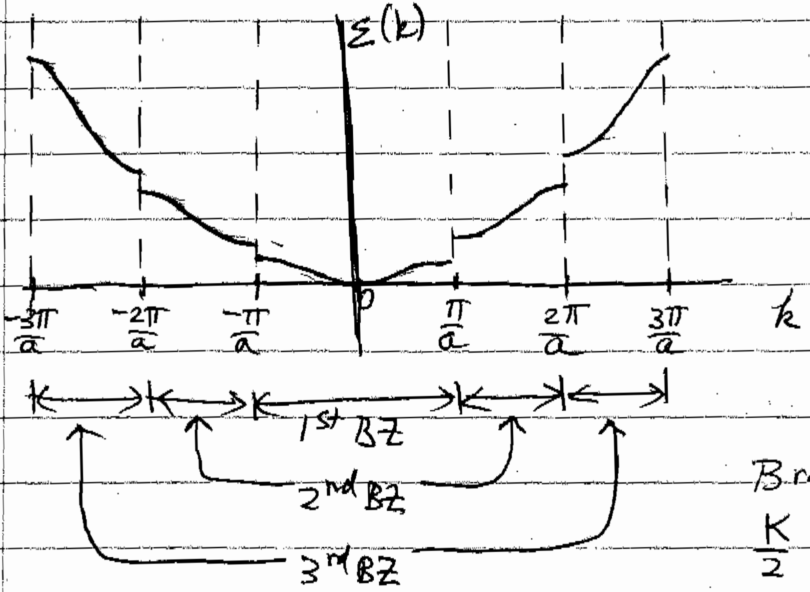
The spatial periodicity of ψ_1 and ψ_2 is $\lambda = \frac{2\pi}{k_{\parallel}} = \frac{2\pi}{(K/2)}$ $= \frac{2\pi}{\pi/a} = 2a$. The spatial periodicity of $|\psi_1|^2$ and $|\psi_2|^2$ is therefore $\frac{1}{2}\lambda = a$. Since ψ_1 and ψ_2 are $\frac{\pi}{2}$ out of phase, then $|\psi_1|^2$ and $|\psi_2|^2$ 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 integers

$K = nb$, $b = \frac{2\pi}{a}$, n integers

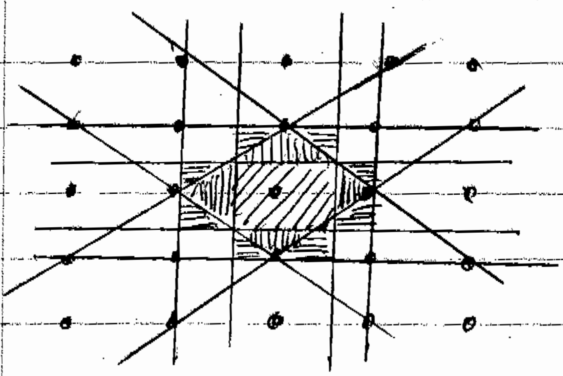
gap open is ε(k) every time k crosses the boundary of a Brillouin Zone

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

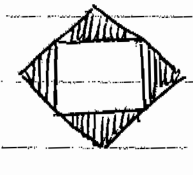
For a 2-dimensional square B.L. of lattice constant a



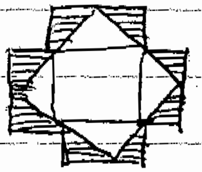
Bragg Planes divide k-space into Brillouin Zones

1st BZ

2nd BZ



3rd BZ



whenever k crosses the surface of a BZ, ~~there~~ then is a discrete jump in the energy ε(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 K a R.L. vector and $\vec{q}$ a vector in the 1st BZ. $\vec{q}$ is unique

⇒ each nth 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 nth BZ with wave vector $\vec{k} = \vec{q} + \vec{K}$ ($\vec{K}$ is the RL vector that translates $\vec{q}$ into the nth BZ)

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