

electrons - a preview

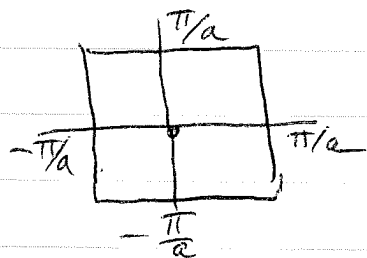
The above argument for X-rays is true for any waves. In particular it is also true for particle waves (where $\vec{p} = \hbar\vec{k}$ gives the quantum wave vector \vec{k}) provided one assumes the collisions of the particle with the crystal are elastic (ie the particle only ~~loses~~ ^{exchanges} momentum but not energy to the crystal). If one shot a high energy electron into the crystal, one could see electron diffraction patterns with Bragg peaks. Such electrons would scatter only if the tip of the wave vector \vec{k} lay on a Bragg plane.

What about a conduction electron inside the metal? In the absence of the periodic ion potential, the electron state would be a plane wave $e^{i\vec{k}\cdot\vec{r}}$. When we turn on the ion potential, such a plane wave would scatter if \vec{k} lay on a Bragg plane. But in the presence of the ion potential, $e^{i\vec{k}\cdot\vec{r}}$ is no longer an exact eigenstate. We will see that the eigenstates in the presence of the ion potential is a mixture of $e^{i\vec{k}\cdot\vec{r}}$ plus all the states $e^{i(\vec{k}+\vec{K})\cdot\vec{r}}$ into which it can be scattered by a Bragg plane. From perturbation theory in quantum mechanics, the extent to which the scattered state $e^{i(\vec{k}-\vec{K})\cdot\vec{r}}$ mixes into the free electron state $e^{i\vec{k}\cdot\vec{r}}$ is determined by

the "energy denominator" $\frac{1}{E(\vec{k}) - E(\vec{k}-\vec{R})}$.
Hence states $e^{i\vec{k}\cdot\vec{r}}$ where \vec{k} is far from any Bragg plane (and so where $\frac{1}{E_{\vec{k}} - E_{\vec{k}-\vec{R}}}$ is small) are very little changed from the free electron plane wave state. It is only states $e^{i\vec{k}\cdot\vec{r}}$ where \vec{k} lies close to a Bragg plane that there will be a strong mixing in of the scattered state $e^{i(\vec{k}-\vec{R})\cdot\vec{r}}$ and the resulting eigenstate is noticeably different from the free electron state (it will look like a reflected standing wave).

This explains why metals with valence $Z=1$ are so well described by the free electron model. When $Z=1$, the Fermi surface lies away from all Bragg planes, so all electron states have little Bragg scattering and free electron states are a very good approximation.

For simplicity, consider a simple cubic BL with lattice constant a and valence $Z=1$. The RL has a 1st Brillouin zone with volume $(\frac{2\pi}{a})^3$



The Fermi wave vector k_F is given by

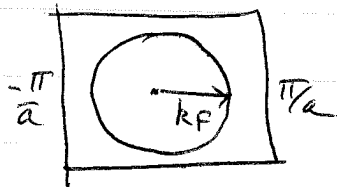
$$\frac{\frac{4}{3}\pi k_F^3}{4\pi^3} = m$$

$$k_F = (3\pi^2 m)^{1/3}$$

For $Z=1$, conduction electron density is $m = 1/a^3$

$$k_F = \frac{(3\pi^2)^{1/3}}{a} \quad \text{and} \quad \frac{k_F a}{\pi} = \frac{3.09}{\pi} < \frac{\pi}{\pi} = 1$$

and so the Fermi surface lies entirely within the 1st Brillouin Zone. All electron states with the



Fermi surface are therefore close to free electron-like, since they are not near any Bragg planes.

Note: volume in k-space of Fermi sphere is

$$\frac{4}{3}\pi k_F^3 = 4\pi^3 m = \frac{1}{2} \left(\frac{2\pi}{a}\right)^3 = \frac{1}{2} \text{ vol } 1^{\text{st}} \text{ B.Z.}$$

This is in general true for any B.L.

⇒ for $z=1$, the Fermi surface ~~almost~~ always lies ~~entirely within 1st B.Z.~~ occupies a volume in k-space equal to $\frac{1}{2}$ the volume of the 1st B.Z.

If $z=2$ however, then conduction electron density $m = 2/a^3$ and Fermi surface will in general cut ~~over~~ across the surface of the 1st B.Z.

The electron states at the BZ surface will not be free electron-like and there is now the possibility for more complicated behavior.

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

$$\begin{aligned}\psi_{\vec{k}}(\vec{r}) &= \sum_{\vec{K}} e^{i(\vec{k}-\vec{K})\cdot\vec{r}} c_{\vec{k}-\vec{K}} \\ &= e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}} \\ &= e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{where } u_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}}\end{aligned}$$

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

$$\begin{aligned}u_{\vec{k}}(\vec{r} + \vec{R}) &= \sum_{\vec{K}} e^{-i\vec{K}\cdot(\vec{r} + \vec{R})} c_{\vec{k}-\vec{K}} = \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{R}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}} \\ &= \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{r}} c_{\vec{k}-\vec{K}} = u_{\vec{k}}(\vec{r}) \quad \text{since } e^{-i\vec{K}\cdot\vec{R}} = 1 \\ &\quad \text{for all } \vec{R} \text{ in R.L.}\end{aligned}$$

This then yields Bloch's Theorem which we prove more rigorously later.

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

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

where $u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$ is periodic on the B.L.

An equivalent alternative statement of Bloch's Theorem is

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

If the wave vector \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

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

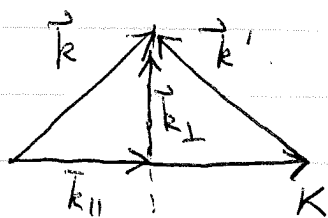
$$= \int d^3r \left[e^{-i\vec{k}\cdot\vec{r}} + e^{-i\phi_1} e^{-i\vec{k}'\cdot\vec{r}} \right] \left[e^{i\vec{k}\cdot\vec{r}} + e^{i\phi_2} e^{i\vec{k}'\cdot\vec{r}} \right]$$

$$= \int d^3r \left[1 + e^{i(\phi_2 - \phi_1)} + e^{-i\phi_1} e^{i(\vec{k} - \vec{k}')\cdot\vec{r}} + e^{i\phi_2} e^{i(\vec{k}' - \vec{k})\cdot\vec{r}} \right]$$

these two terms integrate to zero - proof later

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

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



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

$$\text{write } \vec{k} = \vec{k}_{\parallel} + \vec{k}_{\perp}$$

$$\text{then } \vec{k}' = -\vec{k}_{\parallel} + \vec{k}_{\perp}$$

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

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

Similarly

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

$$= e^{i\phi_2/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} 2 \cos(\vec{k}_{\parallel}\cdot\vec{r} - \frac{\phi_1}{2} - \frac{\pi}{2})$$

$$= e^{i\phi_2/2} e^{i\vec{k}_{\perp}\cdot\vec{r}} 2 \sin(\vec{k}_{\parallel}\cdot\vec{r} - \frac{\phi_1}{2})$$

so

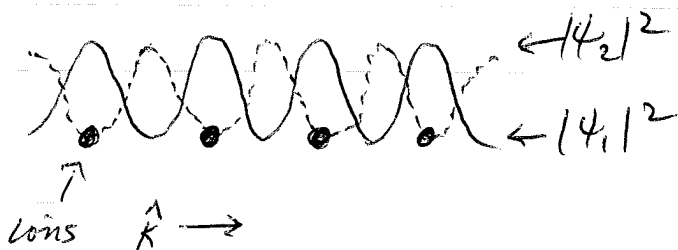
$$\left. \begin{aligned} |\psi_1(\vec{r})|^2 &\sim \cos^2(\vec{k}_{11} \cdot \vec{r} - \phi_1/2) \\ |\psi_2(\vec{r})|^2 &\sim \sin^2(\vec{k}_{11} \cdot \vec{r} - \phi_1/2) \end{aligned} \right\} \text{probability density}$$

reflection from Bragg plane gives standing waves in direction \parallel to \vec{k}

Since $\vec{k}_{11} = \frac{\vec{k}}{2}$ we have $\vec{k}_{11} \cdot \vec{R} = \frac{\vec{k} \cdot \vec{R}}{2} = \pi n$ where n is an integer

$$\Rightarrow |\psi_1(\vec{r})|^2 \text{ and } |\psi_2(\vec{r})|^2 \text{ have the periodicity of the B.L.}$$
$$\circ |\psi_1(\vec{r} + \vec{R})|^2 \approx \cos^2(\vec{k}_{11} \cdot \vec{r} + \pi n - \phi_1/2) = \cos^2(\vec{k}_{11} \cdot \vec{r} - \phi_1/2) = |\psi_1(\vec{r})|^2$$

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,



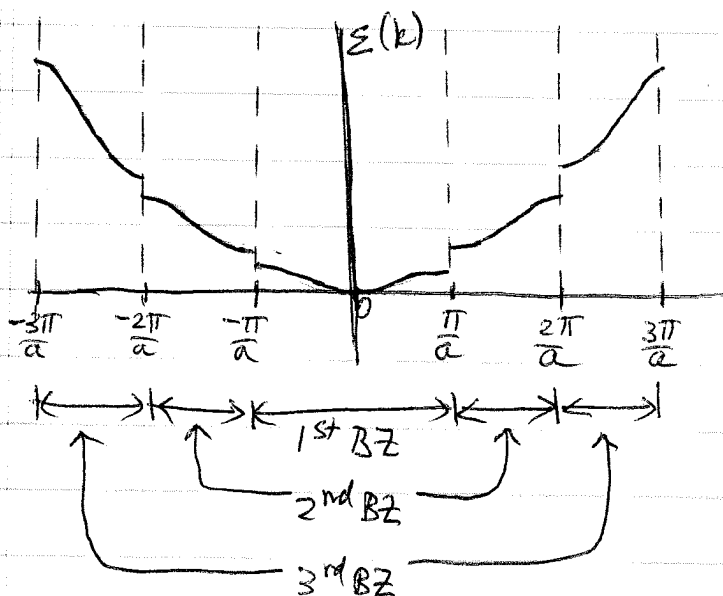
The spatial periodicity of ψ_1 and ψ_2 is $\lambda = \frac{2\pi}{k_{11}} = \frac{2\pi}{(K/2)}$
 $= \frac{2\pi}{\pi/a} = 2a$. The spatial periodicity of $|\psi_1|^2$ and
 $|\psi_2|^2$ is therefore $\frac{1}{2}\lambda = a$. Since ψ_1 and ψ_2 are $\frac{\pi}{2}$
out of phase, then $|\psi_1|^2$ and $|\psi_2|^2$ 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 in between 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, $E_1 < E_2$.

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

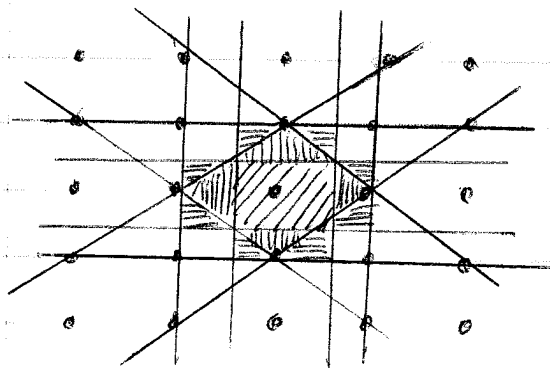
For a 1-dimensional B.L. of lattice constant a . We expect the dispersion relation to look as in the sketch below:



$R = ma$ m integers
 $K = nb$, $b = \frac{2\pi}{a}$, n integers
 gap open in $E(k)$
 every time k crosses
 the boundary of a
 Brillouin Zone

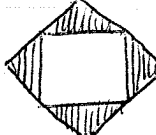
Bragg Planes are at
 $\frac{K}{2} = \left(\frac{2\pi n}{a}\right)\left(\frac{1}{2}\right) = \frac{\pi n}{a}$
 for n integers

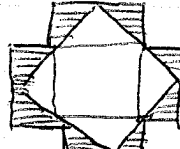
For a 2-dimensional square B.L. of lattice constant a



Bragg Planes divide k -space into Brillouin Zones

1st BZ 

2nd BZ 

3rd BZ 

whenever k crosses the surface of a BZ, there is a discrete jump in the energy $E(k)$

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

Each \vec{k} in k -space can be written as
 $\vec{k} = \vec{g} + \vec{K}$ with \vec{K} a R.L. vector and \vec{g} a
vector in the 1st B.Z. \vec{g} is unique
 \Rightarrow each n^{th} B.Z. may be mapped onto the 1st B.Z.
by translating its points by appropriate R.L. vectors \vec{K}

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

The wavefunctions $\psi_{\vec{g}, n}$ and energies $E_n(\vec{g})$
are called the band structure