PHYS 551 Lecture #20

Title: "Free" electrons in a periodic potential

Bloch's Theorem:

A solution of the Schrödinger equation in a periodic lattice (i.e., with a periodic potential) can be changed by only a phase factor for all lattice translations. In otherwords, the probability density must be the same for all equivalent positions in the lattice. Hence $\psi^*(\vec{r})\,\psi(\vec{r}) = \psi^*(\vec{r}+\vec{R})\,\psi(\vec{r}+\vec{R})$ where $\vec{R} \equiv n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$. In general:

$$\begin{aligned}
\psi_k(\vec{r}) &= e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) \quad \text{where} \quad e^{i\vec{k}\cdot\vec{r}} \text{ is a plane wave} \\
u(\vec{r}) &\equiv \vec{u}(\vec{r}+\vec{R}) \ \text{ and is now assumed periodic} \\
\psi_k(\vec{r}+\vec{R}) &= e^{i\vec{k}\cdot(\vec{r}+\vec{R})}u(\vec{r}+\vec{R}) \\
\psi_k(\vec{r}+\vec{R}) &= e^{i\vec{k}\cdot\vec{R}}e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) \\
\psi_k(\vec{r}+\vec{R}) &= e^{i\vec{k}\cdot\vec{R}}\psi_k(\vec{r})
\end{aligned}$$

Not only does $\psi_k(\vec{r}+\vec{R}) = e^{ik\cdot R}\psi_k(\vec{r})$, it also is multi-valued.

$$\text{Let } \vec{k} = \vec{G} + \vec{k}' \qquad \begin{aligned} e^{i\vec{k}\cdot\vec{R}} &= e^{i(\vec{G}+\vec{k}')\cdot\vec{R}} = e^{i\vec{G}\cdot\vec{R}}e^{i\vec{k}'\cdot\vec{R}} \\ &= e^{i2\pi n}e^{i\vec{k}'\cdot\vec{R}} \end{aligned}$$

so

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

but we could have written equivalently

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

and so ψ_k and $\psi_{k'}$ must have the same phase shift.

Thus a general $\psi(\vec{r})$ solution must use a composite sum

$$\psi(\vec{r}) = \sum_{\vec{G}} \psi_{\vec{k}-\vec{G}}(\vec{r})u_{\vec{k}-\vec{G}}(\vec{r})$$

Notice $\vec{k}$ is the only wave vector on the right hand side

$$\psi_k(\vec{r}) = \sum_{\vec{G}} \psi_{\vec{k}-\vec{G}}(\vec{r})u_{\vec{k}-\vec{G}}(\vec{r})$$

So we must define an additional parameter to specify which solution.

$$\psi_{n,\vec{k}} \;=\; e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r}) \quad n \equiv \text{band index.}$$

In the case of nearly free electrons U_0 is assumed to be constant.

Using the time independent Schrödinger equation, $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U_o\psi((\vec{r}) \;=\; E\psi(\vec{r})$, and letting $\vec{G}=0$ and $\psi_k = A\ e^{i\vec{k}\cdot\vec{r}}$

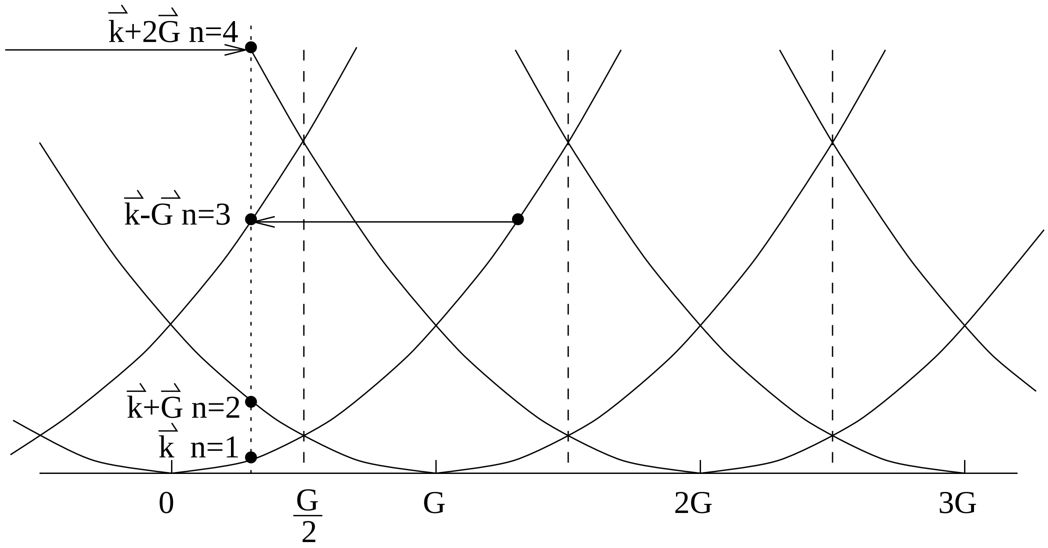
$$\text{Normalization requires} \quad \int_{x-tal} \psi^*\psi\ dV = 1 \qquad A = \frac{1}{\sqrt{V}}$$

with energy eigenvalue, $E = U_0 + \frac{\hbar^2 k^2}{2m}$, and eigenfunction, $\psi_k = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$.

Notice that we could choose another solution $\vec{k} \Rightarrow \vec{k}+\vec{G}$

$$\text{This gives} \;\; \psi = Ae^{i(\vec{k}+\vec{G})\cdot\vec{r}} \;\; \text{and} \;\; \nabla^2\psi = \; -A|\vec{k}+\vec{G}|^2\psi$$

so that $E = U_0 + \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2$



Reduced Zone: Look at all solutions in the first Brillouin zone

Extended Zone: Look at solutions in the appropriate zone

So what happens at the zone boundry?

Bragg reflection of the electrons!

We might therefore expect equal numbers of the two possible solutions.

$$Ae^{i\frac{\vec{G}}{2}\cdot\vec{x}} \quad \text{and} \quad A\ e^{-i\cdot\frac{\vec{G}}{2}\cdot\vec{x}} \;\; \text{where} \;\; |G| = \frac{2\pi}{a}$$

$$
\begin{aligned}
\psi(+) &= \exp(i\frac{G}{2}x) + \exp(-i\frac{G}{2}x) = 2\cos(\pi x/a) \\
\text{and} \qquad \psi(-) &= \exp(i\frac{G}{2}x) - \exp(-i\frac{G}{2}x) = 2i\sin(\pi x/a)
\end{aligned}
$$

$\psi^*(+)\psi(+) \propto \cos^2(\pi x/a)$

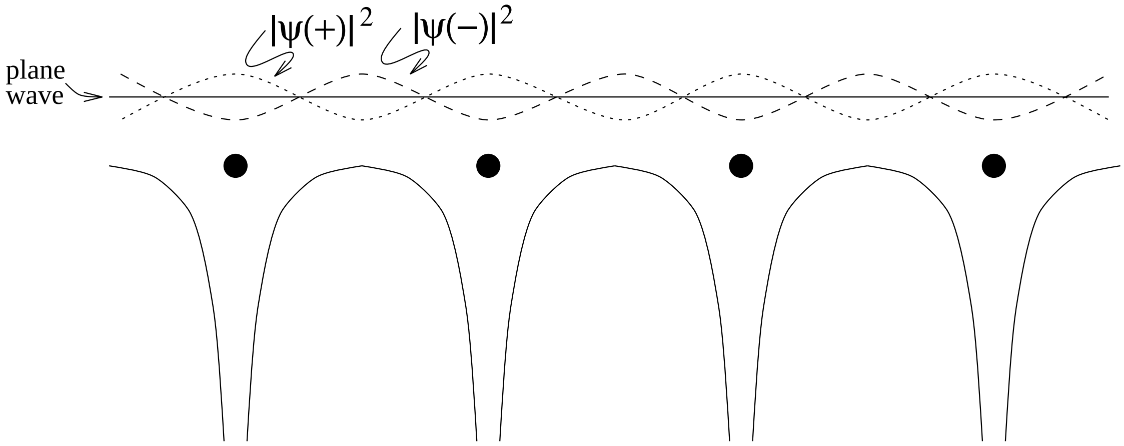
$\psi^*(-)\psi(-) \propto \sin^2(\pi x/a)$

The + solution builds up charge at ions

while the − solution builds up charge between ions

At present U is constant and thus there is no difference in the eigenvalues

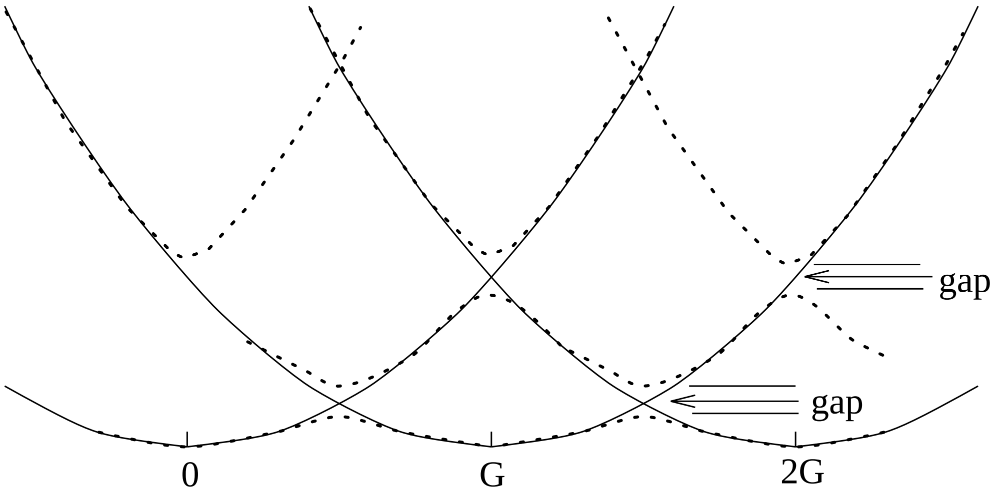
If U is not constant (generally attractive), then



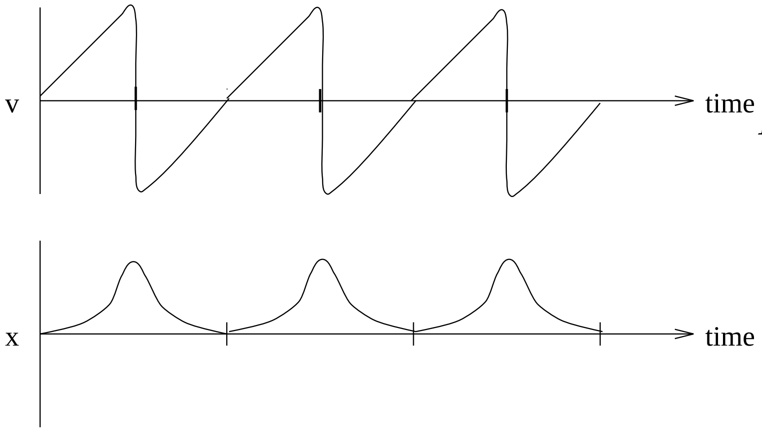
$|\psi(+)|^2$ is lower in energy

$|\psi(-)|^2$ is higher in energy

There are gaps wherever "bands" cross.



If we have a <u>single</u> electron and apply an electric field: (No scattering)



$$\begin{aligned}
m\vec{v} &= \vec{p} = \hbar\vec{k} \\
\vec{k} &= \frac{m}{\hbar}\vec{V} \\
E_{\text{F.E.}} &= \frac{\hbar^2 k^2}{2m} \\
\frac{dE}{dk} &= \frac{\hbar^2 k}{m} \\
|\vec{v}| &= \frac{1}{\hbar}\frac{dE}{dk} \\
\frac{d^2E}{dk^2} &= \frac{\hbar^2}{m} \\
\frac{1}{m} &= \frac{1}{\hbar^2}\frac{d^2E_{\text{F.E.}}}{dk^2} \\
\frac{1}{m^*} &\equiv \text{effective mass} \\
\frac{1}{m^*} &\equiv \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}
\end{aligned}$$

Magnitude of the energy gap

$$\begin{aligned}
E_g &= E_+ - E_- \\
E_+ &= \int_0^1 dx\ \psi^*(+)\, U(x)\, \psi(+) \\
E_- &= \int_0^1 dx\ \psi^*(-)\, U(x)\, \psi(-) \\
\text{if}\ \ U(x) &= U_0\cos(\frac{2\pi x}{a})\ \ \text{with period } a!
\end{aligned}$$

$$E_{\text{gap}} = 2\int dx\ U_0\cos(\frac{2\pi x}{a})[\cos^2(\frac{\pi x}{a}) - \sin^2(\frac{\pi x}{a})]$$

(between 1st and 2nd bands)

We can always decompose U in terms of its *Fourier* components to determine the gap at each and every band crossing.