PHYS 551 Lecture 21

Title: General Solution for an Electron in a Weak Periodic Potential

For any function $f(\vec{r})$, a periodic function in $\vec{r}$, we express this function in terms of a Fourier transform. Hence

$$f(\vec{r}) = \sum_{\vec{G}} A(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

where $\vec{G}$'s are (in this case) the set of reciprocal lattice vectors.

$$\text{The coefficients are} \quad A(\vec{G}) = \frac{1}{V}\int_{cell} f(r) e^{i\vec{G}\cdot\vec{r}} d\vec{r}$$

This relationship can be easily shown:

(1) Multiply by $e^{-i\vec{G}'\cdot\vec{r}}d\vec{r} \implies f(\vec{r})e^{-i\vec{G}'\cdot\vec{r}}d\vec{r} = \sum_{\vec{G}} A(\vec{G}) e^{i(\vec{G}\cdot\vec{r}-\vec{G}'\cdot\vec{r})}d\vec{r}$

(2) Integrate over $\int_{\text{UNIT CELL}} d\vec{r} \implies \int_{\text{CELL}} f(r)e^{-i\vec{G}'\cdot\vec{r}}d\vec{r} = \int \sum_{\vec{G}} A(\vec{G}) e^{i(\vec{G}\cdot\vec{r}-\vec{G}'\cdot r)}d\vec{r}$

(3) Exchange $\int$ with $\sum$ on the right hand side

Note: $\int_{\text{CELL}} e^{i(\vec{G}-\vec{G}')\cdot\vec{r}}d\vec{r} = V_{cell}\ \delta(\vec{G}-\vec{G}')$

$$\text{So} \quad \int_{\text{CELL}} f(r)e^{-i\vec{G}'\cdot\vec{r}}dr = V_{cell}\sum_{\vec{G}} A(\vec{G})\ \delta(\vec{G}-\vec{G}')$$

$$\text{Thus} \quad \int_{\text{CELL}} f(r)e^{-i\vec{G}'\cdot\vec{r}}dr = V_{cell}\ A(\vec{G})$$

$$QED$$

Using the properties of the Fourier transform, we will extend this formalism to the time-independent Schrödinger equation. Recall that the Bloch condition gives the following general wave function:

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

where

$$\sum_{\vec{G}} u(\vec{k}-\vec{G})e^{i\vec{G}\cdot\vec{r}} \text{ is periodic in } \vec{r}$$

and

$$e^{i\vec{k}\cdot\vec{r}} \text{ is a plane-wave solution}$$

NOTE: $u(\vec{k}-\vec{G}) \equiv u(\vec{G})$

The POTENTIAL can also be written in a similar fashion:

$$U(\vec{r}) = \sum_{\vec{G}'} U(\vec{G}')e^{i\vec{G}'\cdot\vec{r}}$$

Notice: $\vec{G}' = 0$ corresponds to a constant potential U_0.

Also since the potential is real, $U^*(G) = U(-G)$

and $(U(-G)e^{-i\vec{G}\cdot\vec{r}} + U(G)e^{i\vec{G}\cdot\vec{r}}) = 2\ \cos(\vec{G}\cdot r)\, U(\vec{G})$

The Schrödinger equation gives:

$$-\frac{\hbar^2}{2m}\,\nabla^2\psi + U(r)\psi = E\psi \qquad \text{Recall } \nabla\cdot\nabla(\psi) = \nabla\cdot(\nabla\psi)$$

Substituting gives:

$$\begin{aligned} -\frac{\hbar^2}{2m}\,\nabla^2\left[\sum_G u(G)e^{i(\vec{k}-\vec{G})\cdot\vec{r}}\right] \;&+\; \sum_{G'} U(G')^{i\vec{G}'\cdot\vec{r}} \sum_G u(G)e^{i(\vec{k}-\vec{G})\cdot\vec{r}} \\ &=\; E\sum_G u(G)e^{i(\vec{k}-\vec{G})\cdot\vec{r}} \end{aligned} \tag{1}$$

Divide by $e^{i\vec{k}\cdot\vec{r}}$ and <u>split</u> U(G=0)

$$\frac{\hbar^2}{2m}\sum_G |\vec{k}-\vec{G}|^2\, u(G)e^{-i\vec{G}\cdot\vec{r}} + \sum_{G'}^{G'\neq 0}\sum_G U(G')u(G)e^{i(\vec{G}'-\vec{G})\cdot\vec{r}} + \sum_{\vec{G}} U_0 e^{i\vec{G}\cdot\vec{r}} = E\sum_{\vec{G}} u(G)e^{-i\vec{G}\cdot\vec{r}} \tag{2}$$

Collecting $\sum_G$ and $\sum_G \sum_{G'}$ terms gives

$$\sum_G \sum_{G'}^{G'\neq 0} U(G')u(G)e^{i(\vec{G}'-\vec{G})\cdot\vec{r}} = \sum_G \left[E - U_0 - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2\right] u(G)e^{-i\vec{G}\cdot\vec{r}} \tag{3}$$

Now multiply by $e^{i\vec{G}''\cdot\vec{r}}$ and integrate $\int_{cell} d\vec{r}$

$$\begin{aligned} \sum_G \sum_{G'}^{G'\neq 0} U(G')u(G)\ \delta(G''+G'-G) \;&=\; \sum_G \left[E - U_0 - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}|^2\right] u(G)\delta(G''-G) \\ \underline{\text{So}} \qquad \sum_{G'}^{G'\neq 0} U(G')u(G''+G') \;&=\; \left[E - U_0 - \frac{\hbar^2}{2m}|\vec{k}-\vec{G}''|^2\right] u(G'') \end{aligned} \tag{4}$$

Clearly this represents a set of simultaneous equations for the entire range of $\vec{G}''$. Typically, using a computer, it is possible to use only a <u>few</u> hundred. In this course, we will use less.

To get some idea of what this all means we will make an extreme initial assumption: $U(\vec{r})$ is so weak and so slowly varying that all U(G) *except* $U(G=0)$ can be, to first order, ignored.

Clearly, if the potential has this form, the system must very close to being an ideal free electron gas. Hence it might be reasonable to assume that only a single $u(G)$ is present in the approximate wavefunctions. Let $u(0)$ be this non-trivial coefficient.
Thus we *assume* $\psi(\vec{r},\vec{k}) \approx u(0)e^{i\vec{k}\cdot\vec{r}}$
Reassessing Eqn. (4) gives

$$0 = \left[E - U_0 - \frac{\hbar^2}{2m}|\vec{k}|^2\right] u(0) \;\text{ if }\; \vec{G}'' = 0 \tag{5}$$

(All left hand side terms are very small: $U(G')\,u(G''+G') = \text{small} \times \text{small}$)
Notice that this is just the energy of the free-electron gas.
Also note that:

$$U(-G'')u(0) = [E - U_0 - \frac{\hbar^2}{2m}|\vec{k} - \vec{G}''|^2]\; u(\vec{G}'') \quad \text{if} \quad \vec{G}'' \neq 0 \tag{6}$$

For Eqn. (5) to hold either $u(0) = 0$ or $E - U_0 = \frac{\hbar^2}{2m}\, k^2$.

Notice that u(0) = 0 is inconsistent with the initial assumption, therefore $E - U_0 = \frac{\hbar^2}{2m}\, k^2$.

Substituting this result into Eqn. (6) and solving for $u(\vec{G}'')$ gives

$$u(G'') = \frac{U(-G'')\;2m}{\hbar^2[k^2 - |\vec{k} - \vec{G}|^2]}\; u(0) \qquad \text{and } G'' \neq 0r \tag{7}$$

Thus $u(\vec{k},\vec{r})$ can be enumerated

$$u(\vec{k},\vec{r}) = \sum_{G}^{G\neq 0} \frac{U(-G)\;2m}{\hbar^2[k^2 - |\vec{k} - \vec{G}|^2]}\; u(0)e^{i(\vec{G}\cdot\vec{r})} + u(0)$$

Notice that $u(\vec{k},\vec{r})$ works in general everywhere except when $k^2 - |\vec{k} - \vec{G}|^2 = 0$; this occurs at <u>ALL</u> band crossings. Thus the particular $u(\vec{G}) \Longrightarrow \infty$! (This violates the initial supposition.) Clearly we must include an additional $u(G)$ term for each band crossing that we want to describe everything accurately. For the band crossing at $\vec{k} = \frac{\vec{G}}{2}$ we need to include the $u(\vec{G})$ term in our initial trial wavefunction. Now Eqn. (4) gives

$$\begin{aligned}
&\text{(A) if } G'' = 0 \qquad & U(G)u(G) &= [E - U_0 - \frac{\hbar^2}{2m}k^2]u(0) \\
&\text{(B) if } G'' = G \qquad & U(-G)u(0) &= [E - U_0 - \frac{\hbar^2}{2m}|k - G|^2]u(G)
\end{aligned}$$

Note: There is no $G' = 0$ on left hand side but a myriad of other terms otherwise. (A) and (B) represent two equations and two unknowns. To be coupled, the determinant must be zero.
Let $E' = -U_0 + E$

$$\text{So}\quad \begin{vmatrix} (E' - \frac{\hbar^2 k^2}{2m}) & -U(G) \\ -U(-G) & E' - \frac{\hbar^2}{2m}|k - G|^2] \end{vmatrix} \begin{vmatrix} u(0) \\ u(G) \end{vmatrix} = 0$$

And solving for E' [recall that $u(G) = u(-G)$] gives

$$E'^2 - \frac{\hbar^2 k^2}{2m} E' - \frac{\hbar^2}{2m} |\vec{k} - \vec{G}|^2 E' + (\frac{\hbar^2}{2m})^2 k^2 |k - G|^2 - U^2(G) = 0$$

$$\text{Let:} \quad A = 1 \quad B = -\frac{\hbar^2}{2m}(k^2 + |\vec{k} - \vec{G}|^2) \quad C = (\frac{\hbar^2}{2m})^2 k^2 |k - G|^2$$

Thus

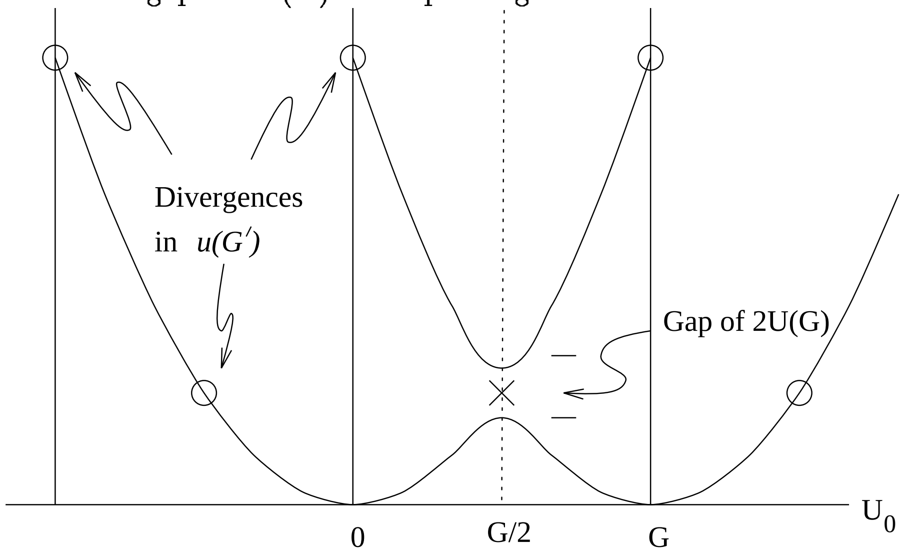
$$E' = \frac{\frac{\hbar^2}{2m}(k^2 + |\vec{k} - \vec{G}|^2) \pm \sqrt{[\frac{\hbar^2}{2m}(k^2 + |\vec{k} - \vec{G}|^2)]^2 - 4C}}{2}$$

So

$$E(k) = U_0 + \frac{\hbar^2}{4m}(k^2 + |\vec{k} - \vec{G}|^2) \pm \frac{1}{2}\sqrt{(\frac{\hbar^2}{2m})^2 (k^2 - |\vec{k} - \vec{G}|^2)^2 + 4U(G)^2}$$

$$\begin{aligned} \text{If} \quad k = 0 \qquad & E(k) = U_0 + \frac{\hbar^2 G^2}{4m} \pm \sqrt{(\frac{\hbar^2}{2m})^2 |\vec{G}|^4 + 4U(G)^2} \\ \text{If} \quad k = \vec{G}/2 \qquad & E(k) = U_0 + \frac{\hbar^2}{4m}(\frac{G}{2})^2 \pm \frac{1}{2}\sqrt{4U(G)^2} \\ & \qquad = U_0 + \frac{\hbar^2}{4m}\frac{G^2}{2} \pm U(G) \end{aligned}$$

Clearly there is a gap of $2U(G)$! Now plotting the two solutions:



Notice that the U(G) coefficient produces a gap at $\vec{G}/2$!

So far we have examined the energy solutions (eigenvalues). Now to investigate the eigenfunctions or wavefunctions (ψ).

Recall Eqn.(A)

$$u(G) = \frac{[E - U_0 \ - \ \frac{\hbar^2 k^2}{2m}]}{U(G)} \ u(0)$$

At the first zone boundary: $\vec{k} \ = \ \vec{G}/2$ and $E = U_0 + \frac{\hbar^2}{2m}(\frac{G}{2})^2 \pm U(G)$

So

$$u(G) = \pm\frac{U(G)}{U(G)} u_0 \ = \ \pm u(0) \begin{array}{l} + \text{ higher energy} \\ - \text{ lower energy} \end{array}$$

$$\psi(\vec{k},\vec{r}) \approx e^{i\vec{k}\cdot\vec{r}}[u(0) \pm u(0)e^{-i\vec{G}\cdot\vec{r}}] \text{ for } \vec{k} = \vec{G}/2$$

$$\begin{aligned} U(\vec{r}) &= U_0 + U(G)e^{i\vec{G}\cdot\vec{r}} + U(-G)e^{-i\vec{G}\cdot\vec{r}} \\ U(\vec{r}) &= U_0 + 2U(G)\cos(\vec{G}\cdot\vec{r}) \ \ (\text{if } U(G) \text{ is real}) \end{aligned}$$

Let $U(G) > 0$ and examine $\psi^*\psi = |\psi|^2$ (Note: $\int |\psi|^2 d\vec{r} = 1$)

Higher energy $|\psi(+)|^2 \ = \ [(1 + e^{-i\vec{G}\cdot\vec{r}})(1 + e^{i\vec{G}\cdot\vec{r}})] \ |u(0)|^2$

Lower energy $|\psi(-)|^2 = \ [(1 - e^{-i\vec{G}\cdot\vec{r}})(1 - e^{i\vec{G}\cdot\vec{r}})] \ |u(0)|^2$

$$\begin{aligned} |\psi(+)|^2 &= 2(1 + \cos(\vec{G}\cdot\vec{r}))|u(0)|^2 \ = \ 4 \ \cos^2(\tfrac{\vec{G}\cdot\vec{r}}{2}) \\ |\psi(-)|^2 &= 2(1 - \cos(\vec{G}\cdot\vec{r}))|u(0)|^2 \ = \ 4 \ \sin^2(\tfrac{\vec{G}\cdot\vec{r}}{2}) \end{aligned}$$

At $|\vec{r}| = 0$ $U(0) = U_0 + 2U(G)$, which is at a maximum

H $|\psi(+)|^2 = 4|U(0)|^2$

L $|\psi(-)|^2 = \ \ 0$

At $\vec{r} = \frac{\vec{a}}{2}$ $U(\frac{\vec{a}}{2}) = U_0 - 2U(G)$, which is at a minimum

H $|\psi(+)|^2 = \ \ 0$

L $|\psi(-)|^2 = 4|U(0)|^2$

Now reexamining $E(k)$ where

$$E(k) = U_0 + \frac{\hbar^2}{4m}(k^2 + |\vec{k} - \vec{G}|^2) \pm \frac{1}{2}\sqrt{(\frac{\hbar^2}{2m})^2(k^2 - |\vec{k} - \vec{G}|^2) + 4U(G)^2}$$

and letting $c = \frac{\hbar^2}{2m}$ which gives

$$E(k) = U_0 + \frac{c}{2}(k^2 + |\vec{k} - \vec{G}|^2) \pm \frac{1}{2}\sqrt{c^2(k^2 - |\vec{k} - \vec{G}|^2) + 4U(G)^2}$$

$+$ solution $+$

k	$E(k)$
$\frac{3}{2}G_1$	$U_0 + c\frac{5}{4}G_1^2 + \frac{1}{2}\sqrt{c^2 4G_1^4 + 4U(G_1)^2} \approx U_0 + c\frac{9}{4}G_1^2$
G_1	$U_0 + c\frac{1}{2}G_1^2 + \frac{1}{2}\sqrt{c^2 G_1^4 + 4U(G_1)^2} \approx U_0 + cG_1^2$
$\frac{1}{2}G_1$	$U_0 + c\frac{1}{4}G_1^2 + \frac{1}{2}\sqrt{0 + 4U(G_1)} = U_0 + c\frac{1}{4}G_1^2 + U(G_1)$
0	$U_0 + c\frac{1}{2}G_1^2 + \frac{1}{2}\sqrt{c^2 G_1^4 + 4U(G_1)^2} \approx U_0 + cG_1^2$
$-\frac{1}{2}G_1$	$U_0 + c\frac{5}{4}G_1^2 + \frac{1}{2}\sqrt{c^2 4G_1^4 + 4U(G_1)^2}$
$-G_1$	$U_0 + c\frac{5}{2}G_1^2 + \frac{1}{2}\sqrt{c^2 9G_1^4 + 4U(G_1)^2}$

$-$ solution $-$

k	$E(k)$
$2G_1$	$U_0 + cG_1^2$
$\frac{3}{2}G_1$	$U_0 + c\frac{1}{4}G_1^2$
G_1	U_0
$\frac{1}{2}G_1$	$U_0 + c\frac{1}{4}G_1^2 - U(G_1)$
0	U_0
$-\frac{1}{2}G_1$	$U_0 + c\frac{1}{4}G_1^2$
$-G_1$	$U_0 + cG_1^2$

k	k^2	$(k-G_1)^2$	$\vert k-G_1\vert$	$\overbrace{k^2+\vert k-G_1\vert^2}^{A}$	$\overbrace{k^2-\vert k-G_1\vert^2}^{B}$	
$\frac{3}{2}G_1$	$\frac{9}{4}G_1^2$	$\frac{1}{4}G_1^2$	$\frac{1}{2}G_1$	$\frac{10}{4}G_1^2$	$\frac{8}{4}G_1^2$	$2G_1^2$
G_1	G_1^2	0	0	G_1^2	G_1^2	G_1^2
$\frac{1}{2}G_1$	$\frac{1}{4}G_1^2$	$+\frac{1}{4}G_1^2$	$-\frac{1}{2}G_1$	$\frac{2}{4}G_1^2$	0	0
0	0	$+G_1^2$	$-G_1$	G_1^2	$-G_1^2$	$-G_1^2$
$\frac{1}{2}G_1$	$\frac{1}{4}G_1^2$	$+\frac{9}{4}G_1^2$	$-\frac{3}{2}G_1$	$\frac{10}{4}G_1^2$	$-\frac{8}{4}G_1^2$	$-2G_1^2$
$-G_1$	G_1^2	$4G_1^2$	$-2G_1$	$5G_1^2$	$-3G_1^2$	$-3G_1^2$
$-\frac{3}{2}G_1$	$\frac{9}{4}G_1^2$	$\frac{25}{4}G_1^2$	$-\frac{5}{2}G_1$	$\frac{34}{4}G_1^2$	$-\frac{16}{4}G_1^2$	$-4G_1^2$
$-2G_1$	$4G_1^2$	$9G_1^2$	$-3G_1$	$13G_1^2$	$-5G_1^2$	$-5G_1^2$