Lecture 23 (April 14, 2008)

Let's talk about the quiz for a few minutes.

We have plane waves (normalized) and periodic boundary conditions. So, you all correctly calculated the volume of k-space for each allowed value of k:

$\left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$ in 3D. In other words the density of these points is $\frac{V}{8\pi^3}$ (number of allowed solutions per unit volume of the k-space). If you include spin, then it will be $2\cdot\frac{V}{8\pi^3}$. If someone asks: "How many states are there in the volume $d\bar{k}$?"

You say $\frac{2V}{8\pi^3}\,d\bar{k}$.

How does the energy density of states come about?

$$\sum_n F(\varepsilon_n) = \frac{2V}{8\pi^3}\int d\bar{k}\, F(\varepsilon_n) = V\int d\varepsilon \int \frac{2}{8\pi^3} d\bar{k}\,\delta(\varepsilon-\varepsilon_n)\,F(\varepsilon)$$

$$= V\int d\varepsilon\, D(\varepsilon)\,F(\varepsilon) \quad \text{if} \quad D(\varepsilon) = \frac{2}{8\pi^3}\int d\bar{k}\,\delta(\varepsilon-\varepsilon_n).$$

Let's evaluate $D(\varepsilon)$ for free electron gas:

The energy is spherically symmetric $\Rightarrow$ polar coordinates.

$$D(\varepsilon) = \frac{2}{8\pi^3}\int_0^\infty 4\pi k^2 dk\,\delta(\varepsilon-\varepsilon_k) = \int_0^\infty \frac{d\varepsilon}{d\varepsilon/dk}\,\frac{2m\varepsilon}{\hbar^2}\,\delta(\varepsilon-\varepsilon_k)$$

$$\boxed{D(\varepsilon) = \frac{m}{\hbar^3\pi^2}\sqrt{2m\varepsilon}}$$ ← note the units of this!

$\frac{\#\text{ states}}{\text{Energy}\cdot\text{Volume}}$.

Lecture 26

Electron in a weak periodic potential

1. consider two vectors in k space:

$\vec{k}$ and $\vec{k}'$ which satisfy $\vec{k} = \vec{k}' + \vec{K}_s$,

where $\vec{K}_s$ is a reciprocal lattice vector.

Obviously

$$\exp(i\vec{k}\cdot\vec{R}_i) = \exp(i\vec{k}'\vec{R}_i)$$

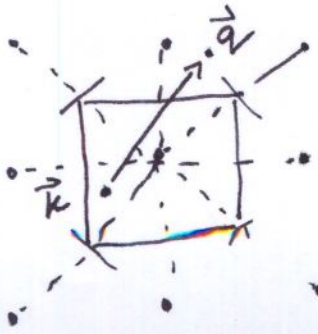
for all direct lattice vectors R_i.

and we will consider these two vectors equivalent.

clearly $\psi_k(r)$ and $\psi_{k+K_s}(r)$ satisfy the same boundary conditions, and we adopt the convention that these functions must be the same:

$$\boxed{\psi_k(r) = \psi_{k+K_s}(r)}$$

This implies that only the 1st BZ is relevant:



$$\boxed{q = k + K_s}$$

note that functions of the form

$e^{i(k+K_s)\cdot r}$ obey Bloch's theorem:

$$e^{i(k+K_s)\cdot(r+R_s)} = e^{ikR_s}\, e^{i(k+K_s)\cdot r}$$

and thus they form a good basis to expand the eigenstates (for each $\vec{k}$):

$$\psi_{n,k}(r) = \sum_s b_{n,k}(K_s)\, e^{i(k+K_s)\cdot r}$$

$\uparrow$ reciprocal lattice vectors.

Often it is written as $\sum_{\vec{G}} b_{n,k}(G)\, e^{i(\vec{k}+\vec{G})\cdot r}$

to leave it orthonormal: $\boxed{(2\pi)^{-3/2} \sum_G b_n(k+G)\, e^{i(k+G)r}}$

This is a plane-wave expansion we have discussed the last time!

note that A&M prefers $-\vec{G}$, but it is the same thing: $\boxed{\psi_{nk} = \sum_K C^n_{k-K}\, e^{i(k-K)r}}$.

If you want to have the proper Bloch form:

$$\psi_{nk}(r) = e^{ikr}\left(\sum_k C^n_{k-K} e^{-iKr}\right) \text{ and}$$

$$\boxed{u^n_k(r) = \sum_K C_{k-K} e^{-iK\cdot r}}$$

or

$$\psi_{nk}(r) = (2\pi)^{-3/2} e^{ikr} \sum_G b_n(k+G) e^{iGr}$$

$$\boxed{u^n(r) = (2\pi)^{-3/2} \sum_G b_n(k+G) e^{iGr}}$$

You now plug this expansion into the schrödinger equation and form your secular determinant just like we did with local orbitals.

Let's take a look at the kinetic energy term first:

$$-\frac{\hbar^2}{2m}\nabla^2 \sum_K C_{k+K}\, e^{i(k+K)\cdot r} =$$

$$= \frac{\hbar^2}{2m} \sum_K (k+K)^2 C_{k-K}\, e^{i(k+K)\cdot r}$$

And now let's look at the potential energy term: $V(r) = \sum_R V(r-R) = \sum_K V_K e^{iKr}$

(your homework will show you that's true).

$$\sum_K V_K e^{iKr} \sum_{K'} C_{k-K'} e^{i(k-K')\cdot r} =$$

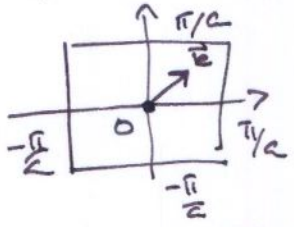
$$= \sum_{K K'} V_K C_{k-K'} e^{i(K-K'+k)\cdot r}$$

We now multiply by a planewave and integrate over the total volume.

$$\boxed{\left(\frac{\hbar^2}{2m}(k+K)^2 - \epsilon_n(k)\right) C^n_{k-K} + \sum_{K'} V_{K'-K} C^n_{k-K'} = 0}$$

Things to remember:

$\vec{k}$ is any point in k-space located inside the first BZ:



$\vec{K}$ is a reciprocal lattice vector!

Our original problem reduced to N independent problems! One for each allowed value of $\vec{k}$!

Q. what does a free electron problem look like in this formalism?

where is the potential? in U_K:

$$V(r) = \sum_K V_K e^{iKr}$$

$$V_K = \frac{1}{v} \int_{cell} dr\, e^{-iK\cdot r} V(r)$$

It's customary to set $V_0 = \frac{1}{v}\int_{cell} dr\, V(r) = 0$

(the average potential in the crystal)

Len Kleinman was the first one to explain that it is arbitrary.

So, if electrons are free $V_K = 0$, $\forall K$.

So we get: $\left(\frac{\hbar^2}{2m}(k-K)^2 - \varepsilon\right) c_{k-K} = 0$

if you call $k-K=q$ $\quad \varepsilon^0 = \frac{\hbar^2}{2m} q^2$ as it should.

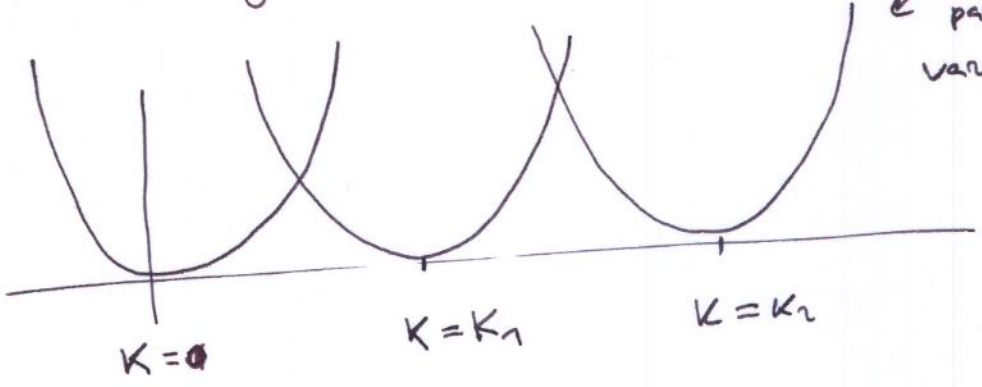
$\psi_k \sim e^{i(k-K)\cdot r}$

This will work unless we have degeneracy:

$\varepsilon_{k-K_1} = \varepsilon_{k-K_2} = \ldots = \varepsilon_{k-K_m}$

Then we are in trouble: we need a linear combination of these plane waves and it is not clear how to choose c_{k-K_m} ...

Let's consider U_K small but not exactly 0.



1. non degenerate case.

$\varepsilon^0 = \frac{\hbar^2}{2m}(k-K_1)^2$, $c_{k-K_1} = 1$, $c_{k-K} = 0$ $K \neq 1$.

what will happen to it when we turn the perturbation on?

$$(\epsilon - \epsilon^0_{k-k_1})\, c_{k-k_1} = \sum_{k'} V_{k'-k}\, c_{k-k'}$$

we have set $V_0 = 0$, so on the RHS $k \neq k'$

If we didn't have V, c_{k-k} were 0 for $k \neq k'$ so the RHS is $O(V^2)$

for $k \neq k_1$

$$(\epsilon - \epsilon^0_{k-k})\, c_{k-k} = \sum_{k'} V_{k'-k}\, c_{k-k'}$$

and $$c_{k-k} = \frac{1}{\epsilon - \epsilon^0_{k-k}} \sum_{k'} V_{k'-k}\, c_{k-k'} =$$

$$= \frac{1}{\epsilon - \epsilon^0_{k-k}} (V_{k_1-k}\, c_{k-k_1}) + \sum_{k' \neq k_1} \frac{V_{k'-k}\, c_{k-k'}}{\epsilon - \epsilon^0_{k-k}}$$

(very small.)

$$c_{k-k} = \frac{V_{k_1-k}\, c_{k-k_1}}{\epsilon - \epsilon^0_{k-k}} + O(V^2)$$

plug this back into my equation for c_{k-k_1}:

$$(\epsilon - \epsilon^0_{k-k_1})\, c_{k-k_1} = \sum_{k'} V_{k'-k_1} \frac{V_{k_1-k'}\, c_{k-k_1}}{\epsilon - \epsilon^0_{k-k'}} + O(V^3)$$

need to solve by iteration, to first order:

$$\epsilon = \epsilon^0_{k-k_1} + \sum_{k} \frac{|V_{k-k_1}|^2}{\epsilon^0_{k-k_1} - \epsilon^0_{k-k}} + O(V^3)$$

small corrections!

Lecture 27

Last time: we wrote the wave function:

$$\psi_k(r) = \sum_{lK} C_{k-lK}\, e^{i(k-lK)r} \qquad (1)$$

we expanded the periodic potential in a lattice Fourier series:

$$V(r) = \sum_{lK} V_{lK}\, e^{iK\cdot r} \qquad (2)$$

And we got the schrödinger equation

$$\left(\frac{\hbar^2}{2m}(k-lK)^2 - \varepsilon\right) C_{k-lK} + \sum_{lK'} V_{lK'-lK}\, C_{k-lK'} = 0 \qquad (3)$$

For the free electron ($V_{lK} = 0$) this procedure gives $\epsilon^0_{k-lK} = \frac{\hbar^2}{2m}(k-lK)^2$ $\psi_k \sim e^{i(k-lK)\cdot r}$

what about a weak potential?

For a non-degenerate case, starting with

$\epsilon = \epsilon^0_{k-lK_1}$, $C_{k-lK} = 0$ for $K \neq lK_1$

(in other words $\sum_{lK} C_{k-lK}\, e^{i(k-lK)\cdot r} = C_{k-lK_1}\, e^{i(k-lK_1)\cdot r}$)

we got the following result:

$$c_{k-k} = \frac{V_{k_1-k}\, c_{k-k_1}}{\epsilon^{\circ}_{k-k_1} - \epsilon^{\circ}_{k-k}}$$

$$\epsilon = \epsilon^{\circ}_{k-k_1} + \sum_{k} \frac{|V_{k-k_1}|^2}{\epsilon^{\circ}_{k-k_1} - \epsilon^{\circ}_{k-k}} \qquad (4)$$

In other words, not much is happening!

Now consider a degenerate case:

we get k such that

$\epsilon^{\circ}_{k-k_1}, \epsilon_{k-k_2}, \ldots \epsilon_{k-k_m}$ are about the same

(not necessarily exactly equal but less than V different)

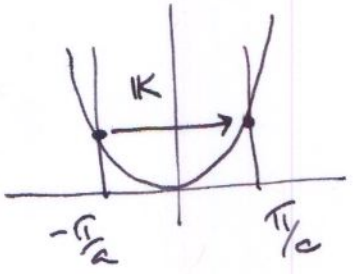
But they are different from other ϵ_{k-k}'s.

In this case equation (3) needs to be treated with care.

Another way to see it is to look at the denominators in equations (4): they blow up!

A & M deals with this in detail in chapter 9.

Let me consider the simplest case here, namely the case when only two levels of free electrons are almost degenerate. Think of a 1D problem:



I will shift the origin to K_1. So

$$\boxed{q = k - K_1 \quad \text{and} \quad K = K_2 - K_1}$$

Then equation 3 gives for the two levels:

$$(\epsilon - \epsilon_q^\circ)\, c_q = U_K\, c_{q-K}$$

$$(\epsilon - \epsilon_{q-K}^\circ)\, c_{q-K} = U_{-K} c_q = U_K^* c_q \qquad (V \text{ is real!!!})$$

This is a 2×2 matrix equation

$$\begin{vmatrix} \epsilon - \epsilon_q^\circ & -U_K \\ -U_K^* & \epsilon - \epsilon_{q-K}^\circ \end{vmatrix}$$

$$\boxed{\epsilon = \tfrac{1}{2}\left(\epsilon_q^\circ + \epsilon_{q-K}^\circ\right) \mp \sqrt{\left(\frac{\epsilon_q^\circ - \epsilon_{q-K}^\circ}{2}\right)^2 + |V_K|^2}}$$

Ok, when $\epsilon_q^\circ = \epsilon_{q-K}^\circ$?

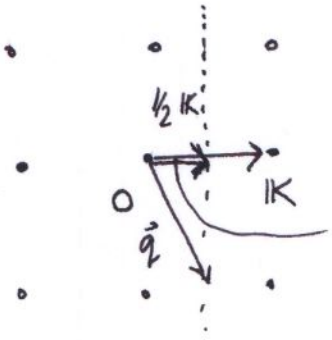
$$\boxed{\frac{\hbar^2 q^2}{2m} = \frac{\hbar^2}{2m}(q-K)^2} \quad ?$$

how can that be?

$$q^2 = \vec{q}\cdot\vec{q} = |q|^2$$

$$(q-k)^2 = (\vec{q}-\vec{K})(\vec{q}-\vec{K}) = |q|^2 - 2\vec{q}\cdot\vec{K} + K^2 = 0$$

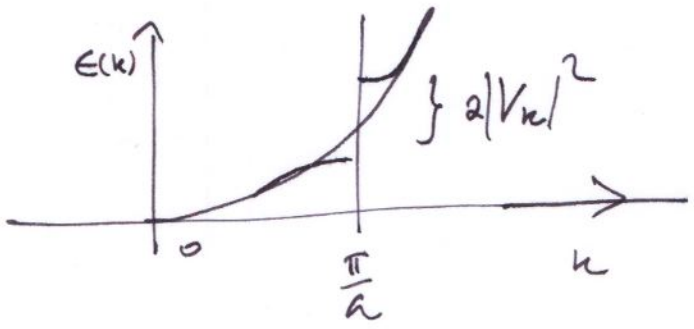
in other words $\boxed{-\vec{q}\cdot\vec{K} + \frac{1}{2}K^2 = 0}$



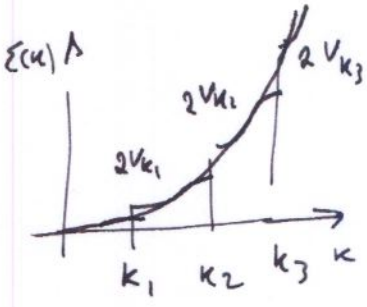
do you see that this condition means that $\vec{q}$ lies on the BZ boundary? (which is AKA the Bragg plane defined by $\vec{K}$).

In other words, when $\vec{q}$ hits the zone boundary there is a strong perturbation of the free electron energy $\frac{\hbar^2 q^2}{2m}$ how big?

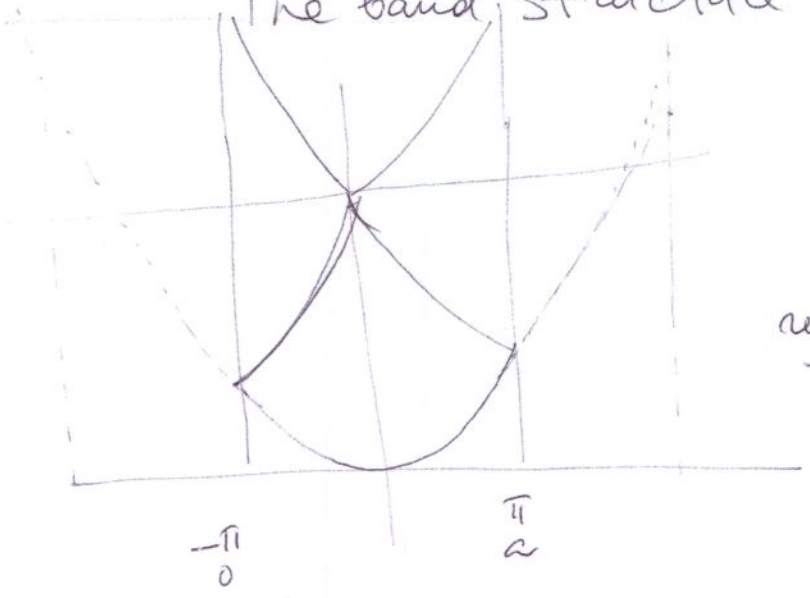
$$\boxed{\epsilon = \frac{\hbar^2 q^2}{2m} \pm |V_K|^2}$$ the level splits in two!



more generally

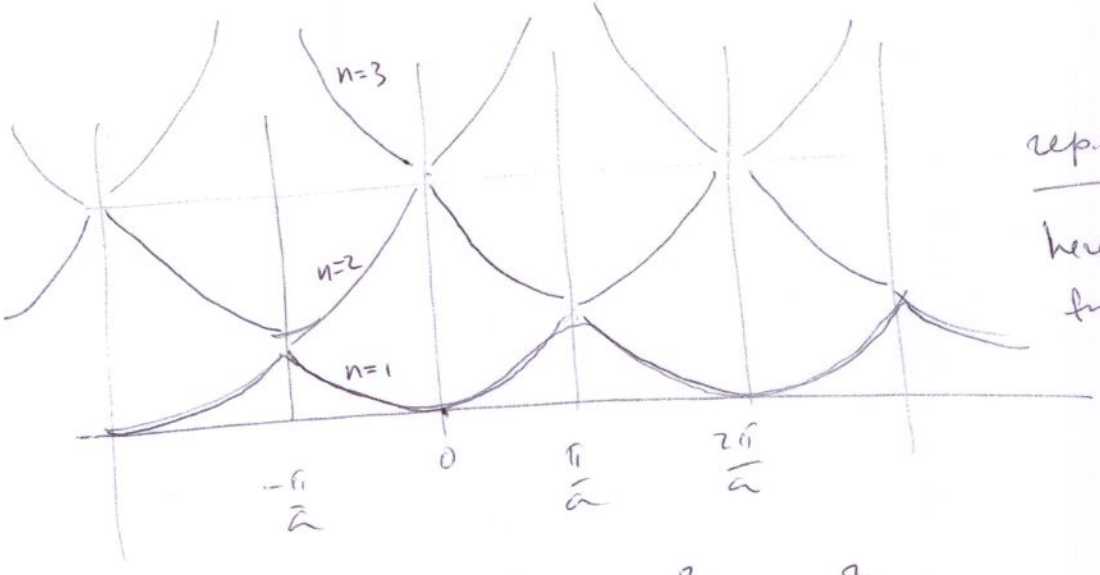


The "band structure" of free electrons:



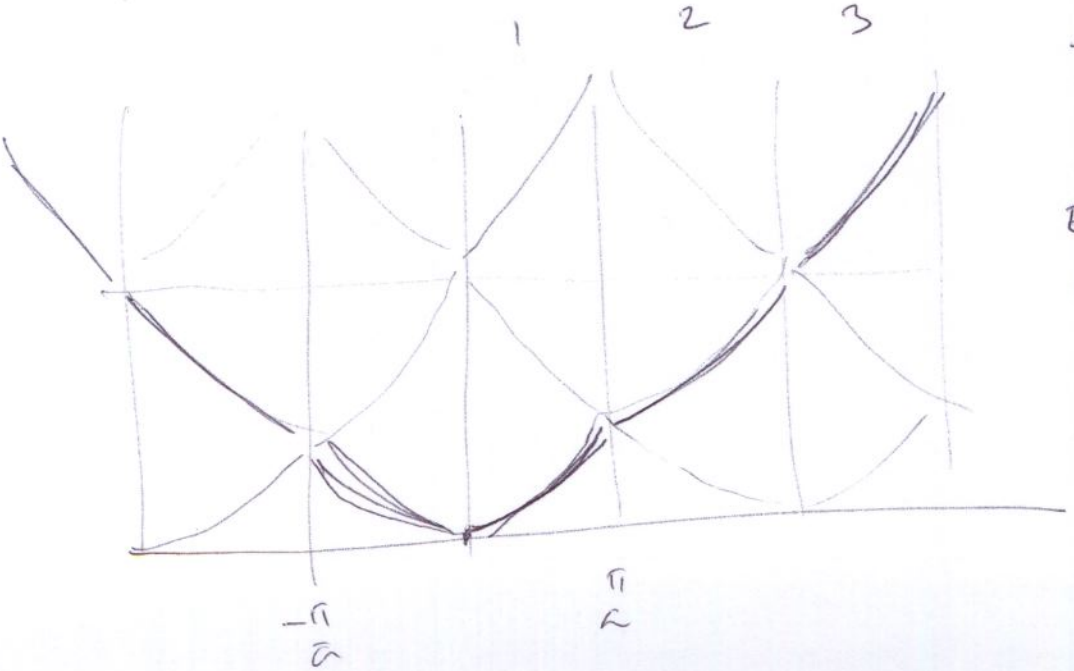
reduced zone picture

$$\psi_n(k,r) = \psi_n(k+K_m, r)$$



repeated zone picture

here $E_n(k)$ is a periodic function (and multi valued!)



extended zone picture

$E_m(k)$ is considered only in the m-th zone!

General properties

$\psi_n(k+G, r) = \psi_n(k, r)$ ← periodic in Reciprocal space!

$$\int_{\text{all space}} \psi_n^*(k,l)\, \psi_\ell(q,l)\, d^3r = \delta_{n\ell}\, \delta(q-k)$$

$$\left[\psi_n(k,l) = (2\pi)^{-3/2} \sum_G \ldots \right]$$

You can use a different normalization

$$\psi_n(k,l) = \frac{1}{\sqrt{N\Omega}} \sum_G$$

(N: number of cells; Ω: cell volume)

then $$\int_{\text{all space}} \psi_n^*(k,l)\, \psi(q,l)\, d^3r = \delta_{n\ell}\delta_{qk}.$$

Also $$\int_{\text{cell}} u_n^*(k,l)\, u_\ell(k,l)\, d^3r = [\Omega/(2\pi)^3]\,\delta_{n\ell}$$

$$\sum_n \int_{\text{all } k\text{-space}} \psi_n^*(k,l)\, \psi_n(k,l')\, d^3k = \delta(l-l')$$

The real PW equation is eq. 3. If you only knew V_k's you will be OK. We will talk more about it Monday (James Chelikowsky will give the lecture).