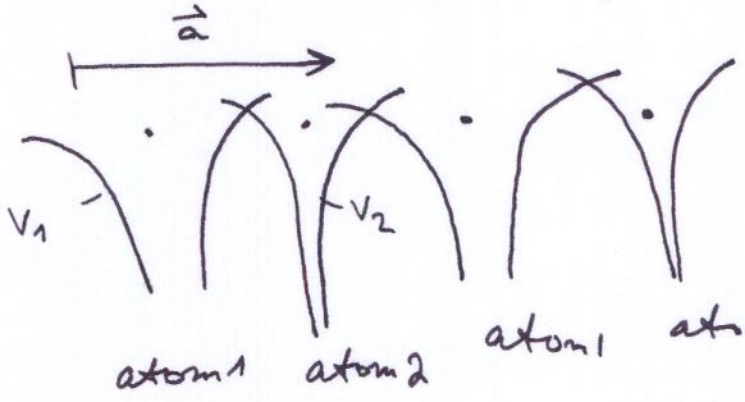
Lecture 21

Electron in a periodic potential.

Let's build a solid. What do we need? a lattice $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$, a bassis $(\vec{b}_1, \vec{b}_2, \dots \vec{b}_n)$ and n atoms to populate this geometric construction. Let's say we have a recipe for the effective one electron potential, then the whole thing will look something like this:



$$U(\vec{r}) = \sum_n \sum_{i=1}^{2} V_i(\vec{r} - \vec{a}_n)$$

This potential is periodic $U(\vec{r} + \underset{\sim}{a_n}) = U(\vec{r})$

$\underset{\sim}{R}$ a Bravais lattice vector

The Hamiltonian is also periodic, in other words it commutes with the translation operator $\hat{T}_{a_n}$.

So the wave function satisfies the Block theorem!

$$\boxed{\psi(z+an) = e^{ik(an)}\psi(z)}$$ (see our discussion of crystal vibrations).

more generally $\psi(\bar{z}+\bar{R}) = e^{i\bar{k}\bar{R}}\psi(z)$ or:

if you know the wave function in one cell you can get the value in another cell by multiplying by a phase factor!!! (Bloch, 1928)

It is convenient to incorporate $\vec{R}$ as an argument of the wave function:

$$\boxed{\psi(k,z) \equiv e^{ik\cdot z}u(k,z)} \leftarrow \text{just for kicks!}$$

Let's try the Block theorem:

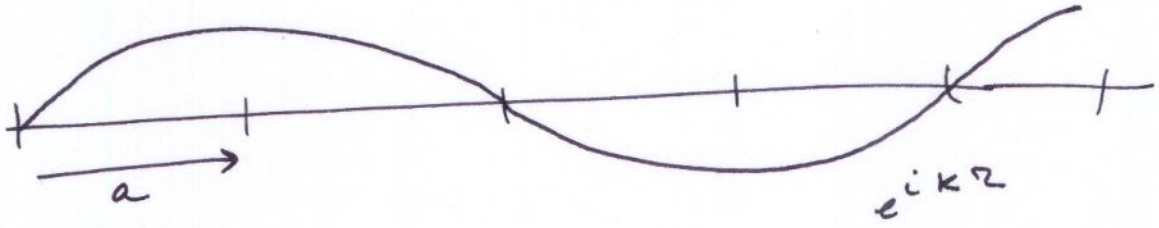
$$\psi(k, z+R) = e^{ik(z+R)}u(k, z+R)$$

Now, if $\underline{u(k,z+R) = u(k,z)}$ ← a cell periodic function

then $\psi(k,z+R) = e^{ik\cdot R}\psi(k,z)$ just as we wanted!!! (this is also known as Floquet theorem)

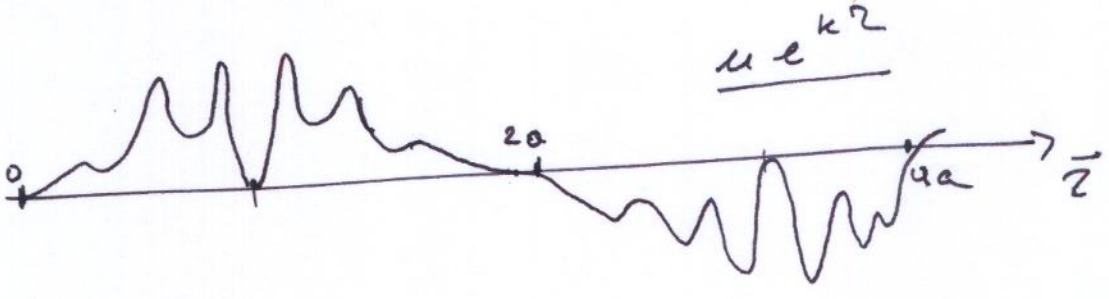
What this $u(r,z)$ might look like?

Then you modulate it by a plane wave!

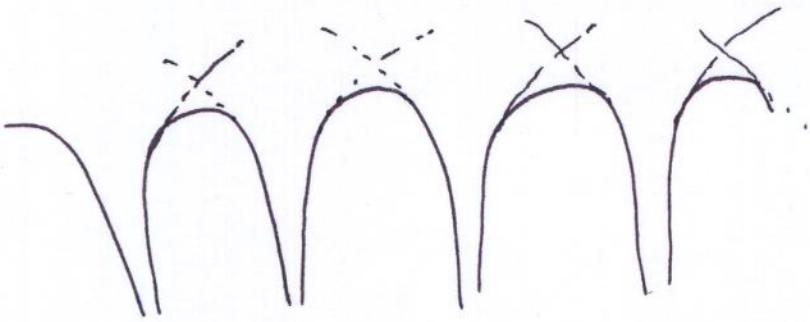


$k = \frac{\pi}{2a}$ since $\lambda = 4a$ and $k = \frac{2\pi}{\lambda}$.

The product looks something like this:



Let's consider a simple case: one atom per unit cell, and it is hydrogen.



& know the solution for one well:

$\psi = R_{nl}(r)\, Y_{lm}(\Omega)$, which for the ground state is $R_{10} Y_{00} = \frac{1}{\sqrt{\pi}} e^{-r} = \varphi_0(r)$

$R_{20} \sim (2-r) e^{-r/2} = \varphi_1(r)$

Q: <u>can I use them to build something cell periodic?</u>

How about this:

$$U(k, r) = \sum_R e^{-ik(r-R)} \varphi_0(r-R) \quad ?$$

Let's try it:

$$U(k, r+R') = \sum_R e^{-ik(r+R'-R)} \varphi_0(r+R'-R) =$$

$$= \sum_R e^{-ik(r-(R-R'))} \varphi_0(r-(R-R')) = \sum_{\tilde{R}} e^{-ik(r-\tilde{R})} \varphi_0(r-\tilde{R})$$

So it works!

$$u(k,r) = u(k, r+R')$$

This is a general property of all "lattice sums"!

Ok, now I can write the Bloch wave:

$$\psi(k,r) = e^{ikr}\, u(k,r)$$

$$\psi(k,r) = e^{ikr} \sum_R e^{-ik(r-R)} \varphi_0(r-R) =$$

$$= \sum_R e^{ikR} \varphi_0(r-R).$$

$$\boxed{\psi(k,r) = \sum_R e^{ikR} \varphi_0(r-R)}$$

What would you do if you had more states or atoms in the unit cell? Let's say we want to include $R_{20} Y_{00}$? Call it $\varphi_1(r-R)$

Now you will have $\psi_1(k,r)$ and $\psi_0(k,r)$.

In General $\psi_n(k,r)$ or $\psi_{nk}(r)$

↑ so-called Band index!

The wavefunction is then written as

$$\psi(k,r) = \left(\sum_R e^{ikR}\varphi_0(r-R)\right)c_0 + \left(\sum_R e^{ikR}\varphi_1(r-R)\right)c_1$$

Does it obey the Bloch theorem?

$$\psi(k,r+R) = \sum_{R'} e^{ikR'}\varphi_0(r+R-R') =$$

$$= e^{ikR}\sum_{R'} e^{ik(R'-R)}\varphi_0(r-(R'-R)) =$$

$$= e^{ikR}\sum_{\tilde{R}} e^{ik\tilde{R}}\varphi_0(r-\tilde{R}) = e^{ikR}\psi(k,r).$$

so it works! Note the change of variables

$R'-R=\tilde{R}$ another ~~reciprocal~~ Bravais lattice vector!

Again, we shall use Born-von Karman periodic boundary conditions: $\psi(r+Na_i)=\psi(r)$

$N=N_1N_2N_3$ the total # of primitive cells in the crystal. Together with the Bloch theorem we get $k=\sum_i \frac{m_i}{N_i}\vec{b}_i$ in reciprocal space with

$\Delta k = (2\pi)^3/V$ for every value.

Lecture 22

Last time we have established that a wave function for an electron in a periodic potential has the form of a Bloch wave:

$$\psi(k,r) = e^{ikr}\, u(k,r),$$

where $u(kr)$ is a periodic function.

We then considered a model system built of hydrogen atoms and used an LCAO ansatz to build $u(k,r)$:

$$u(k,r) = \sum_R e^{-ik(r-R)}\, \varphi_0(r-R)$$

where $\varphi_0 \sim \frac{1}{\sqrt{\pi}} e^{-r}$ is the ground state of a hydrogen atom. We came up with the following wf:

$$\boxed{\psi(k,r) = \sum_R e^{ikR}\, \varphi_0(r-R)}$$

Let's see if it is a proper Bloch wave:

$$\psi(k, r+R') = \sum_R e^{ikR}\, \varphi_0(r+R'-R) =$$

$$= e^{ikR'} \sum_R e^{ik(R-R')} \varphi_0(r+R'-R) =$$

$$= e^{ikR'} \sum_R e^{ik(R-R')} \varphi_0(r-(R-R')) = e^{ikR} \psi(k,R).$$

OK, so it is a Block wave.

I also want to normalize it:

$$\boxed{\psi_k(r) = \frac{1}{\sqrt{N}} \sum_R e^{ik\cdot R} \varphi_0(r-R)}$$

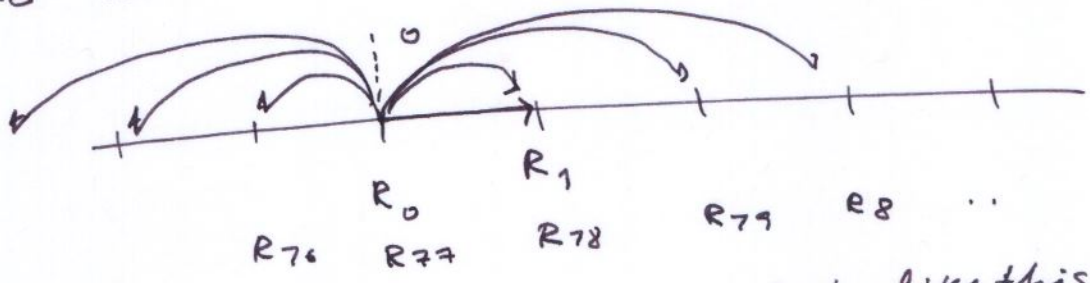
Let's calculate the energy of an electron in this state:

$$E_k = \frac{\int \psi_k^* H \psi_k \, dr}{\int \psi_k^* \psi_k \, dr}$$

$$\int \psi_k^* H \psi_k \, dr = \frac{1}{N} \sum_R \sum_{R'} e^{ik(R-R')} \int \varphi_0^*(r-R') \left[\frac{p^2}{2m} + \sum_{R''} V(r-R'')\right] \varphi$$

$$\int \psi_k^* \psi_k \, dr = \frac{1}{N} \sum_R \sum_{R'} e^{ik(R-R')} \int \varphi_0^*(r-R') \varphi_0(r-R) \, dr$$

Let's take a closer look at the second equation. It is a double sum over the lattice. In the outer sum $\sum_R$ let's pick just one term R_{77} $R = R_{77} = R_0$ and call R_0 the original cell: $R_0 = 0$

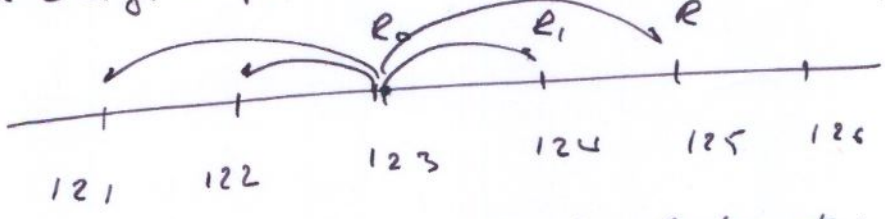


what do we get? The inner sum now looks like this:

$$\frac{1}{N}\sum_{R'} e^{ik(R_0 - R')} \int \varphi_0^*(\vec{r} - \vec{R}')\, \varphi_0(\vec{r} - \vec{R}_0)\, d\vec{r} =$$

$$= \frac{1}{N}\sum_{\vec{R}'} e^{ik(+\vec{R}')} \underbrace{\int \varphi_0^*(\vec{r} - \vec{R}')\, \varphi_0(\vec{r})\, d\vec{r}}_{S(\vec{R}')}$$

Now let me take another term in the outer sum, let's say $R = R_{123}$, again a can choose it to be the origin for this particular term:



and again the inner sum looks like this:

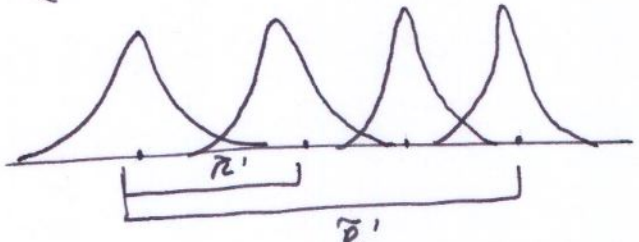
$$\frac{1}{N}\sum_{\tilde{R}'} e^{ik(+\tilde{R}')} \quad S(\tilde{R}') \qquad !!!$$

Do you get it? They are all the same, all N of them! In other words, my double sum is actually N single sums:

$$\frac{1}{N} N \sum_{\tilde{R}'} e^{ik(+\tilde{R}')} \quad S(\tilde{R}')$$

↑ infinite !!! OR at least very large...

Well, like with many things in life, it is true only in principle:



The overlap matrix is actually short range!!!

How low will you go? One choice is

$S(0) = 1$
$S(R) = 0$, $\forall R$ } This is called orthogonal TB!

Or, you can keep just the nearest neighbors.

in one dimension: $1 + e^{-ika} S + e^{ika} S = 1 + 2S\cos ka$

in 3D:  (simple cubic)

you get $1 + 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$.

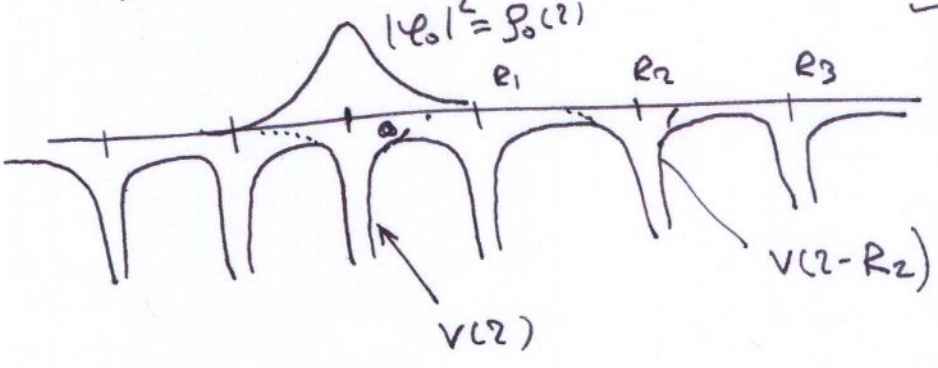
We now turn to $\int \psi_k^* H \psi_k$. It is similar but a bit more complicated. It is again $\frac{1}{N}\sum_R$ like before, but the integral is not so simple:

$$\sum_R e^{ikR} \int \varphi_0(r-R)\left[\frac{p^2}{2m} + \sum_{R''} V(r-R'')\right]\varphi_0(r)\,dr =$$

$$= \sum_R e^{ikR} \int \varphi_0(r-R)\left[\frac{p^2}{2m} + V(r-R) + \sum_{R''\neq R} V(r-R'')\right]\varphi_0(r)\,dr =$$

$$= \sum_R e^{ikR}\left[\varepsilon_0 S(R) + \int \varphi_0^*(r-R)\sum_{R''\neq R} V(r-R'')\,\varphi_0(r)\,dr\right]$$

for $R=0$ we have $\varepsilon_0 + \int \rho_0(r)\sum_{R''\neq 0} V(r-R'')\,dr$

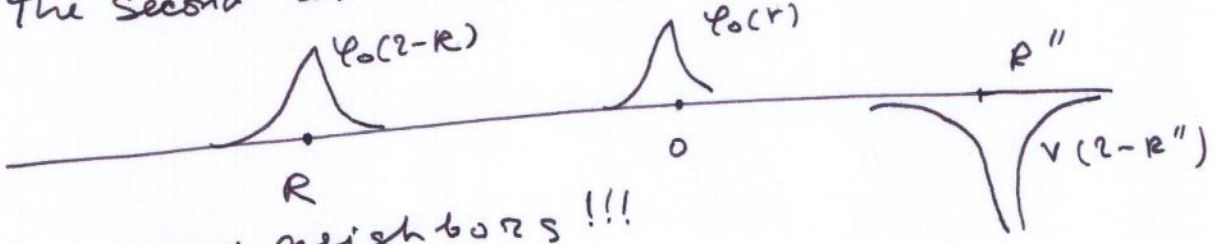


The first one is just -13.6 eV! The second one is called the Crystal field.

For other terms in this sum we have:

$$\sum_{R\neq 0} e^{ikR}\left[\varepsilon_0 S(R) + \int \varphi_0^*(2-R)\varphi_0(2)\sum_{R''\neq R} V(2-R'')\,d\tau\right]$$

The second term is pretty small. With the exception of



The nearest neighbors !!!
so we can drop it. Then ε_k is given by:

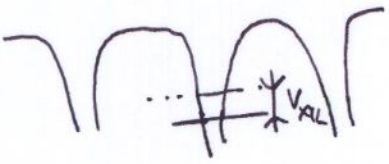
$$\varepsilon_k = \frac{\varepsilon_0 + V_{XTL} + \sum_R{}' e^{ikR}\varepsilon_0 S + \sum_{NN} e^{ikR}\int \varphi_0(2-R)V(2-R)\varphi_0(2)}{1 + \sum_R{}' e^{ikR}\underbrace{\int \varphi_0(2-R)\varphi_0(2)\,d\tau}_{S(R)}}$$

Let me now be a radical: $S(R) = 1 \quad R=0$
$S(R) = 0 \quad \forall R\neq 0$.

$$\boxed{\varepsilon_k = \varepsilon_0 + V_{XTL} + 2V_{SS}(\cos k_x a + \cos k_y a + \cos k_z a)}$$

↑ Heisenberg uncertainty principle at work!

you lower the energy of an atom by bringing all other potential wells:



Since the electron knows it can delocalize $\Delta x \uparrow \Rightarrow \Delta p \downarrow \rightarrow \frac{\Delta p^2}{2m} \downarrow$.

Let's call this renormalized atomic level energy $\tilde{E}_0$. Pick a k along the x axis,

e.g. $k = (100)$

$$E_{100} = \tilde{E}_0 + 2V_{sss}(2 + \cos k_x a)$$

Now pick $k = (111)$

$$E_{111} = \tilde{E}_0 + 6V_{sss}\cos ka$$