Lecture 21

The plan:

1. LCAO & variational principle.
2. filling the band.
3. 2 atoms per cell (1D).
4. Another source of band gaps.

Remember, we will have a quiz Wednesday.

Lecture 23

Last time we have introduced the tight-binding approximation (also known as the Hückel theory).

Let's trace the steps:

1. build a Block wf from atomic orbitals

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

2. calculate the expectation value of the Hamiltonian.

3. Assume the wf centered on different sites to be orthogonal: $\int \varphi^*(\vec{r}-\vec{s})\,\varphi(\vec{r})\,d\vec{r} = \delta_{s0} = S(\vec{s})$

4. Renormalize the atomic energy by the x-tal field potential $\tilde{E} = \epsilon + \int |\varphi_0|^2 \sum_{NN} V(\vec{r}-\vec{R}_{NN})\,d\vec{r}$

5. Use the nearest neighbor approximation:

$$\langle \varphi(\vec{r}-\vec{R}) | \sum_{T\neq R} V(\vec{r}-\vec{T}) | \varphi(\vec{r}) \rangle = \langle \varphi(\vec{r}-\vec{R}) \sum_{NN} V(\vec{r}-\vec{T}_{NN}) | \varphi(\vec{r}) \rangle$$

we called the matrix elements between the s-orbitals VSSσ and got the following expression:

$$E_k = \tilde{E}_0 + 2\,V_{ssb}\,(\cos k_x a + \cos k_y a + \cos k_z a)$$

for a simple cubic lattice.

This is the nearest-neighbor orthogonal model.

The NN OTB is easily generalized to more complex cases. But before I do this let me remind you the logic of the variational estimate:

you have $h\varphi_i = \varepsilon_i \varphi_i$ and you make an ansatz $\varphi_i = \sum_\alpha C_{i\alpha}\,\Phi_\alpha$, and you write an estimate of the energy with this φ:

$$\frac{\sum_\alpha \sum_\beta C^*_{i\alpha} C_{i\beta} \langle \alpha | \hat{h} | \beta \rangle}{\sum_\alpha \sum_\beta C^*_{i\alpha} C_{i\beta} \langle \alpha | \beta \rangle}$$ and you compute a variation:

For simplicity allow me to use an orthogonal basis $\langle \alpha | \beta \rangle = 0$ for $\alpha \neq \beta$.

$$\delta \frac{\langle \psi | h | \psi \rangle}{\langle \psi | \psi \rangle} = \delta \frac{\sum\sum C^* C \langle \alpha | h \beta \rangle}{\sum C^* C} = 0$$

what do I vary you may ask? C^*_α is the answer.

$\{\Phi_\alpha\}$ or $[\,|\alpha\rangle\}$ is a fixed function set.

$$\frac{\sum C^* C \left(\sum_{\alpha'} c_{i\alpha'} \langle \alpha | h | \alpha' \rangle \right) - \left(\sum\sum C^* C \langle \beta | h | \alpha \rangle \right) c_{i\alpha}}{\left(\sum C^* C \right)^{1/2}} = 0$$

$$\boxed{\sum_{\alpha'} c_{i\alpha'} \langle \alpha | h | \alpha' \rangle - E\, c_{i\alpha} = 0}$$

This is a linear uniform system of equations. The eigenstates can be computed directly from the <u>secular equation</u>:

$$\det \left| h_{\alpha\alpha'} - E \delta_{\alpha\alpha'} \right| = 0 ,$$

where $h_{\alpha\alpha'} = \langle \alpha | h | \alpha' \rangle$.

In terms of this theory I correctly guessed that coefficients for our hydrogen solid were

$\frac{1}{\sqrt{N}} e^{ikR} = C_k(R)$, and my choice of basis is

$\{ |\alpha - R\rangle \}$ or $\{ \varphi_0(\alpha - R) \}$ hydrogen functions located at each lattice node!!!

Lecture 25

Q: How do we populate the band?

What is the Fermi momentum and energy?

$$E_F = \alpha + 2\beta \cos k_F a$$

k_F: the wave vector of the fastest electron!

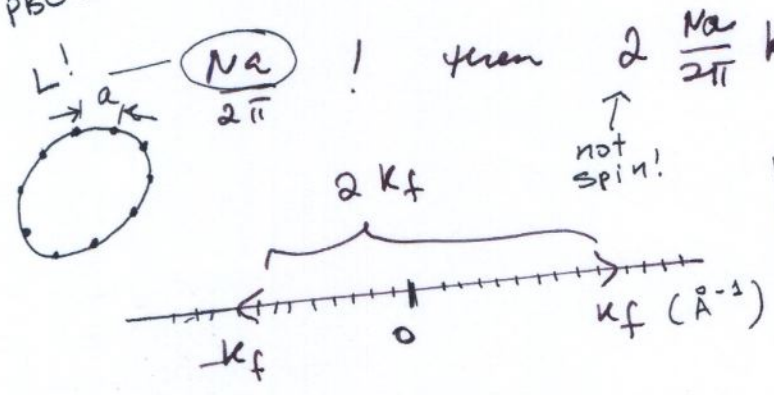
$\alpha \leftrightarrow \tilde{\epsilon}$, $\beta \leftrightarrow V_{sso}$

$$\leftrightarrow \quad \epsilon_k = \tilde{\epsilon} + 2V_{sso}\cos k_x a$$

That's easy!

How many states per unit length in the k-space?

PBC:



$$\frac{Na}{2\pi}\,!\ \text{then}\ \ 2\,\frac{Na}{2\pi}k_f = M$$

(2: not spin!)

$$k_f = \frac{M}{Na}\,\frac{2\pi}{2} = \frac{M\pi}{Na}$$

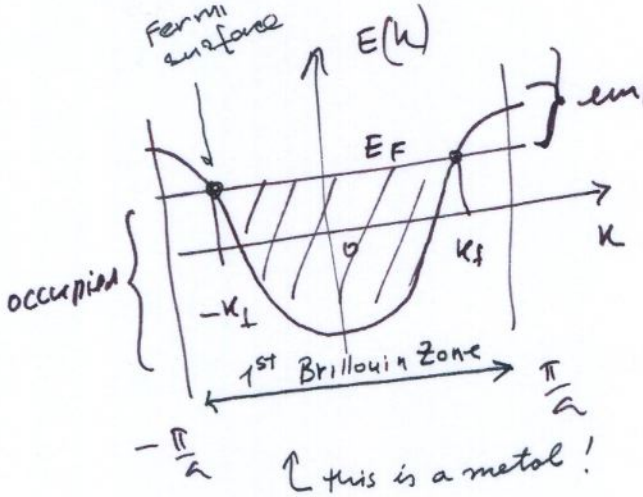
M is the number of the occupied states.

with ν electrons per atom: $N\nu = 2M$ (spin!)

If $\nu = 2$, then

$$k_f = \frac{M}{Na}\,\frac{2\pi}{a} = \frac{\pi}{a}$$

The band is full!!



Set $\alpha = \upsilon$

Note that both N and M are infinite, but the ratio is finite!!!

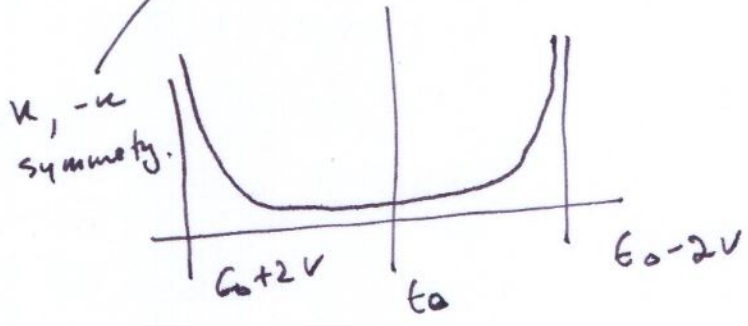
Density of States

Remember in 1D the density of states in the k-space is $L/2\pi$. This is not very exciting.

Q: What is the density of states as a function of energy?

$$D(E) = \frac{dS}{dE} = \frac{dS}{dk}\left|\frac{dk}{dE}\right| = \frac{dS/dk}{dE/dk} =$$

$$= 2\,\frac{L}{2\pi}\,\frac{1}{2Va\sin ka} \overset{L=Na}{=} \frac{N}{\pi}\,\frac{1}{\left(4V^2-(E-\epsilon_0)^2\right)^{1/2}}$$



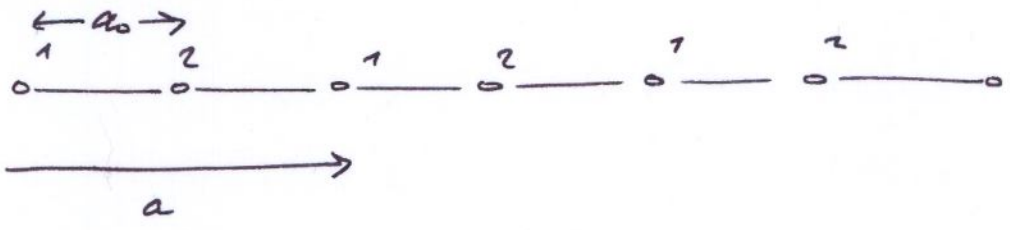
per atom we get $d(E) = D(E)/N$

$$d(E) = \frac{1}{\pi}\,\frac{1}{\left(4V^2-(E-\tilde{\epsilon}_0)^2\right)^{1/2}}$$

$$\int_{\epsilon_0+2V}^{\epsilon_0-2V} d(E)\,dE = 1 \qquad \text{(check this!)}$$

(integrate over the entire band)

Let's now focus on a 1D problem. Orthogonal basis and nearest neighbor interactions only.



I will double the unit cell. Who can tell me what I might expect? I agree, let's see how it works out. Since I have two atoms in the unit cell I can't just use one Bloch wave in my variational guess. What should I do? Indeed, I will form two:

$$|1\rangle = \frac{1}{\sqrt{N}} \sum_R e^{ikR} \phi_0(r-R)$$

$$|2\rangle = \frac{1}{\sqrt{N}} \sum_R e^{ikR} \phi_0(r-R-a_0)$$

The wave function then is a linear combination of these two:

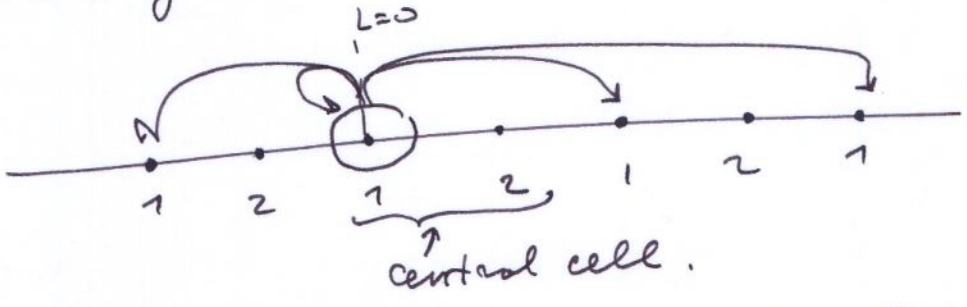
$$\psi_i = c_{1i}|1\rangle + c_{2i}|2\rangle$$

and I need to write down a secular equation (now it will be a matrix!)

$$H_{\alpha\beta}(k) = \frac{1}{R}\sum_{R} e^{ikR} \langle \alpha | \sum_{NN} V | \beta \rangle$$

and here we should be careful. We should have a very clear picture of what these α and β are standing for!

Let's say $\alpha = 1$ and we look at $\underline{\underline{22}}$



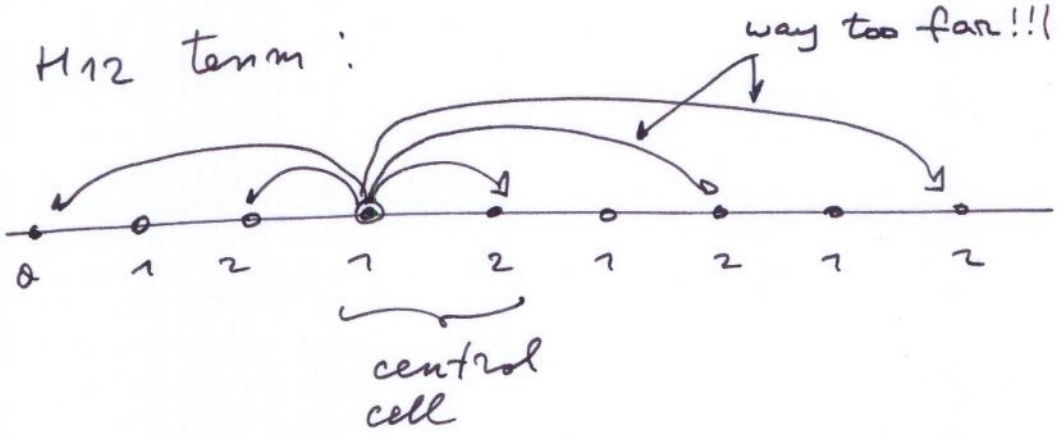
so I pick the orbital on atom (1) and I need to couple it to all other atom 1 orbitals. One is a self interaction term, and it's ok!

$$\int |\varphi(r-0)|^2 \sum_{NN} V(r - R_{NN})\, dr$$ so this just

gives the renormalized on-site atomic energy ϵ_0. All other terms we have to discard since we have the NN model!!!!

Obviously, the exact same analysis will apply to H_{22}.

Let's now consider a more complicated H_{12} term:



As you can see only two terms shall contribute

$$H_{12} = V_{ss}\left(1+e^{-ika}\right)$$

$$H_{21} = V_{ss}\left(1+e^{+ika}\right)$$

Note, the matrix is <u>hermitian</u> as it should!

The secular determinant is then:

$$\begin{vmatrix} \epsilon_0 - \lambda & V_{ss}\left(1+e^{-ika}\right) \\ V_{ss}\left(1+e^{ika}\right) & \epsilon_0 - \lambda \end{vmatrix} = 0$$

$$(\epsilon_0-\lambda)^2 - V_{ss}^2\left(1+e^{ika}+e^{-ika}+1\right) = 0$$

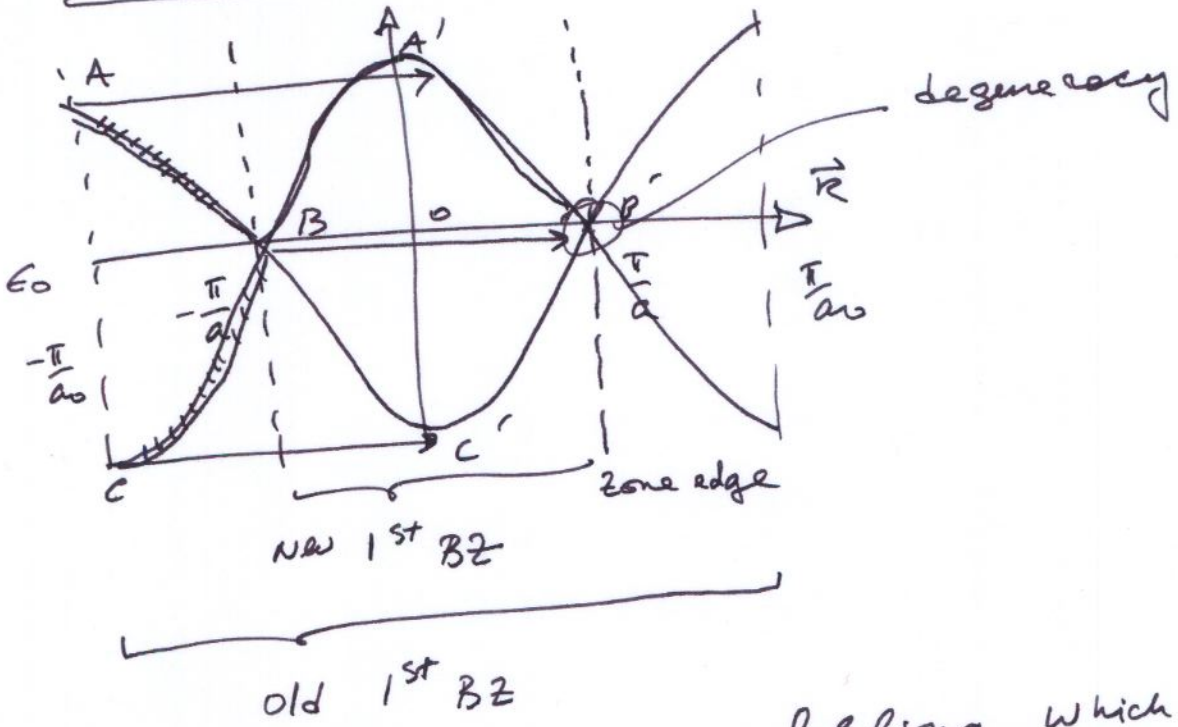
$$(\epsilon_0 - \lambda)^2 - 2V_{ss}^2 (1 + \cos ka) = 0$$

Now recall that $a = 2a_0$!

$$\cos(2\varphi) = \cos^2\varphi - \sin^2\varphi \qquad 1 = \cos^2\varphi + \sin^2\varphi$$

$$(\epsilon_0 - \lambda)^2 = 4\cos^2 k\frac{a}{2}$$

$$\lambda = \epsilon_0 \pm 2\cos k\frac{a}{2}$$



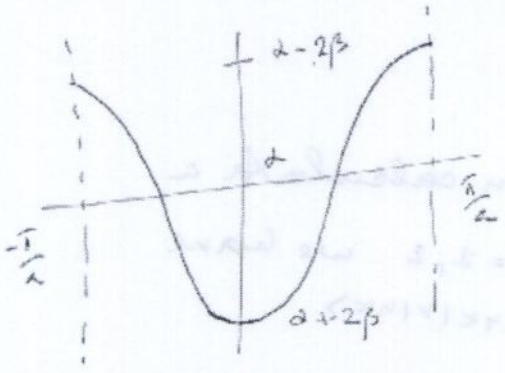
This is the so-called zone folding, which is no folding really, just a translation. As you can see, no information is lost ! Instead of a big piece of cosine ∩ we got a bubble ◇ in half the space. What will happened if 1, 2 differ?

Lecture 24 SSP

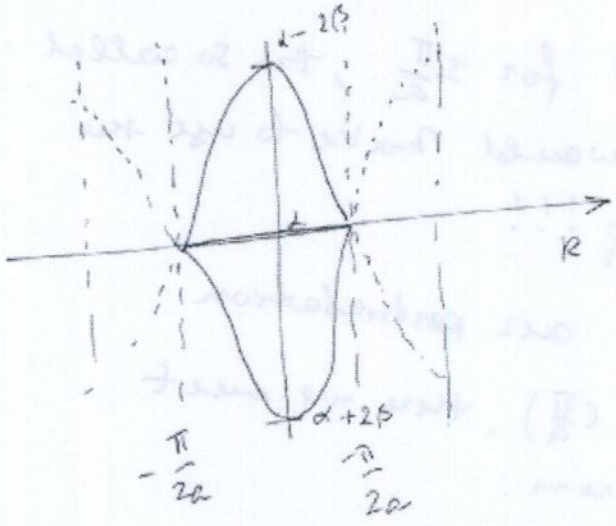
04.18.06

Band gaps continued...

So we have established that if we use the periodic boundary conditions for an infinite periodic 1D chain (or for a ring) we get a band:



We then formally depicted the same chain with a unit cell twice as big and got the following result:



So far no new information just as we have expected. The only interesting feature is a two-fold degeneracy at the "zone-edge".

Imagine now we have a perturbation which makes every other atom slightly different*:

*) actually any perturbation commensurate with 2a will do.

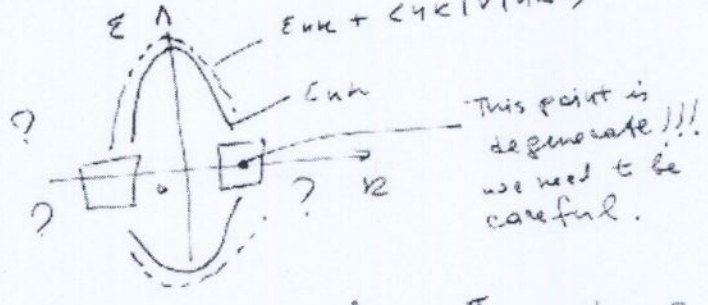
Now let's think in terms of the perturbation theory.

we have our eigen vectors:

$$\Psi_k^n = C_{1k}^n \frac{1}{\sqrt{N}} \sum_L e^{ikL} |1,L\rangle + C_{2k}^n \frac{1}{\sqrt{N}} \sum_L e^{ikL} |2\,L\rangle$$

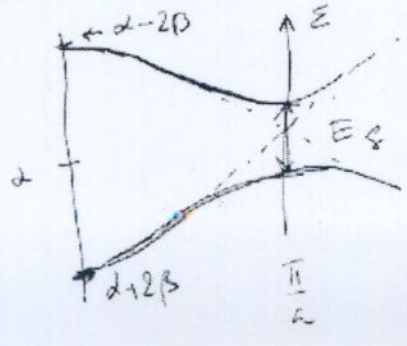
Bloch waves

So for any energy $\varepsilon^n(k)$ we can calculate a shift $\langle nk|V|nk\rangle$. for $n = 1, 2$ we have two bands:



This works everywhere except for $\pm\frac{\pi}{a}$, the so called zone boundaries !! there we would have to use the degenerate perturbation theory !!!

We will need to diagonalize our perturbation in the basis of $\Psi_1(\frac{\pi}{a})$ and $\Psi_2(\frac{\pi}{a})$. there we meet the so-called no crossing theorem:



we have opened a gap !!!

Another source of Band gaps

Consider linear chain of atoms with spacing "a". Let's say each atom has two states $|1\rangle$ and $|2\rangle$. Take a simple model:

$\langle 1|H|1\rangle = \varepsilon_1$

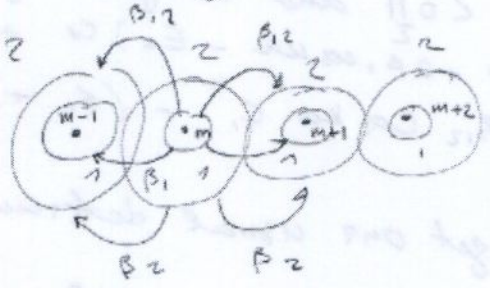
$\langle 2|H|2\rangle = \varepsilon_2 \qquad \varepsilon_2 > \varepsilon_1$

As far as hopping integrals keep only these:

$\langle m,1|H|m\pm1,1\rangle = \beta_1$

$\langle m,1|H|m\pm1,2\rangle = \beta_{12}$

$\langle m,2|H|m\pm1,2\rangle = \beta_2$



Five parameters! $[\varepsilon_1, \varepsilon_2, \beta_1, \beta_2, \beta_{12}]$

As before $\psi_k^n = \left(\frac{1}{\sqrt{N}}\sum_m e^{ikma}|m,1\rangle\right) C_1^n(k) + \left(\frac{1}{\sqrt{N}}\sum_m e^{ikma}|m,2\rangle\right) \times C_2^n(k)$

I guess the wave function to be a linear combination of Bloch waves build out of atomic orbitals.

We also require $|C_1^n(k)|^2 + |C_2^n(k)|^2 = 1$

Now plug it into the Schrödinger eqn:

$$C_1 \sum_n e^{ikna} \hat{H} |n,1\rangle + C_2 \sum_n e^{ikna} H |n,2\rangle =$$

$$= E_n(k) \left[\left(\sum_m e^{ikma} |m,1\rangle \right) C_1 + (\quad) C_2 \right]$$

Project on $\langle 0, \frac{1}{2}|$ by multiplying from the left

by $\langle 0 \frac{1}{2}|$ and integrating:

$$\left.\begin{aligned} (\varepsilon_1 + 2\beta_1 \cos ka - E_n) C_1 + 2\beta_{12} \cos(ka) C_2 = 0 \\ 2\beta_{12} \cos ka \, C_1 + (\varepsilon_2 + 2\beta_2 \cos ka - E_n) C_2 = 0 \end{aligned}\right\}$$

we get our usual determinant:

$$\begin{vmatrix} \varepsilon_1 + 2\beta_1 \cos ka - E_k & 2\beta_{12} \cos ka \\ 2\beta_{12} \cos ka & (\varepsilon_2 + 2\beta_2 \cos ka - E_k) \end{vmatrix} = 0$$

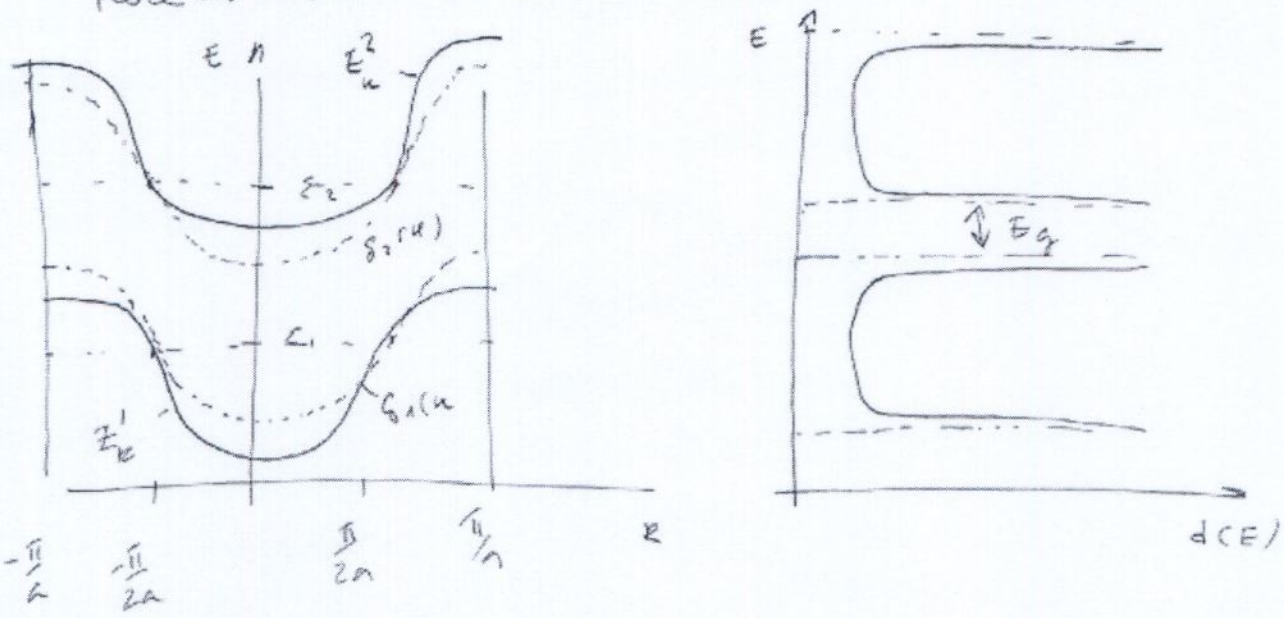
You will get two solutions

$$E_n^{1/2} = \frac{g_1(k) + g_2(k)}{2} \pm \left(\left(\frac{g_1(k) - g_2(k)}{2} \right)^2 + 4\beta_{12}^2 \cos^2 ka \right)^{1/2}$$

where $g_1(k) = \varepsilon_1 + 2\beta_1 \cos ka$

$g_2(k) = \varepsilon_2 + 2\beta_2 \cos ka$

Here is what it looks like:



This is another source of gaps in the energy spectrum.

Note, that you still can't tell whether the system is a metal or insulator!!!

For that you need to know how electrons fill these bands. We will talk about this next time.

Also note, that the gap is controlled by the initial "atomic" level separation $(\varepsilon_1 - \varepsilon_2)$ and by the width of each band $4\beta_i$. Band can and do overlap, and that would close the gap: