

## Part V: Electronic Band Structure

Now that we know what types of lattices are possible, and how to measure them, let us try to figure out what happens to the valence electrons when they move in such lattices, i.e. what energies and wavefunctions can they have. We've already seen a simple model (the tight-binding model in 1D) – here we will discuss the general case and try to understand when simple models like the tight-binding model are valid, and when not.

To start with, let me remind you what happens to electrons in free space (i.e., when there are no nuclei on an ordered lattice in the neighbourhood, just the electrons). As usual, we will ignore electron-electron interactions, so we need only find the spectrum for a single electron and then occupy the lowest levels with all the electrons we have available.

Since there are no interactions, the Hamiltonian for a single electron has only the kinetic energy

$$\vec{H}_0 = -\frac{\hbar^2}{2m}\nabla^2$$

Because this system is invariant to all translations, we expect the wavefunctions to be plane-waves:

$$\phi_{\vec{k}}^{(0)}(\vec{r}) \propto e^{i\vec{k}\cdot\vec{r}}$$

where  $\vec{k} = \vec{p}/\hbar$  is the momentum of the electron, up to a factor of  $\hbar$ . Indeed, this guess works and the corresponding eigenenergy is:

$$E_0(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m} = \frac{\vec{p}^2}{2m}$$

i.e. the expected kinetic energy. Note that here there are no restrictions on the allowed momenta: any value of  $\vec{k}$  is allowed, meaning that there are eigenstates for any energy  $E > 0$  (there are no eigenstates with  $E < 0$ ; check if you're not sure why).

Since the energy increases monotonically with  $|\vec{k}|$ , if we have a finite concentration of electrons, in the ground-state they will occupy all the states with  $|\vec{k}| < k_F$ , where  $k_F$  is determined by the electron concentration: the more electrons there are, the larger  $k_F$  is. This momentum is known as the **Fermi momentum**, and the corresponding energy  $E_F = \frac{\hbar^2 k_F^2}{2m}$  is the **Fermi energy** – i.e., the energy of highest state occupied by electrons, in the ground-state.

So what happens if we introduce a lattice of nuclei? (ions, to be more precise). For simplicity, and so that I can draw pictures, let me assume that the lattice is 1D; however, everything I say next generalizes straightforwardly to 2D and 3D. Let's also assume that we have a simple crystal with a single atom in the basis, although again, things generalize straightforwardly to more complicated cases. Suppose that we have  $N$  atoms placed at their lattice locations  $X_n = na$ , where  $a$  is the lattice constant and  $n = 1, \dots, N$ . We will do again the trick of assuming periodic boundary conditions, and then letting  $N \rightarrow \infty$ , so that the boundary condition we use becomes irrelevant.

Then, the total potential felt by any of the valence electrons is:

$$V_{tot}(x) = \sum_{n=1}^N V_a(x - na)$$

where  $V_a(x)$  is the potential created by an ion located at the origin, and the sum is simply the contribution of all the ions. So now we need to solve Schrödinger's equation:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_{tot}(x) \right] \phi(x) = E\phi(x)$$

with the periodic boundary condition

$$\phi(x + Na) = \phi(x), \text{ for any } x.$$

This is because the length of the chain is  $L = Na$ , and if it is closed and we go around it by  $L$ , we return to the original point so we should find the same value for the wavefunction.

Let's use intuition to "guess" what the solutions should look like. What do we expect?

(i) the solution must have plane-wave like character, because the symmetry tells us that the probability to be in any unit cell must be the same, irrespective of which unit cell we're talking about. However,

(ii) we expect that the wavefunction varies from place to place inside the unit cell, since, for example, the probability to find the electron should be higher near an ion than in between two ions.

Putting these together, let's try the guess:

$$\phi_k(x) = e^{ikx} u_k(x)$$

where  $u_k(x) = u_k(x + a)$  is a periodic function. This has the right character, because it leads to a probability  $|\phi_k(x)|^2 = |u_k(x)|^2$  which is a periodic function, just as we want it to be. Another way to see this is that, with our guess:

$$\phi(x + a) = e^{ik(x+a)} u_k(x + a) = e^{ika} e^{ikx} u_k(x) = e^{ika} \phi(x),$$

i.e. moving one unit cell over leaves the magnitude of the wavefunction unchanged, but it adds a phase, just as it should (remember, we want many eigenfunctions, not just the one with  $\phi(x + a) = \phi(x)$ , and we need the plane-wave for that). By the way, in 3D, the guess would be  $\phi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$ , where now  $u_{\vec{k}}(\vec{r})$  is periodic in the 3D unit cell.

It turns out that this guess works perfectly. In fact, one can prove that any Schrödinger's equation with a periodic potential has eigenfunctions of this type, which are known as **Bloch wavefunctions**. What is left to do is to figure out what is  $u_k(x)$  and its corresponding eigenenergy  $E_k$ , so that the equation is satisfied. This is a matter of math.

Before discussing how to do that, let's look more carefully at the momentum  $k$ , since eigenstates in a periodic potential are also characterized by it, like in free space. There is, however, a major difference between the two. As I said above, in free space the momentum can have any value, without any restriction. For our 1D crystal, the wavefunction must also satisfy the periodic boundary condition  $\phi(x + Na) = \phi(x)$ . For a Bloch wavefunction, though,  $\phi(x + Na) = e^{ikNa} \phi(x)$ , so we must have  $k = \frac{2\pi}{Na} m$ , where  $m$  is an integer. One can again show that only  $N$  of these solutions are distinct (just like the discussion we had for the tight-binding model), so we must restrict  $k \in (-\frac{\pi}{a}, \frac{\pi}{a}]$ , i.e. to the first Brillouin zone! This is another illustration of what I said when we discussed crystals, that any property that depends on the momentum is periodic, and we only need find what happens inside the Brillouin zone which is the unit cell of the reciprocal lattice.

Before looking at how this works in a simple but non-trivial example, let's first make sure that we regain the correct solution if  $U_a(x) \rightarrow 0$ . This, of course, leads us back to free electrons, but zero is also a periodic potential so we should be able to put the free electron solution in the Bloch form, and with the restriction on the values of  $k$  if we adopt the periodic boundary condition. The way this works is illustrated in the figure below. On the right, I show the dispersion in free space: the usual parabola with any momentum allowed. If I choose to view the free space as a periodic lattice (without any potential), then the correct description is shown on the right. I placed a parabola at each reciprocal lattice point, so now the eigenstates are periodic – but I only count the states inside the first Brillouin zone, since the other unit cells are just repeating these. So now we've restricted the

momentum, but for each value of  $k$  we have many solutions  $E_n^{(0)}(k)$ ,  $n = 0, 1, 2, \dots$ . Overall we have the same spectrum, it's just a different way to index the states. By the way, this “re-arrangement” of the states to fall all inside the Brillouin zone is known as “folding”.

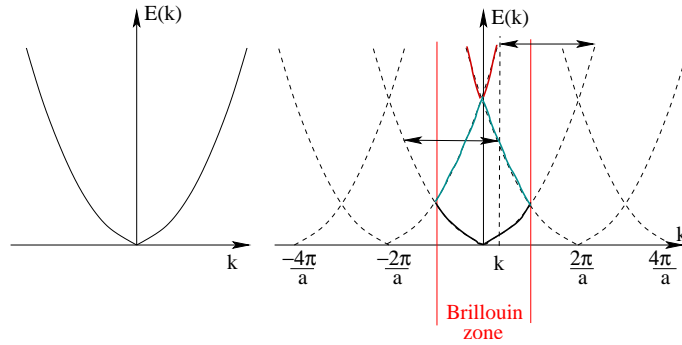


Figure 1: Free space eigenstates. Left: the usual parabola, where any  $k$  is allowed and we have a single eigenstate for a given  $k$ . Right: the corresponding band-structure if we take the vacuum to be a periodic crystal with lattice constant  $a$  (and no potential). Now the momenta are restricted to the BZ, but for each  $k$  we have an infinite number of bands  $E_n^{(0)}(k)$ . The thick coloured lines show the  $n = 0, 1, 2$  bands. For any given  $k$  in the BZ, we can see to what  $K$  of the original parabola that particular energy corresponds. I showed 3 such correspondences (horizontal lines with arrows).

To be a bit more precise, let's consider the first 3 bands,  $n = 0, 1, 2$ , for a given  $k$  (see right figure). I illustrated the corresponding states in both representations – in the usual free space language, they correspond to different momenta,  $K_0 = k, K_1 = k - \frac{2\pi}{a}, K_2 = k + \frac{2\pi}{a}$ . The energies, then, are  $E_0^{(0)}(k) = \frac{\hbar^2 k^2}{2m} = E_0(K_0)$ ;  $E_1^{(0)}(k) = \frac{\hbar^2 (k - \frac{2\pi}{a})^2}{2m} = E_0(K_1)$ ;  $E_2^{(0)}(k) = \frac{\hbar^2 (k + \frac{2\pi}{a})^2}{2m} = E_0(K_2)$ , and so on and so forth, I hope you agree that we can map all the points in one spectrum to points in the other.

How about the wavefunctions, can we put them in the Bloch form? For  $n = 0$  this is trivial, since here  $\phi_{K_0}^{(0)}(x) = e^{iK_0 x} = e^{ikx} = \phi_{0,k}(x)$ , so it has the expected Bloch form  $\phi_{0,k}(x) = e^{ikx} u_{0,k}(x)$  with  $u_{0,k}(x) = 1$ , which is certainly periodic. How about for  $K_1$ ? In this case, the eigenstate is:

$$\phi_{K_1}^{(0)}(x) = e^{iK_1 x} = e^{i(k - \frac{2\pi}{a})x} = e^{ikx} u_{1,k}(x) = \phi_{1,k}(x)$$

where for the  $n = 1$  band, it follows that we must have  $u_{1,k}(x) = e^{-i\frac{2\pi}{a}x}$ . Is this a periodic function? The answer is yes, since  $u_{1,k}(x+a) = e^{-i\frac{2\pi}{a}(x+a)} = e^{-i\frac{2\pi}{a}x} e^{-i2\pi} = u_{1,k}(x)$ . And so on and so forth, you can check that for each band  $n$ , the phase difference between the corresponding  $K_n$  and  $k$  is a multiple of  $2\pi/a$  and gives a different periodic part  $u_{n,k}(x)$  for the Bloch wavefunction  $\phi_{n,k}(x) = e^{ikx} u_{n,k}(x)$  of that band. By the way, it is good that different bands have different  $u_{n,k}(x)$ , because wavefunctions with different  $n$  and/or different  $k$  have to be orthogonal.

So this scheme works for free space, if we choose to view it as a periodic potential. As the rule says, we find that  $k$  is indeed restricted to the Brillouin zone. The price is that we have many bands (different eigenstates for the same  $k$ ), each of which has a Bloch wavefunction with a different periodic part. Turns out that this is what happens in the general case, too – we will have (infinitely) many bands in the Brillouin zone, however their energies  $E_n(k)$  will, of course, depend on the particular potential we choose, as will the periodic parts of their Bloch wavefunctions,  $\phi_{n,k}(x) = e^{ikx} u_{n,k}(x)$ . To find the specific  $E_n(k)$  and  $u_{n,k}(x)$ , we need to solve Schrödinger's equation.

Let me show you how it works in a simple case – for our 1D universe with  $\delta$ -function attraction between ions and electrons, i.e.  $V_a(x) = -U_0 a \delta(x)$  (By the way, why does the constant in front have units of energy·distance if  $V_a(x)$  is an energy? Figure that out. Once you do that, you'll see that we

need to use the lattice constant  $a$ , which is our natural lengthscale in this problem, as the length. That leaves  $U_0$  as an energy which we can adjust at will: the larger it is, the stronger the attraction).

First, let me quickly review the solution for a single ion; you have already solved this for hmw 2, so I will just give the main points. Let's start with the bound states, with  $E = -\frac{\hbar^2\kappa^2}{2m} < 0$ . If we put this in SE and use the fact that the solution must be normalizable, we find that  $\phi(x) = Ae^{\kappa x}$  if  $x < 0$ , and  $\phi(x) = Be^{-\kappa x}$  if  $x > 0$ . The constants are found from "sewing" the solutions together at the origin. Continuity of the wavefunction leads to  $A = B$ , while the jump of the derivative:

$$-\frac{\hbar^2}{2m} \left[ \frac{d\phi}{dx} \Big|_{x=+\epsilon} - \frac{d\phi}{dx} \Big|_{x=-\epsilon} \right] = U_0 a \phi(0)$$

(see hmw 2 for justification) leads to  $\kappa = \frac{mU_0 a}{\hbar^2}$ . So there is a single bound state, with wavefunction:

$$\phi_B(x) \propto e^{-\kappa|x|} = e^{-\frac{|x|}{a_B}}$$

where the "Bohr" radius is  $a_B = \frac{1}{\kappa} = \frac{\hbar^2}{mU_0 a}$  defines the "spread" of the wavefunction, and energy

$$E_B = -\frac{\hbar^2\kappa^2}{2m} = -\frac{U_0^2}{\frac{2\hbar^2}{ma^2}}.$$

This tells us that the larger  $U_0$  is (the stronger the attractive potential), the more negative the energy of the bound state, and the smaller  $a_B$  is. This means that by decreasing  $U_0$ , we can go from the limit where  $a_B \ll a$ , which is the tight-binding limit where our tight-binding model should work well, to the limit with  $a_B \gg a$ , which is the **nearly free electron limit**. These are sketched below.

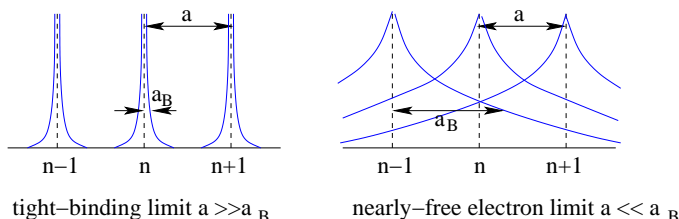


Figure 2: Left: tight-binding limit, where  $a_B \ll a$ . Right: nearly free electron limit, where  $a_B \gg a$ .

For a single ion, then, the spectrum for negative energies has only this one level at energy  $E_B$ . Let's see what happens for a lattice of such ions, at negative energies  $E = -\frac{\hbar^2\lambda^2}{2m}$ ; for what values of  $\lambda$  do we now find eigenstates?

We need to solve the SE for the potential  $U_{tot}(x) = -U_0 a \sum_{n=0}^{N-1} \delta(x - na)$ . The Bloch theorem guarantees that the wavefunctions must be such that  $\phi_k(x+a) = e^{ika} \phi_k(x)$  – this is very nice, because it means that we only need solve SE inside one unit cell, and match the boundaries accordingly.

So consider the unit cell  $0 < x < a$ . The potential at all these  $x$  values is zero, so the wavefunction in this interval must be  $\phi_k(x) = \alpha e^{\lambda x} + \beta e^{-\lambda x}$  (note that since this is for a finite interval, I cannot drop either exponential). According to Bloch's theorem, the potential in the next unit cell,  $a < x+a < 2a$ , must be  $\phi_k(x+a) = e^{ika} \phi_k(x) = e^{ika} (\alpha e^{\lambda x} + \beta e^{-\lambda x})$ . All we need to do now, is to "sew" together the wavefunctions at  $x = a$ , where we have a delta function in the potential. This works just as before. Continuity at  $x = a$  implies:

$$\alpha e^{\lambda a} + \beta e^{-\lambda a} = e^{ika} (\alpha + \beta)$$

while the jump in the derivative results in:

$$-\frac{\hbar^2}{2m} \left[ e^{ika}(\alpha\lambda - \beta\lambda) - (\alpha\lambda e^{\lambda a} - \beta\lambda e^{-\lambda a}) \right] = U_0 a e^{ika}(\alpha + \beta)$$

So we have two homogeneous equations for  $\alpha, \beta$ , and we know that a non-trivial solution is possible only if the determinant is zero. After some boring algebra, this condition becomes:

$$\cosh(\lambda a) - \frac{\sinh(\lambda a)}{\lambda a_B} = \cos(ka)$$

where I used the shorthand notation  $\cosh(x) = \frac{1}{2}(e^x + e^{-x})$ ,  $\sinh(x) = \frac{1}{2}(e^x - e^{-x})$ .

So what happens here is that for each value of  $k$  (inside the Brillouin zone), this equation will give us one or more solutions  $\lambda_n(k), n = 1, 2, \dots$  (however many solutions we get) and therefore we find the allowed energies  $E_n(k) = -\frac{\hbar^2 \lambda_n(k)^2}{2m}$ .

This equation is too complicated to admit simple analytical solutions, but we can still figure out a lot about its solutions in various asymptotic cases. Let me define the function:

$$f(x) = \cosh(x) - \frac{a}{a_B} \frac{\sinh x}{x}$$

Then  $\lambda = x/a$  is the solution when  $f(x) = \cos(ka)$ . Since  $-1 \leq \cos(ka) \leq 1$ , we need to figure out what's the shape of  $f(x)$ , and in particular when it has values between  $-1, 1$ . At the origin,  $f(0) = 1 - \frac{a}{a_B}$ . This is definitely less than 1. If  $a > 2a_B$ , then  $f(0) < -1$ . As  $x$  increases, you should be able to convince yourself that this function increases monotonically. In particular, at large  $x$  we can discard the  $e^{-x}$  exponentials as being small, and we find  $f(x) \rightarrow \frac{e^x}{2} \left(1 - \frac{a}{a_B} \frac{1}{x}\right)$ , which diverges as  $x \rightarrow \infty$ .

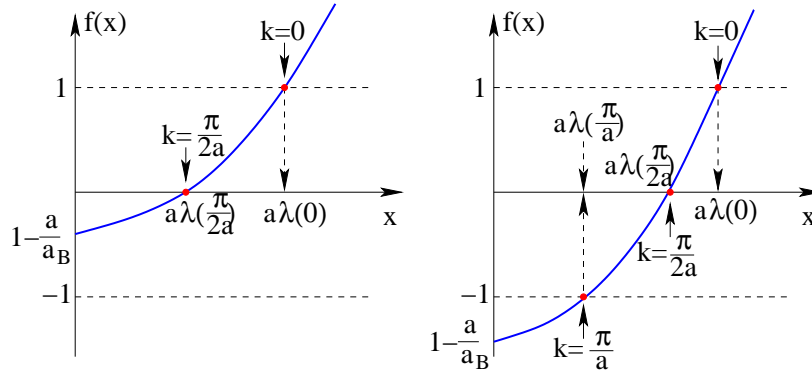


Figure 3:  $f(x)$  sketched when (left)  $a < 2a_B$ , and (right)  $a > 2a_B$ . The solutions for  $f(x) = \cos(ka)$  with  $k \in (-\frac{\pi}{a}, \frac{\pi}{a}]$  lie in between between  $-1, 1$ .

This function is sketched above, for both  $a < 2a_B$  and  $a > 2a_B$  cases. Let me start with the second case, first. Here, there is a single solution  $x$  for  $f(x) = \cos(ka) \in [-1, 1]$ , so we expect a single solution for  $\lambda = x/a$ , and therefore a single band at negative energies  $E = -\frac{\hbar^2 \lambda^2}{2m}$ .

Let's find it in the limit  $a \gg a_B$ , i.e. in the tight-binding limit. Now  $f(0)$  starts at a very negative value, so by the time it crosses the  $[-1, 1]$  interval the values of  $x$  are large and we can use the simpler asymptotic expression, i.e. here:

$$f(x) \approx \frac{e^x}{2} \left(1 - \frac{a}{a_B} \frac{1}{x}\right) = \cos(ka) \rightarrow x = \frac{a}{a_B [1 - 2e^{-x} \cos(ka)]}$$

This is still a transcendental equation so we don't have an exact solution, but we can get an accurate one by iterations. If the exponential wasn't there, the solution would be  $x = \frac{a}{a_B} \gg 1$  in this limit. As a result,  $e^{-x}$  is small and leads to a tiny correction, so the actual solution won't be too far from  $\frac{a}{a_B}$ . So I can replace the  $x$  in the exponential with  $a/a_B$ , to find:

$$x = \lambda(k)a \approx \frac{a}{a_B \left[ 1 - 2e^{\frac{-a}{a_B}} \cos(ka) \right]} \approx \frac{a}{a_B} \left[ 1 + 2e^{\frac{-a}{a_B}} \cos(ka) \right]$$

(this is just a Taylor expansion, since the exponential continues to be small). Remembering that  $1/a_B = \kappa$  for the bound state, we find:

$$\lambda(k) = \kappa \left[ 1 + 2e^{\frac{-a}{a_B}} \cos(ka) \right]$$

leading to the energies:

$$E_B(k) = -\frac{\hbar^2 \lambda(k)^2}{2m} \approx E_B \left( 1 + 4e^{\frac{-a}{a_B}} \cos ka \right) = E_B - 2t \cos(ka)$$

if we define the hopping  $t = 2|E_B|e^{\frac{-a}{a_B}}$ . Before continuing, note that I dropped the term that goes like  $e^{\frac{-2a}{a_B}}$  from the square – this is because I know that it is much smaller than the ones I kept, and moreover I already neglected such terms when I did the Taylor series above, and in the iterational solution, etc. So it's simply not meaningful to keep it here.

So for  $a \gg a_B$  we regain the tight-binding eigenenergy we expected to be valid here, with the correct expression for the hopping  $t$  (see hmw2). If we kept higher order corrections they would account for the contributions of the overlap  $S$  and the shift  $\Delta E$  etc, which are ignored at this level of approximation. The left panel below shows the allowed energy band, i.e. the energy interval where we find solutions in the limit when  $N \rightarrow \infty$ , so that all  $k$  inside the BZ are allowed. The right picture shows the dispersion for one particular value of  $a/a_B$ , in the tight-binding limit. The larger  $a/a_B$  is, the narrower the band becomes, because the hopping between nearest sites is smaller and smaller. In the limit  $a/a_B \rightarrow \infty$  we basically have isolated atoms, each with their allowed level at  $E_B$ .

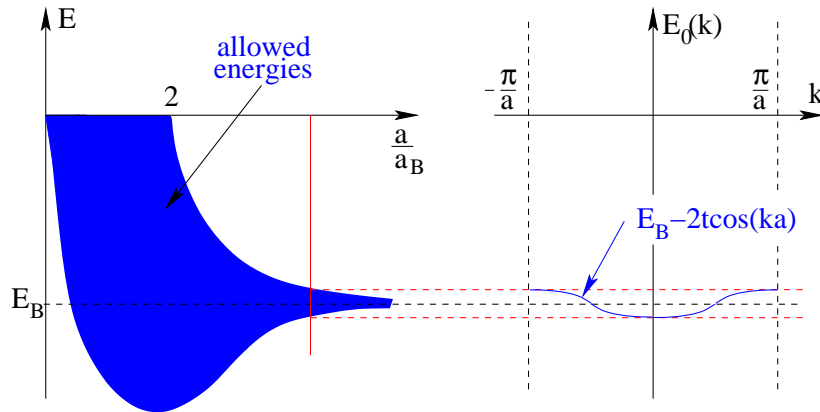


Figure 4: Left: allowed band of energies with  $E < 0$ , as a function of  $a/a_B$ . Right: For a particular value of  $a/a_B$ , indicated by the dashed line, I showed the dispersion  $E_B(k)$  vs  $k$ , in the Brillouin zone.

How about the wavefunctions, do they come out correctly? In the tight-binding limit we obtained the solutions  $|\phi_k\rangle = \sum_n e^{ikna} |n\rangle$ , which, when projected in real space, means that  $\phi_k(x) = \langle x | \phi_k \rangle =$

$\sum_{n=0}^{N-1} e^{ikna} \phi_B(x - na)$ . Remember that the bound level eigenfunctions are simple exponentials. For  $0 < x < a$ , the ones that contribute most are the  $e^{-x/a_B}$  part from the ion at  $n = 0$ , and then  $e^{\frac{x-a}{a_B}}$  part from the ion at  $n = 1$  – all other ions' contributions are very much smaller than these terms, since they are further away from this interval. Keeping only these two largest contribution, the tight-binding approximation says that for  $0 < x < a$  we should find:

$$\phi_k(x) \propto e^{\frac{-x}{a_B}} + e^{ika} e^{\frac{x-a}{a_B}}$$

Let's see what the exact solution predicts in this limit. This requires us to find  $\alpha, \beta$  so that we have the wavefunction. We can use either equation, let's use the simpler one:

$$\alpha e^{\lambda a} + \beta e^{-\lambda a} = e^{ika}(\alpha + \beta) \rightarrow \frac{\alpha}{\beta} = \frac{e^{ika} - e^{-\lambda a}}{e^{\lambda a} - e^{ika}}$$

But in this limit  $\lambda \approx \frac{1}{a_B} \rightarrow e^{\lambda a} = e^{\frac{a}{a_B}} \gg 1$ , thus we can simplify the fraction:

$$\frac{\alpha}{\beta} \approx \frac{e^{ika}}{e^{\lambda a}} \rightarrow \alpha = \beta e^{ika} e^{\frac{-a}{a_B}}.$$

Putting this into our solution on the  $0 < x < a$  interval,  $\phi_k(x) = \alpha e^{\lambda x} + \beta e^{-\lambda x} \approx \alpha e^{\frac{x}{a_B}} + \beta e^{\frac{-x}{a_B}}$  (since  $\lambda \approx \frac{1}{a_B}$ ) gives us, up to a normalization constant, the expected solution.

What happens when we decrease  $a/a_B$ , i.e. we bring the ions closer and closer together? For one, the hopping increases so the bandwidth  $4t$  becomes larger. From the discussion of the exact  $f(x)$ , you can see that something happens at  $a/a_B = 2$  – only above it are we guaranteed to find solutions for all  $k$  in the BZ. What happens for smaller  $a/a_B$ , as the figure above hopefully suggests, is that we need to worry about positive energies (so far we only discussed  $E < 0$  eigenstates). So let's look at the spectrum there, too.

The  $E = \frac{\hbar^2 K^2}{2m} > 0$  case is studied just like before. Everything mirrors what we did for  $E = -\frac{\hbar^2 \lambda^2}{2m} < 0$  if we replace  $\lambda \rightarrow iK$ . In particular, we now find that for each  $k$ , the allowed values of  $K$  (which determine the energy) are given by the equation:

$$\cos(Ka) - \frac{\sin(Ka)}{Ka_B} = \cos(ka)$$

Let's define again a function  $g(x) = \cos(x) - \frac{a}{a_B} \frac{\sin x}{x}$ , and solve  $g(x) = \cos(ka) \rightarrow K = x/a$ . What does  $g(x)$  look like? Its two components are sketched below; the  $\cos$  function oscillates, while the  $\frac{\sin x}{x}$  oscillates but also decays slowly with increasing  $x$ .

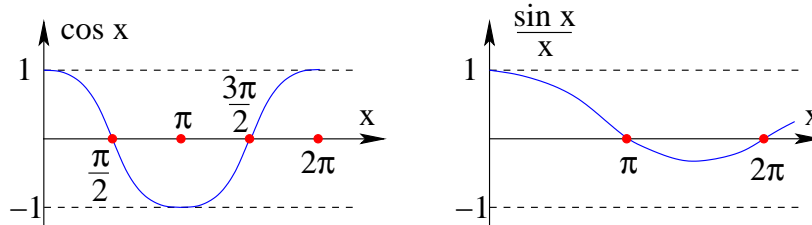


Figure 5: Left:  $\cos(x)$  vs  $x$ . Right:  $\sin(x)/x$  vs  $x$ .

Let's see first what happens for  $a \gg a_B$ . In this case, the  $\sin$  term is large near the origin and dominates there, so  $g(x)$  looks like in the next plot. I also drew the lines for  $g(x) = 1$  (this gives

solutions for  $k = 0$ ) and  $g(x) = -1$ , which corresponds to solutions for  $k = \pm \frac{\pi}{a}$ . As we increase  $k$  we sweep between the two. Unlike for  $E < 0$ , where we found a single solution for each  $k$ , here we have an infinity of them, so they predict an infinity of bands at positive energies. The full spectrum looks like sketched on the right, with the tight-binding band at negative energy, and all these other allowed bands separated by gaps at positive energies. Note how the “curvature” of the bands alternates.

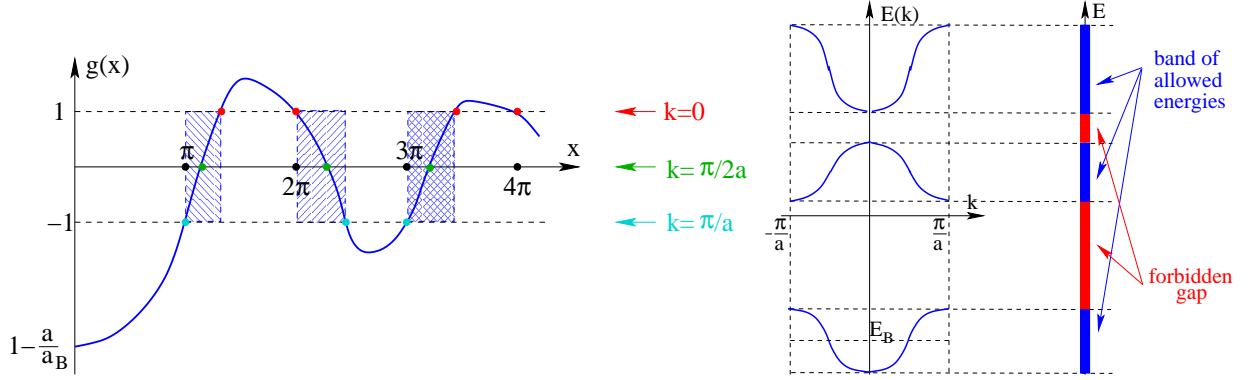


Figure 6: Left: Solution of  $g(x) = \cos(ka)$  in the limit  $a/a_B \gg 1$ . Right: Full spectrum in the limit  $a \gg a_B$ .

Ok, so now finally let's see what happens as  $a/a_B$  becomes small. In this limit, the function  $g(x)$  looks like below. The contribution of the sin term is very small, so  $g(x)$  barely crosses above 1 or below -1. We still get allowed bands separated by forbidden energy ranges, but they are wider. The bottom of the lowest band nicely matches up with what we found there for the negative spectrum, so the whole spectrum here looks like shown in the right panel:

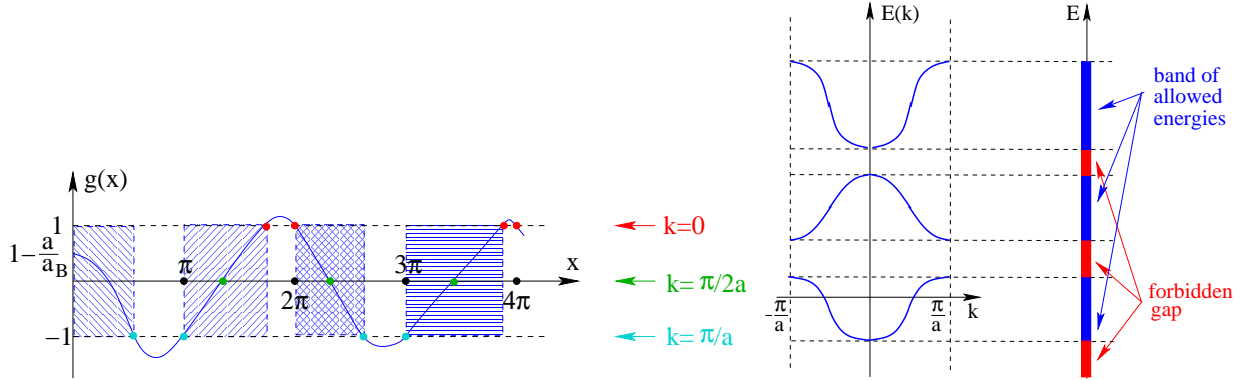


Figure 7: Left: Solution of  $g(x) = \cos(ka)$  in the limit  $a/a_B \ll 1$ . Right: Full spectrum in the limit  $a \ll a_B$ .

This is starting to look like the free electron spectrum, which it should evolve into when  $a/a_B \rightarrow 0$  (for  $a_B \rightarrow \infty$  when  $U_0 \rightarrow 0$ , i.e. when there is no potential). Indeed, as we make  $a/a_B$  smaller, the bottom of the lowest band comes closer to zero while the gaps above start to close, and we regain the folded band structure from Fig. 1. If you wish to check this statement, you can calculate, for example, the energies of the first two bands at  $k = \pi/a$ . I did this, and found  $E_0(k = \frac{\pi}{a}) = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 \left[1 - \frac{4a}{\pi^2 a_B}\right]$ , while for the second band, I find  $E_1(k = \frac{\pi}{a}) = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 \left[1 + \frac{4a}{\pi^2 a_B}\right]$ . So the first bands ends just below the  $\frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2$  expected in vacuum for  $k = \frac{\pi}{a}$ , while the second band starts just a bit above it. The gap between them is proportional to  $a/a_B$ , and indeed closes as  $U_0 \rightarrow 0$ .



This calculation tells us that in the presence of a periodic potential, we generically expect to see a spectrum consisting of allowed energy bands which are separated by gaps. Of course, real atoms have many bound states, not just one like our “pretend” atoms. However, this is not going to change things significantly. Each level has a characteristic distance over which it decays exponentially, and “deeper” levels decay faster because they are located closer to the nucleus. For a given lattice constant  $a$ , the low-lying levels decay much faster than  $a$  so they are well-described by tight-binding models. For higher-energy orbitals, which are more extended, the tight-binding approximation is not going to be accurate anymore, and we’ll need to do better. In any event, if we consider what happens as we decreased the lattice constant from infinity (corresponding to isolated atoms, each with its own atomic spectrum), we should get something like sketched below:

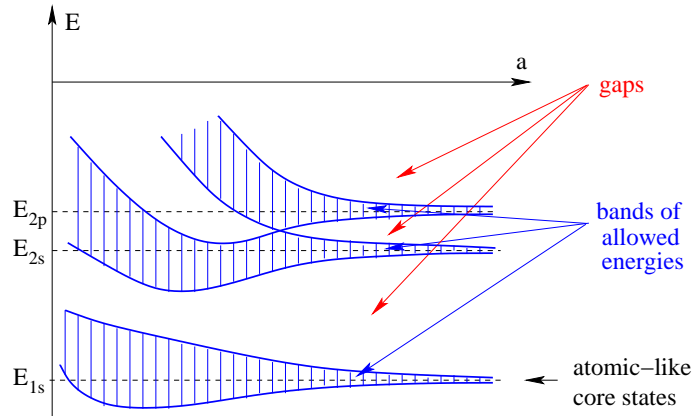


Figure 8: General evolution of the energy bands in a solid, as the lattice constant is decreased.

The precise locations of the allowed energy bands will, of course, depend on what type of crystal we have (remember, from hmw 2, the difference in  $E(k)$  for different lattices even in the tight-binding limit), and what is the equilibrium value for  $a$ , etc etc. But there will certainly be energy bands separated by forbidden gaps. Higher bands have larger hopping constants because their orbitals are more spread-out, so their width increases faster; they are also closer together, so we expect that they start overlapping at some point or other (when this happens, the simple tight-binding approximation definitely fails and we need to work harder to find an accurate solution).

So this is the generic picture for the single-electron spectrum of a crystal. Now we have to fill the lowest levels with all the electrons contributed by all the atoms. There are two possible outcomes:

(i) the last band that contains electrons is only partially full. In this case, the material is a metal – if we apply a small electric field, there are free levels just above the occupied ones, so we can easily excite electrons and make them move preferentially in the direction of the field, to get an electric current (we’ll discuss this more carefully very soon).

(ii) the last band that contains electrons is completely full, in the ground-state. In this case, the material will not be a metal; to excite electrons to empty levels, we need to give them an energy at least equal to the gap so that we can move them into the next band. This is why applying a small electric field will not start a current flowing, so this is not a conductor. If the gap is larger than  $\approx 2\text{eV}$ , we call this an insulator; if it is less than  $\approx 2\text{eV}$ , we call such a material a semiconductor.

The next topic we’ll work on is to understand a bit the difference in the macroscopic properties of metals vs. insulators/semiconductors. Not just transport properties (how currents flow or don’t flow through them), but also optical properties (what do they look like) and thermal properties.

Before that, for completeness’ sake let me just mention that we can measure directly the energy

bands using photo-emission spectroscopy. This is when a beam of high-energy photons is shined onto a sample, and some of them are absorbed by electrons inside which therefore receive enough energy to escape the crystal. Detectors measure the energy and momentum of the escaping electrons, and from conservation of energy and momentum, one can extract information about was the energy and momentum, i.e.  $E_n(k)$ , of the electrons while in the crystal. This technique is known as Angle-Resolved Photoemission Spectroscopy (ARPES), and the Damascelli lab here at UBC does such measurements. You can look at their webpage for more information and some nice pictures of experimentally measured electronic bands.

In terms of calculating band structures going beyond simple models like tight-binding, one uses so called ab-initio methods, or density functional theory. A lot of care is needed with the interpretation, though, because this theory only guarantees to predict the (total) ground-state energy and density of electrons in the ground-state, and this only if a certain functional is known. We do not know that functional but we can compute an approximate form for the jellium model, and that is usually used for everything (so-called LDA approximation). This works pretty well for systems with weak electron-electron interactions, but not for systems with strong interactions. Various ways to fix the problem are proposed for the latter problems, but this is still very much work in progress.