Electronic Hamiltonians - part I

In this section we discuss how to deal with electronic Hamiltonians, i.e. the first step in our sequence of approximations. We treat the ions as being frozen in their equilibrium positions, so the electrons are moving in the resulting periodic potential and also experience electron-electron interaction. We will first ignore the electron-electron interactions, i.e. set them to zero. Although this may seem a very strange things to do, it is actually a fairly good approximation in some cases. We will revisit this issue toward the end of the section, but roughly speaking, what happens is that the repulsion between two electrons is nearly compensated (screened) by the attraction with the positive charges present in the same region. This compensation works very well for electrons that are far apart, less so if they are spatially close. For simplicity, we begin by assuming that we can completely ignore electron-electron interactions. This allows us to study exactly models of non-interacting electrons moving in periodic potentials, to understand the typical aspects of electronic band-structures. Then, we will consider the role of (weak) electron-electron repulsions using the Hartree-Fock approximation, and we will revisit screening using the Random Phase Approximation.

1 General considerations

The beauty of **non-interacting Hamiltonian** (this is the generic name used for models where e-e interactions are ignored, even though the electrons do interact with the ions!) is that they can always be solved exactly. The first step is to find the single-electron eigenstates for the Hamiltonian of interest: $\hat{H}|\gamma\rangle = E_\gamma|\gamma\rangle$. This we can always do because it is a single-electron problem – and as we'll see next, symmetries of the lattice will help us a lot in figuring out what this basis of one-particle eigenstates is.

Once we know all $E_\gamma, |\gamma\rangle$, we use this one-particle basis to write the Hamiltonian in 2ndQ. We define the corresponding operators $c_\gamma^\dagger, c_\gamma$, and the Hamiltonian is simply $\hat{H} = \sum_\gamma E_\gamma c_\gamma^\dagger c_\gamma$. Indeed, this says that adding an electron in state γ to the system, increases its energy by E_γ – which is true for non-interacting electrons.

If we work with an isolated system with a given number N of electrons, then the N-particle ground-state (GS) is obtained by occupying the lowest-energy N amongst the γ levels $|GS\rangle_N = \prod_{\gamma \in GS} c_\gamma^\dagger |0\rangle$, and the corresponding GS energy is $E_{GS,N} = \sum_{g \in GS} E_\gamma$, where the product/sum are over the levels occupied in the GS. I explicitly used the index N for both because they depend on N, but often times that is not written explicitly. Excited states are obtained by moving electrons from the lowest states into higher ones.

If we work with an open system, which is in contact with a heat reservoir of temperature T and a particle reservoir with chemical potential μ, then the number of particles is not fixed. In equilibrium, each one-particle level γ is filled according to the Fermi-Dirac distribution

$$n_\gamma = \langle \hat{n}_\gamma \rangle = \frac{1}{e^{\beta(E_\gamma - \mu)+1}}$$

In the limit $T \to 0$, the system goes to its GS and we find that $n_\gamma = 1$ if $E_\gamma < E_F$, while $n_\gamma = 0$ if $E_\gamma > E_F$. E_F **is the Fermi energy** (equal to the value of μ when $T = 0$) and is defined as the energy of highest one-particle state occupied in the ground-state of the system. Its value will depend on how many electrons there are in the system – the more electrons, the bigger E_F. Of course, the average number of electrons in the system is $N = \langle \hat{N} \rangle = \sum_\gamma \langle \hat{n}_\gamma \rangle$. I'll still call this quantity N even though it is usually not an integer (the value changes continuously with μ and T).

However, for us these values will be of the order 10^{23}, so an extra .2653 or some such decimal part will really not make any difference, we can pretend that the number is an integer if we so wish. Fluctuations $\delta N = \sqrt{\langle (\hat{N}\rangle - N)^2}$ about its average can be calculated straightforwardly, and for large systems with large corresponding N, it is always the case that $\delta N/N \sim 1/\sqrt{N} \to 0$. In other words, even though the number of particles fluctuates, in the thermodynamic limit the fluctuations become vanishingly small and it's essentially as if the number is fixed to its average value.

Hopefully this is all well-known, the main point I wanted to make is that in the absence of electron-electron interactions each electron is on its own, so if we can solve the problem for a single electron, we know the answer for an isolated system with any number of electrons, or for any open system in equilibrium at some given μ, T.

2 Non-interacting electrons in a periodic potential

For simplicity, let's assume that we put together many Li atoms ($1s^2 2s^1$ electronic structure) in a crystal, and see how we would model this if we can ignore electron-electron interactions. From what we have discussed, we expect the $2s$ electrons to be the valence electrons, so we're considering 1 valence electron per Li^+ ion.

For simplicity, let me consider a 1D model of a chain of such ions, placed equidistantly from each other (of course, in reality Li would crystallize as a 3D crystal, but you should be able to deal with 3D lattices if you understand how the 1D case works). We can label these with an index $n = 1, ..., N$, where we will let $N \to \infty$, in the end. Let a be the lattice constant, so the position of the nth ion is $R_n = na$. To describe the valence electrons, we introduce creation and annihilation operators $c_{n\sigma}^{\dagger}, c_{n\sigma}$ for an electron at site n with spin σ. To be more precise, $c_{n\sigma}^{\dagger}|0\rangle$ is the one-electron state for which $\langle x, \sigma' | c_{n\sigma}^{\dagger} |0\rangle = \delta_{\sigma,\sigma'}\phi_{2s}(x - R_N) = \delta_{\sigma,\sigma'}\langle x|n\rangle$, i.e. in fact the electron is created into the $2s$ orbital of the nth ion. Because this is the only orbital that we include in our model, we can say that the electron is at site n without creating confusion.

This $2s$ orbital has some characteristic lenghtscale a_B (its Bohr radius) over which it is spread away from its ion. Our approximation to keep only these orbitals is a reasonable approximation if the distance between neighbour ions is much bigger than the "size" of the $2s$ orbital, so that there is no confusion to which orbital an electron belongs. This is sketched below to the left, and is known as a "tight-binding" limit. One can also consider the "nearly-free electron limit", which would be valid if the atomic orbitals spread over many lattice sites, so that you couldn't be sure to which orbital an electron which is close to ion n, let's say, belongs in reality. This is sketched to the right. We will discuss this second case later on.

Another way to see why we need to treat these cases differently, is to remember that we are allowed to introduce creation and annihilation operators only for the states of an orthonormal, one-particle basis. In the tight-binding limit (left panel) the $2s$ orbitals are not truly orthogonal, there is always some tiny overlap – but it is a good approximation to pretend that they are if $a \gg a_B$. (To be truly correct, we should use Wannier orbitals instead of the atomic-like orbitals – they look quite similar but are properly orthogonalized. The differences between the two sets are not relevant for what we're doing in this course, so I will ignore them in the following). In the nearly-free limit, it is clear that the there is huge overlap between consecutive orbitals, they are nowhere near close to being an orthogonal basis and we'd get nonsense if we pretended that they were, like we can do in the tight-binding case. This is why we'll have to treat cases with nearly-free electrons quite differently.

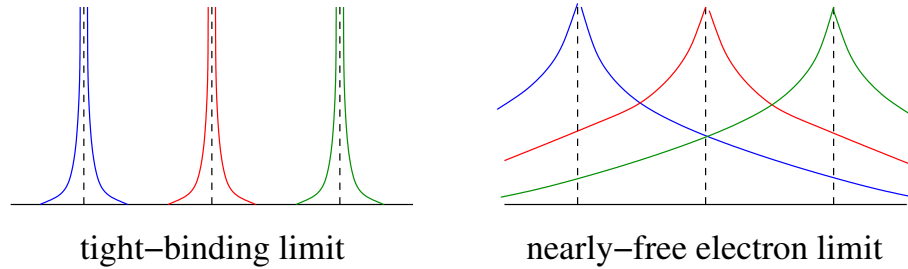tight–binding limit   nearly–free electron limit

Figure 1: Contrast between a tightly-bound model, with orbitals small compared to the lattice constant (left) and a nearly-free model, with orbitals spread over many lattice constants.

2.1 Tight-binding models

For our tight-binding model, we assume $\langle n|m \rangle = \int dx \phi_{2s}(x - R_n)\phi_{2s}(x - R_m) = \delta_{nm}$. As I just said, this orthogonality is necessary in order to be able to associate creation and annihilation operators that satisfy the proper algebra to these states (remember that we can do so only for a basis of orthonormal one-particle states. If the orbitals are not orthogonal, we first have to define a new basis of orthogonal states – we'll assume that this has been done).

Deriving a Hamiltonian for this approximation proceeds just like we did in the Hubbard case, and we will get the same result. If we make the additional approximation that we can ignore even the on-site repulsion $U \to 0$, we obtain the 1D tight-binding Hamiltonian:

$$\hat{H} = \epsilon \sum_{n,\sigma} c_{n\sigma}^\dagger c_{n\sigma} - t \sum_{n,\sigma} \left(c_{n\sigma}^\dagger c_{n+1,\sigma} + h.c. \right) \tag{1}$$

As we should know very well by now, the first term counts the on-site energy to have the electrons at any given site, which up to some small corrections can be thought of as the atomic energy of this orbital. If each atom keeps its electron 100% of the time, for instance when $a \to \infty$ and we have a collection of isolated atoms, the total energy would be given by this term and equal $N\epsilon$. The second term describes hopping: if the electron is at site n, attraction from the neighbouring ions can make it move either to $n + 1$ or to $n - 1$. This is known as **nearest-neighbour hopping** (nn hopping). As we discussed, the electron will also feel attraction from ions further away, and could hop directly two or more lattice sites, to one of those, so in principle longer-range hopping should be present in the Hamiltonian. However, remember that the hopping integral decreases exponentially with the distance between sites, so nearest-neighbour hopping is by far the largest term. In many cases it is a good approximation to ignore longer-range hopping, and we will do so. It can be easily included and once you understand the solution with only nn hopping, you should be able to include longer-range hopping and figure out its effects.

As mentioned several times, it is always advisable to start by assuming a finite-size system, which here would mean a finite number N of atoms (we can let $N \to \infty$ at the end, if we wish). One issue we have to be careful with is what happens at the ends of the chain. I will use the so-called **periodic boundary conditions** (PBC), which state that if the electron is at site 1, it can hop either to 2 or to N, and if the electron is at site N, it can hop either to N-1 or to 1. In other words, it's as if the chain is actually closed into a circle, and 1 and N are nearest neighbours as well. Mathematically, this means that $c_{n+N,\sigma}^\dagger = c_{n,\sigma}^\dagger$ for any n. In other words, if you move N sites along the chain, you get back to the original site.

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The reason we prefer to use PBC in all our problems is because they make the calculations simpler, as we'll see soon. The logic is that for a macroscopic crystal, with $N \sim 10^{23} \gg 1$, it should not matter how we "end" the crystal, because the vast majority of the contributions comes from the bulk sites and the small contributions from the surface must be negligible by comparison. So we can choose whichever situation makes calculations easiest, and PBC do. (As a good physicist you should be skeptic of everything I say and you should check this statement, by repeating the calculation we do next for a chain with **open boundary conditions** OBC, i.e. where an electron at site 1 can only hop to 2, and one at N can only hop to N-1, and show that the difference in the total energy because of the BC is indeed $\mathcal{O}(N)$. This might show up in a homework problem, but if not let me know if you need help with it).

Now that we have the Hamiltonian, the path is clear: first, we need to find its single-particle eigenstates $\hat{H}|\gamma, \sigma\rangle = E_{\gamma,\sigma}|\gamma, \sigma\rangle$ (Because the spin is a good quantum number, it will be part of the set of quantum numbers, so I'll write it separately and let γ be all the other quantum numbers apart from spin, needed to identify one-particle eigenstates). For this problem the most general form of these eigenstates is $|\gamma, \sigma\rangle = \sum_n \phi_\gamma(n) c_{n\sigma}^\dagger |0\rangle$ – the rhs is the most general one-particle state with spin-σ that we can write. So all that is left to do is to find the coefficients $\phi_\gamma(n)$ and the corresponding energy E_γ, and we're done (Q: why did I drop the spin, and when am I not allowed to do that?). For our simple 1D Hamiltonian written above, this eigenproblem can be solved "by brute force", as you'll find out in the next homework. However, that is not a good way to go because it's harder and harder to do this for more complicated models, and in higher dimensional systems, etc. So instead we'll discuss how we use symmetries to figure out what the quantum numbers γ must be, and the corresponding $\phi_\gamma(n)$.

Because of the PBC, this problem is invariant to lattice translations - there is no way to distinguish between any one site and any other site, the properties are all the same everywhere. *Invariance to translations automatically implies that momentum must be a good quantum number.* You might worry that that is true only for continuous translations, but it turns out to be true for a discrete group of translations, like we have here, as well. The difference is that we're now dealing with a quasi-momentum, or crystal momentum, instead of a momentum – we'll soon see what the difference is. In any event, it is customary to be lazy and call it a momentum (not quasi, or crystal). So without any further work, we know that $\gamma \to k$. We know that the wavefunctions associated with a momentum are plane-waves, so we must have $\phi_\gamma(n) \to \phi_k(n) = e^{ikR_n}/\sqrt{N}$ (when properly normalized to the N-site chain). This makes sense, it says that in any eigenfunction, the probability to find the electron at any site is $1/N$ so the homogeneity is enforced. The operators associated with these eigenstates, then, ca be read directly from $|\gamma, \sigma\rangle \to |k, \sigma\rangle = c_{k,\sigma}^\dagger |0\rangle$, and we find the dependence of the "new" operators on the "old" operators:

$$ c_{k\sigma}^\dagger = \sum_n \frac{e^{ikR_n}}{\sqrt{N}} c_{n\sigma}^\dagger \qquad\qquad c_{k\sigma} = \sum_n \frac{e^{-ikR_n}}{\sqrt{N}} c_{n\sigma} $$

which can be inverted to (check!):

$$ c_{n\sigma}^\dagger = \sum_k \frac{e^{-ikR_n}}{\sqrt{N}} c_{k\sigma}^\dagger \qquad\qquad c_{n\sigma} = \sum_n \frac{e^{ikR_n}}{\sqrt{N}} c_{k\sigma} $$

The normalization is defined such that the new operators also satisfy the proper algebra $\{c_{k,\sigma}, c_{k',\sigma'}^\dagger\} = \delta_{k,k'}\delta_{\sigma\sigma'}$ etc, in other words their corresponding wavefunctions are properly orthogonal.

Another way to see that these $|k, \sigma\rangle = c_{k,\sigma}^\dagger |0\rangle$ *must* be the eigenfunctions, is to realize that they describe Bloch states: $\langle x, \sigma'|k, \sigma\rangle = \sum_n \frac{e^{ikR_n}}{\sqrt{N}} \phi(x - R_n)\delta_{\sigma,\sigma'}$, where $\phi(x) = \langle x, \sigma|c_{0,\sigma}^\dagger\rangle$ is

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the wavefunction associated with the valence orbital centred at the origin (the other orbitals are centred about their respective lattice sites). You should already know from an introductory solid-state course what Bloch functions are (we'll review them very soon): they are wavefunctions with the property that $\phi(x + a) = e^{ika}\phi(x)$ (this is in 1D, and needs to be generalized appropriately for higher D). The Schrodinger equation in a periodic potential is guaranteed to have Bloch-type eigenfunctions.

In our problem, because we have only one orbital per unit cell, there is a single Bloch function that we can write for any given momentum k, which is exactly the one I wrote above using the symmetry argument. Because I know that the eigenstates are of Bloch-type, it follows that these unique Bloch functions that I can write must be the eigenstates! **Note**: Later we'll discuss cases where we have two or more orbitals per unit cell, and we'll see that then we can define two or more Bloch-states out of those orbitals, for any given k. In that case, the Hamiltonian will decide which linear combinations of the Bloch states with the same k are the actual eigenstates; but here there is a single Bloch state, so this is it.

If we plug these eigenfunctions into Eq. (1) and do a bit of algebra, we find that

$$\hat{H} = \sum_{k,\sigma} E(k)c_{k,\sigma}^{\dagger}c_{k,\sigma}$$

where $E(k) = \epsilon - 2t\cos(ka)$. In other words, to the one-electron eigenstate $c_{k\sigma}^{\dagger}|0\rangle = \sum_{n=1}^{N}\frac{e^{ikna}}{\sqrt{N}}c_{n\sigma}^{\dagger}|0\rangle$ corresponds the eigenenergy $E(k) = \epsilon - 2t\cos(ka)$. Because the electrons are non-interacting, many-electron solutions are trivial as well: the eigenstate $c_{k_1\sigma_1}^{\dagger}...c_{k_p\sigma_p}^{\dagger}|0\rangle$ has the eigenenergy $E(k_1) + ... + E(k_p)$, i.e. the sum of individual contributions.

But we have one more question to answer: can the momentum k be any number, or are there some restrictions? We are using PBC, *i.e.* that $c_{n+N,\sigma} = c_{n,\sigma}, c_{n+N,\sigma}^{\dagger} = c_{n,\sigma}^{\dagger}$, for any n (we're removing/adding the electron from/to the same site). If we use the link between $c_{n\sigma}$ and $c_{k\sigma}$ from the line above, we find that we must have

$$e^{ikNa} = 1 \rightarrow k = \frac{2\pi m}{Na}, m = 0, \pm 1, \pm 2, ...$$

So only certain values of the momentum are allowed but it seems that we have an infinite (but countable) number of eigenstates, one for each integer.

More careful thinking shows that this is not true, in fact we have distinct answers only for N consecutive values of m, and then we repeat the same eigenfunctions and eigenvalues: if $k_m = \frac{2\pi m}{Na}$ then $k_{m+N} = k_m + \frac{2\pi}{a}$, and you can easily check that $c_{k,\sigma} = c_{k+\frac{2\pi}{a},\sigma}$ and $E(k) = E(k + \frac{2\pi}{a})$. Because we don't find anything new, we can't pretend those to be distinct states/operators, so we throw them out. More generally, we have periodicity $k' = k + pb$ where p is any integer and $b = \frac{2\pi}{a}$ is the reciprocal lattice vector for this lattice: periodicity in real space leads to periodicity in the momentum space, and viceversa.

So we actually only have N distinct allowed k values. We could choose these as being $m = 0, 1, 2, ..., N - 1$ or any other choice of N consecutive integers. Because we like symmetry, the traditional choice is $m = -\frac{N}{2} + 1, ..., -1, 0, 1, ...\frac{N}{2}$, i.e. values symmetrically placed about the origin. In other words, we only consider values such that $-\frac{\pi}{a} < k \le \frac{\pi}{a}$. This interval is the **Brillouin zone**. The allowed values for k and the corresponding eigenenergies in a chain with $N = 21$ sites are sketched below.

Sanity check: is it reasonable that we have $2N$ eigenstates (N possible values for k, times 2 for spin-up and spin-down)? Maybe we didn't find all of them – we always have to worry about
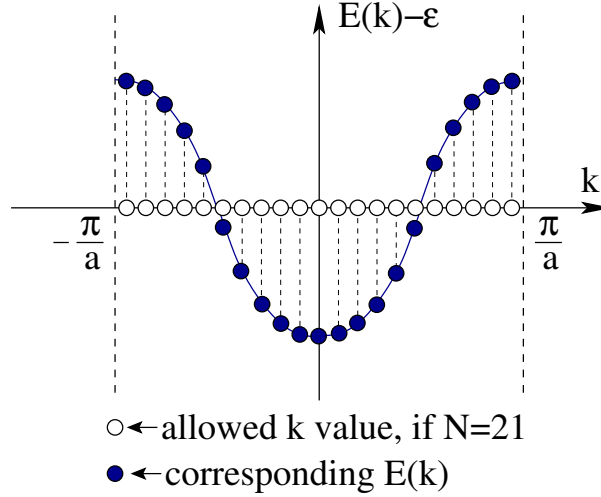
Figure 2: Allowed momenta k and corresponding eigenenergies $E(k)$ (white and blue circles, respectively) inside the first Brillouin zone $-\frac{\pi}{a} < k \le \frac{\pi}{a}$. For a chain with N sites there are precisely N allowed values, equidistantly placed.

this when we "guess" the solution, like we did here. The answer is: all is good. Our Hilbert space is $2N$-dimensional, because it was spanned by the $2s$ orbitals located at $n = 1, ..., N$ and with $\sigma = \pm 1$. The eigenstates form a basis, so there must be precisely $2N$ of them, as well. We found $2N$, so we have all of them (by the way, I forgot to mention that these eigenstates must be orthonormal. You can check by direct calculation that this is indeed the case).

So at this point we finished solving the one-particle problem, and we know its eigenfunctions and eigenvalues. Before moving on to dealing with the many-electron system, let me emphasize again why PBC are so lovely: they make the system invariant to lattice translations, so we know immediately that momentum is a good quantum number (with minor complications such as the restriction to equally spaced values inside the BZ, which is why it's actually a crystal momentum, it's not the free particle momentum that has no such restrictions). Knowing the quantum number tells us the shape of the eigenfunction – Bloch states, in this particular case. So we don't need to calculate it, it's already decided, and all that is left for us to do is find the corresponding energies. By contrast, consider what happens if we have OBC. In this case, there is no invariance to translations: sites near the edges are different from sites that are far from the edges. So we don't have symmetries to tell us what are the quantum numbers and therefore what shape the wavefunctions must have, therefore we have to calculate them from scratch. For a system with N sites and if spin is a good quantum number, that means diagonalizing a $N \times N$ matrix, which takes some work. In simple cases (like this specific problem) we can use tricks to figure out the solutions, as you may see in the homework. But in general one can't do this by hand and computers are needed, and things are certainly more complicated. Now, if we know that both OBC and PBC give us the same results in the thermodynamic limit, it should now be obvious why we prefer the PBC! There are cases where the translation symmetry is broken by something else, for instance by disorder (if there is some randomness in the system because of disorder, then sites close to disorder are different than sites far from it and again, the invariance to translations is gone). Such problems, by and large, need to be solved numerically. We will not discuss them in this course,

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but I want you to be aware of them, and to appreciate the power of symmetries.

Onwards: what is the solution for our chain of Li, i.e. when we have N electrons in the system so that precisely half of the states are filled? We have to place the N electrons in these one-particle states, obeying Pauli's principle. In the ground-state they occupy the lowest available levels, to minimize the total energy. That means that electrons occupy the half of the states with energies $E(k) < \epsilon$ (these are the states with momenta $-\frac{\pi}{2a} < k \leq \frac{\pi}{2a}$ and spin $\sigma = \pm 1$), and we leave empty the other half of the states, with energy $E(k) > \epsilon$. So clearly the total energy is lower than the $N\epsilon$ we would have if each Li kept its electron. The ground-state eigenstate is:

$$|GS\rangle = \prod_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, \sigma} c^\dagger_{k,\sigma}|0\rangle$$

and the ground-state energy is:

$$E_{GS} = \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, \sigma} E(k) = N\epsilon - 4t \sum_{\frac{-\pi}{2a} < \epsilon < \frac{\pi}{2a}} \cos(ka)$$

In the limit $N \to \infty$, the sum can be turned into an integral. This should not be surprising, because the allowed values of k come closer and closer together. As you should be able to show, in this limit:

$$\sum_{k=k_{min}}^{k_{max}} f(k) = \frac{Na}{2\pi} \int_{k_{min}}^{k_{max}} dk f(k)$$

where k_{min} and k_{max} are the limiting values for the allowed k, in our case $\pm\pi/2a$. If you do the integral, you'll find that:

$$\frac{E_{GS}}{N} = \epsilon - \frac{4}{\pi}t < \epsilon$$

So there is a gain of $4t/\pi$ per atom in cohesion energy, because the valence electrons become delocalized over the whole system (each one can be found anywhere in the system with equal probability). This gain increases if we bring the atoms closer and t becomes larger, so it might suggest that the ions should sit as close as possible to make t as large as possible and therefore the energy as low as possible. However, remember that the full Hamiltonian also includes the repulsion between the clouds of core electrons, which will start increasing fast if we decrease the distance between ions – so in fact there is some equilibrium distance between ions where the total energy is minimized. For other types of lattices (and in higher dimension), the expression of $E(k)$ will be different, and as a result the prefactor multiplying t changes, so different lattices lead to different cohesion energies. The one with lowest energy will be the preferred structure that will be observed in reality.

2.2 Free electrons (jellium model without interactions)

The discussion above was for "tight-binding" models. Let's now see what happens in the opposite limit of free electrons; after that we'll discuss the "nearly-free" electron case. Remember that the jellium model assumes that the ions are "spread out" in a uniform density of positive charge. If we ignore the electron-electron interactions, the resulting Hamiltonian (see previous chapter, but now for 1D system) becomes:

$$\hat{H} = \sum_{k,\sigma} \epsilon_k a^\dagger_{k,\sigma} a_{k,\sigma}$$

where $\epsilon_k = \frac{\hbar^2 k^2}{2m}$ is the free-electron kinetic energy, and the operators are associated with plane-waves with momentum k: $\langle x, \sigma' | a_{k,\sigma}^\dagger | 0 \rangle = \delta_{\sigma,\sigma'} e^{ikx}/\sqrt{L}$, where L is the length of the 1D crystal. Note that these operators are very different from the $c_{k,\sigma}$ we found in the previous section: those created/annihilated electrons in Bloch states that are linear combinations of the $2s$ orbitals, not in these plane-waves! This is why I'll call them a instead of c.

This difference is also clear if we look at the allowed k values in this case. Again we impose PBC, meaning that nothing should change if we translate $x \to x + L$. From the definition above, this obviously is true only if $e^{ikL} = 1 \to k = \frac{2\pi}{L} m, m = 0, \pm 1, \pm 2, \dots$. This looks similar to what we had before (there $L = Na$) except now there is no restriction on the values of m! For the tight-binding chain, the restriction appeared because the values of the plane-waves only mattered at $R_n = na$. However, in this jellium model they matter at each $x \in [0, L]$, so each allowed value gives a different, acceptable solution. Thus any integer m and so any $k = \frac{2\pi}{L} m$ is allowed, in other words there is no restriction to a Brillouin zone like before.

If you think about it, this jellium model is the limiting case of the "nearly-free electrons" limit depicted on the right-hand side of Fig. 1. The limit $a_B \gg a$ is obtained when we let $a \to 0$ – indeed, in this case instead of distinct ions, we see a continuous distribution of positive charge. Having $a \to 0$ also means that the Brillouin zone extends to cover the whole axis since $\pm \frac{\pi}{a} \to \pm \infty$, which is what we just found; and finally, in this limit we find $E(k) = \epsilon - 2t \cos(ka) \to \epsilon - 2t + (ta^2)k^2$. If we define an effective mass m such that $\frac{\hbar^2}{2m} = ta^2$, then up to an unimportant constant, $E(k) \to \epsilon_k$ as well (it is reasonable that ta^2 might stay finite as $a \to 0$, because remember that hopping integrals increase with decreasing distance). So formally the results map onto one another, although the wavefunctions are somewhat more complicated, as we'll see later.

If we have N electrons in this system, in the GS they will again occupy all states up to a k_F, so:

$$|GS\rangle = \prod_{|k| < k_F, \sigma} a_{k,\sigma}^\dagger |0\rangle$$

and

$$E_{GS} = \sum_{|k| < k_F, \sigma} \epsilon_k = 2 \sum_{|k| < k_F} \epsilon_k$$

where the Fermi momentum is such that:

$$N = \sum_{|k| < k_F, \sigma} 1 = 2 \sum_{|k| < k_F} 1$$

Again, in the limit $L \to \infty$, the allowed values of k become dense and we can replace the sums with integrals: $\sum_{k_1}^{k_2} f(k) = \frac{L}{2\pi} \int_{k_1}^{k_2} dk f(k)$. We then find: $N = 2k_F L/\pi \to k_F = \pi n/2$, where $n = N/L$ is the electron density, and we can then go and calculate the GS energy $\frac{E_{GS}}{N} = \frac{\hbar^2 \pi^2 n^2}{24m}$ and any other quantities that we are interested in. Note: I expect you to be able to do similar calculations in higher dimensions. I expect you saw them before in undergraduate-level solid state and also statistical mechanics courses. If they give you any trouble, come and talk to me.

2.3 Free electrons in a periodic potential: band structures

At this point you're probably feeling a bit confused because these two cases look very different from one another, so it's not all that clear what they have in common and how one may go from

one to the other by varying the ratio a_B/a. I think the best way to understand this is to actually solve a problem – we'll do this next for the simplest non-trivial example that I know (still in 1D).

Let's again 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 ions placed at their lattice locations $X_n = na$, where a is the lattice constant and $n = 1, .., N$, and N valence electrons whose behavior we're trying to understand. We will again assume PBC and at the end we will let $N \to \infty$, so that the boundary condition 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. Because there are no electron-electron interactions we can solve the problem for a single electrons, and then make a Slater determinant from the one-electron eigenstates. So 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

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

At this point I expect you remember that such periodic potentials always lead to so-called **Bloch eigenstates**. I could jump directly to using them, but because this is a key point, let me briefly review one way to derive them (if this is not enough to jog your memory, please do some reading!).

Let's try to guess what the solution of this Schrödinger equation must look like:

(i) the solution must have some plane-wave like character, because the symmetry of the problem 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; 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:

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

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 phase-factor 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 single-particle 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 the 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. 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 always the case when we have a model with a 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 $U_a(x) \to 0$. 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 that k if limited to be inside the Brillouin zone. The way this works is illustrated in the next figure. On the left, 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 and don't give anything new. So now we've restricted the momentum, but for each value of k we have many solutions $E_n^{(0)}(k)$, $n = 0, 1, 2, ...$. 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 know as "folding".

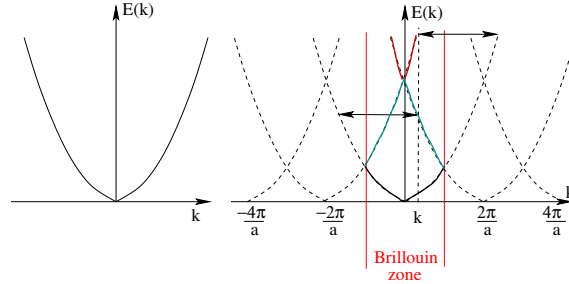Figure 3: Free space eigenstates. Left: the usual parabola for free space, where any k is allowed and we have a single eigenstate for a given k. Right: the corresponding band-structure if we take the vacuum to be a periodic crystal with lattice constant a (and no potential). Now the momenta are restricted 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 2 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

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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: $u_{1,k}(x + a) = e^{-i\frac{2\pi}{a}(x+a)} = e^{-i\frac{2\pi}{a}x}e^{-i2\pi} = u_{1,k}(x)$. 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. It 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 for the specific Hamiltonian of interest.

Let me show you how it works in a simple case – when we have the simplest, δ-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 understand that we need to use the lattice constant a, which is our 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. I expect you have solved this problem in an introductory QM course, and even if not that you can figure it out – but ask for pointers if you need help. Of course, there are eigenstates for all positive energies $E > 0$ (when the electron is not bound to the ion), but those are free states where the electron roams about, not "atomic-like" states where the electron is bound to the nucleus. For this potential, it turns out that there is only one bound state with wavefunction (up to a normalization constant):

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

and energy

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

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

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 varying 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**. For your convenience, these limits are sketched on the next page, again.
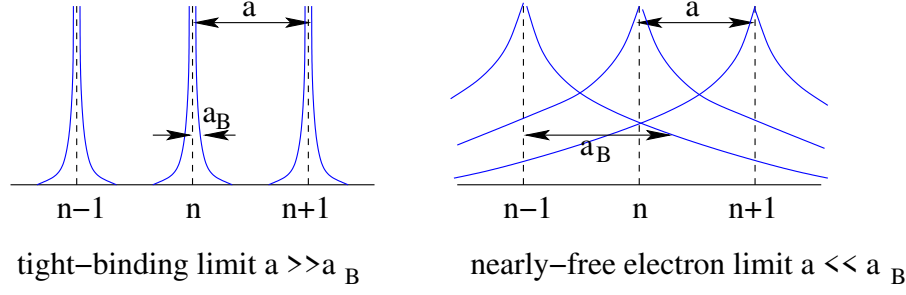
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Figure 4: Left: tight-binding limit, where $a_B \ll a$. Right: nearly free electron limit, where $a_B \gg a$.

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 λ 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 $\phi_k(x) = \alpha e^{\lambda x} + \beta e^{-\lambda x}$. According to Bloch's theorem, the wavefunction in the next unit cell, $a < x + a < 2a$, must be $\phi_k(x + a) = e^{ika}\phi_k(x) = e^{ika}\left(\alpha e^{\lambda x} + \beta e^{-\lambda x}\right)$. All we need to do now, is to "sew" together the wavefunctions at $x = a$, where we have a delta function in the potential. Continuity at $x = a$ implies:

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

while the jump in the derivative because of the δ-function results in:

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

So we have two homogeneous equations for α, β, 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 $\cosh(x) = \frac{1}{2}\left(e^x + e^{-x}\right)$, $\sinh(x) = \frac{1}{2}\left(e^x - e^{-x}\right)$.

So what happens here is that for each value of k (inside the Brillouin zone), this equation will give us one or more solutions $\lambda_n(k), n = 1, 2, ..$ (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 that 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 $f(x) \to \frac{e^x}{2}(1 - \frac{a}{a_B}\frac{1}{x})$, which diverges as $x \to \infty$.
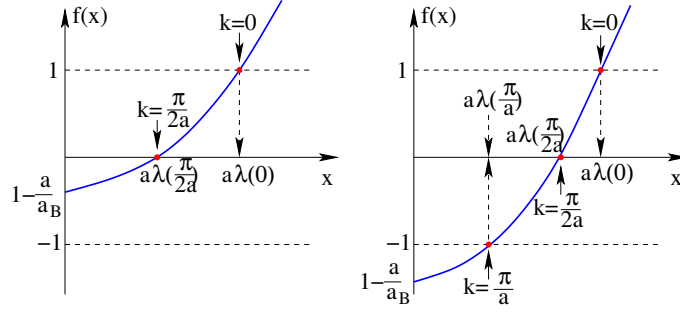

Figure 5: $f(x)$ sketched when (left) $a < 2a_B$, and (right) $a > 2a_B$. The solutions for $f(x) = \cos(ka)$ with $k \in (-\frac{\pi}{a}, \frac{\pi}{a}]$ lie in between between -1,1.

This function is sketched above, for both $a < 2a_B$ and $a > 2a_B$ cases. Let me start with the second case which contains the tight-binding limit $a \gg a_B$. 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 very large and we can use the simpler asymptotic expression, i.e. here:

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

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 (which is a large value, consistent with our asymptotic approximation). 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:

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

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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, 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. Moreover, we also have the correct expression for the hopping t (if you remember how this is defined as the overlap between neighboring orbitals, you can check this statement). The left panel below shows the allowed energy band, i.e. the energy interval where we find solutions in the limit when $N \to \infty$, 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 becomes exponentially small. In the limit $a/a_B \to \infty$ we basically have isolated atoms, each with their allowed level at E_B.
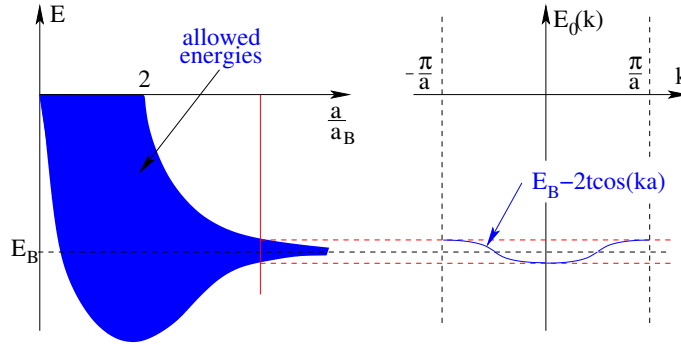

Figure 6: Left: allowed band of energies with $E < 0$, as a function of a/a_B. Right: For a particular value of a/a_B, indicated by the dashed line, I showed the dispersion $E_B(k)$ vs k, in the Brillouin zone.

How about the wavefunctions, do they come out correctly? In the tight-binding limit we obtained the solutions $c_{k,\sigma}^\dagger |0\rangle = \sum_n \frac{e^{ikna}}{\sqrt{N}} c_{n,\sigma}^\dagger |0\rangle$, whose wavefunctions are (ignoring the spin) $\phi_k(x) = \langle x|c_k^\dagger|0\rangle = \sum_{n=0}^{N-1} \frac{e^{ikna}}{\sqrt{N}} \phi_B(x - na)$. Note that these are indeed Bloch states! (as they should be, as, discussed, because the tight-binding model corresponds to a periodic potential.)

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 the $e^{\frac{x-a}{a_B}}$ 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 α, β so that we have the wavefunction. We can use either equation, let's use the simpler one:

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

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

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

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. So our simple tight-binding model gives the correct eigenenergies and eigenfunctions in the correct limit – but only for this band! There are higher energy bands (see below) which are completely missing from the tight-binding model, although the full Hamiltonian has them. If, however, we only need to know where the tight-binding band is, which is the case when we only have electrons enough to partially populate it, and the other bands are way above and never come into play – then the tight-binding model is an excellent approximation, and one that makes life much simpler.

What happens when we decrease a/a_B? 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 $\lambda \to iK$. 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 $g(x) = \cos(ka) \to K = x/a$. 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.
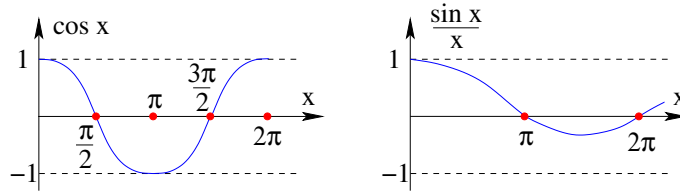

Figure 7: Left: $\cos(x)$ vs x. Right: $\sin(x)/x$ vs x.

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.

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
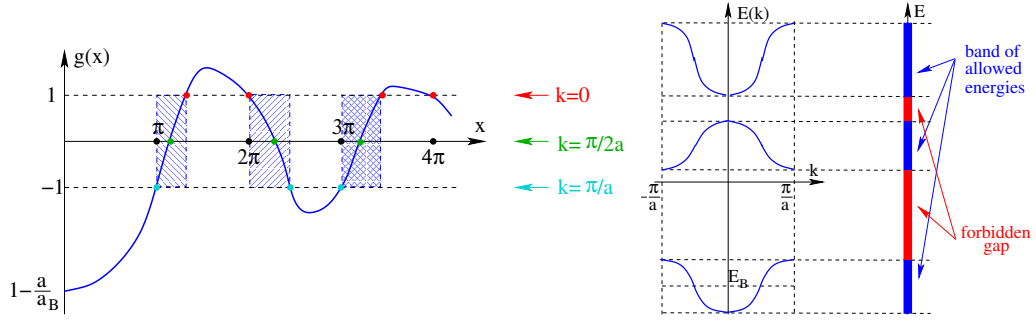
Figure 8: Left: Solution of $g(x) = \cos(ka)$ in the limit $a/a_B \gg 1$. Right: Full spectrum in the limit $a \gg a_B$.

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:
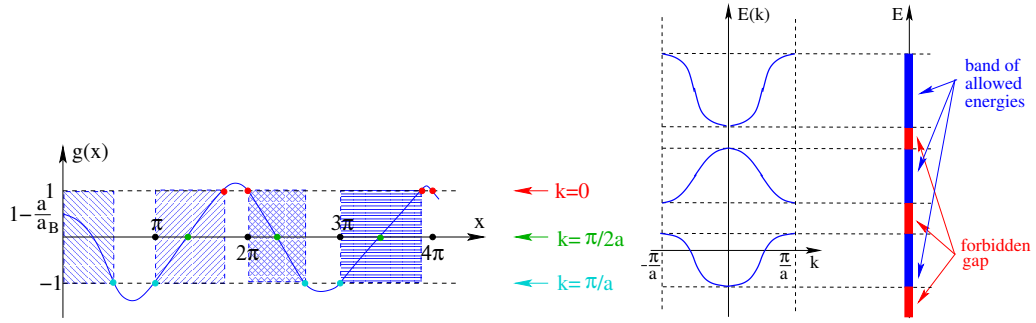

Figure 9: Left: Solution of $g(x) = \cos(ka)$ in the limit $a/a_B \ll 1$. Right: Full spectrum in the limit $a \ll a_B$.

This is starting to look like the free electron spectrum, which it should evolve into when $a/a_B \to 0$ ($a_B \to \infty$ when $U_0 \to 0$, 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. 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 $U_0 \to 0$.

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
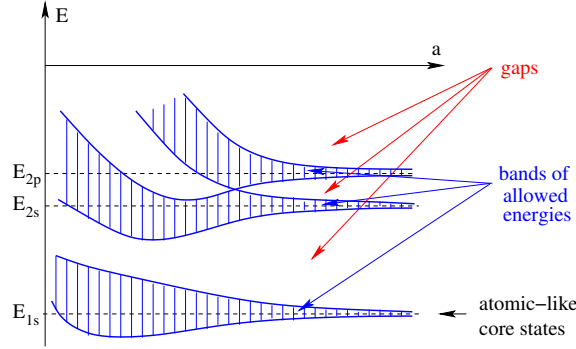
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Figure 10: General evolution of the energy bands in a solid, as the lattice constant is decreased.

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 next.

The precise locations of the allowed energy bands will, of course, depend on what type of crystal we have, and what is the equilibrium value for a, etc etc. But there will certainly be energy bands characterized by a momentum $\vec{k}$ restricted to the first Brillouin zone, 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 $\approx$ 2eV, we call this an insulator; if it is less than $\approx$2eV, we call such a material a semiconductor.

Based on the solution for the tight-binding model, you might expect that any time we have one (or an odd number) of valence electrons per ion we should get a metal. This is not true! To obtain the ground-state with the lower-half of the tight-binding band full, we made the crucial approximation that we can ignore electron-electron interactions. If those interactions cannot be ignored, then the many-electron wavefunction is not a Slater determinant of one-electron states and all these arguments fail. It turns out that for a Hubbard model in 3D, if U is sufficiently large, a gap opens up and splits the occupied states from the empty states, so the system is an insulator (in 1D, this happens for any $U > 0$). We distinguish such insulators from the ones discussed above, which occur even in the absence of interactions. Those are called **band insulators** (and are a bit boring although extremely important for current technologies), whereas the ones that arise because

of electron-electron interactions are called **Mott insulators**. We'll discuss a bit more about these later on.

Before finishing this section, let me 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 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 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 **density functional theory**, also known as **ab-initio methods**. These are based on the Hohenberg-Kohn theorem, which is an amazing result – please take a bit of time to read about this in a standard textbook (for example, Taylor and Heinonen pp. 182-192). These days there are free (and also commercial, of course) software packages to deal with this approach, and some of you may end up using some of these. Even if you don't, you should have a basic understanding of the underlying ideas, which are fairly simple to grasp. Let me just say that a lot of care is needed with the interpretation of these results, 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 approximation for the jellium model, and that is used for any model (the so-called LDA approximation). This works pretty well for systems with weak electron-electron interactions, but not for systems with strong interactions. Various improvements and ways to fix the problem are proposed for the latter problems, but this is still very much work in progress.