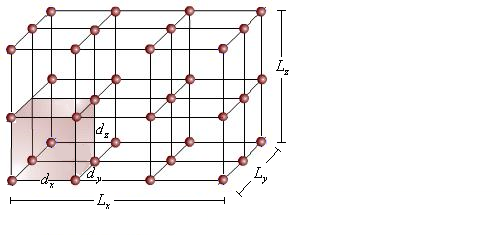
**Crystal Excitations**

**Bloch’s Theorem**

Let’s consider Bloch’s theorem…this is basically a reprisal of the discussion in the QM folder. So consider a typical lattice:



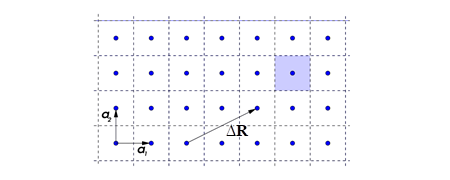
and the Hamiltonian,



Due to the periodic arrangement of the molecules, the crystal clearly possesses a discrete translational symmetry, i.e., it commutes with the translation operator:



where is the momentum operator of course (setting ℏ = 1), and Δ**R** is any displacement going from one lattice site to the next, illustrated below, again, unfortunately in 2D:



And we can say Δ**R** = m1**a**1 + m2**a**2 + m3**a**3, where m1,2,3 are any integers, and the a’s are the primitive lattice basis vectors. So this means that the two operators can be simultaneously diagonalized, which means that the eigenfunctions of our Hcrystal may be written as the eigenfunctions of D(ΔR). What are the eigenfunctions of D(ΔR)? Well let’s figure that out. The eigenvector equation would read,



putting this equation in position space we get:



So we see that the requirements of crystal symmetry are that ψ(**r**) change by some constant number λ every change BLV displacement Δ**R**. So ψ(r) doesn’t necessarily have to be periodic. Can we learn anything more about what λ can be? Let’s put the eigenvector equation in momentum space,



So using the momentum representation, we have found the eigenvalue, λ = e-i**k**·Δ**R** where **k** can be any real vector (since **p** could be any real vector). But this **k** will not end up representing physical momentum, because, thanks to Vcrystal, the eigenstates do not have well-defined momenta. Rather, this **k** will be the crystal momentum. Okay, so now plugging in our eigenvalue, into the eigenvector equation for D, we have:



after a little thought, we can now see that the most general solution to this equation is:



where u(r) is a function periodic over every Δ**R**. This is called Bloch’s theorem. The advantage afforded us by Bloch’s theorem is that we no longer have to solve the Schrodinger equation over the entire volume. Now we can just solve it over one primitive cell, and then Bloch’s theorem tells us what the rest of the wavefunction must look like.

**Restrictions on k**

There are some restrictions on what these **k** can be however. The first is purely formal. **k** cannot range over values which would duplicate the d.o.f. encompassed within u(r). This means **k** can only range over the k-space encompassed by a single reciprocal lattice cell. For instance, consider ψ**k**(r) and ψ**k**+**G**(r), where **G** is a RLV. Then,



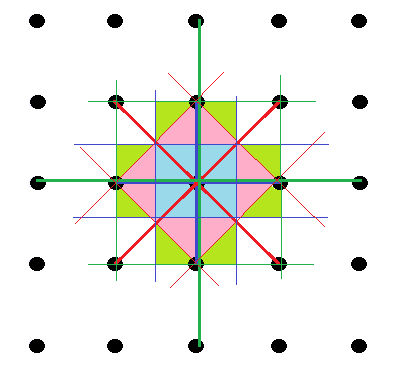
But ei**G**·**r** is itself a function periodic with respect to any displacement vector Δ**R**, since by definition **G**·Δ**R** = 2πp (again, see previous file). So really it is just another u(r). So basically, to uniquely define a wavefunction we must restrict **k** to within the ‘volume’ of a single RLV cell, or in other words, a Brillouin zone (BZ). Recall that for a lattice with RLV’s **b**1, **b**2, **b**3 …,



So a ‘conventional’ choice for the BZ would be (other choices possible, but α’s should span width 1):



But as we discussed in the Interaction file, there is another cell beside the conventional one that is more often employed. It’s the Wigner-Seitz cell. So consider a RL, and we’ll draw blue thick lines to the nearest neighbors in k-space, and red thick lines to the next nearest neighbors, and then green thick lines to the next-next nearest neighbors.



Then draw the Bragg planes (which from our top-down perspective look like skinny lines) which bisect these thick lines. Then the 1st BZ is the set of k-points (blue region) which are closer to the origin than the origin’s nearest neighbors. This is implicitly the characterization we used before. Another way to say it is that it’s the set of points for which the origin is their nearest neighbor. These are also the set of points that don’t require us to cross any Bragg plane to get to. It’s also the Wigner-Seitz cell. The 2nd BZ would be the set of k-points (pink region) for which the origin is their next nearest neighbor. And these would also be the set of points that only require us to cross a single Bragg plane to get too (from the origin). The 3rd BZ would be the set of k-points (green region) for which the origin is their next next nearest neighbor. And these would also be the set of points that only require us to cross two Bragg planes to get to. And so on. Note the volume in k-space of the 1st BZ is the same as that of the 2nd BZ is the same as that of the 3rd BZ, etc. In this way, we might characterize the BZ our k’s must lie in, at least for a rectangular RL, as:



Well this isn’t the only restriction. Turns out the α’s can take on only discrete values. This is because the wavefunction must be periodic over the length of the crystal. u(r), being periodic over any unit cell, is already periodic over the crystal. But the ei**k**·**r** factor is not, automatically. Supposing that over the course of the crystal there are Ni cells in **a**i direction, then we must have, setting **L**i = Ni**a**i (no implicit summation over indices):



Filling in our generic **k**, we have:



Since this equation must hold for any i, we must have, generally:



where again, p is just any integer. Mindfull of the restriction above, that αi lie between - ½ and ½, now we can say p must range between -Ni/2 and Ni/2. Or basically:



For example, a rectangular lattice with side lengths a1,2,3, would have the following **b**’s:



and consequently,



So yeah.

**General features of u(r)**

So u(r) is a function periodic over the unit cell. And it’s equation can be ascertained by filling ψ into the Schrodinger equation:



Doing so we have:



and so we have:



which looks just like the usual Schrodinger equation except that there is an extra linear term – this doesn’t make the equation fundamentally any more difficult to solve. And it obeys periodic boundary conditions in both its value and derivative, so we’d say, for instance,



where **a**i=1,2,3 is any of the primitive basis lattice vectors. There will in general be n = (1, 2, 3, …, ∞) such solutions for a given k. These correspond to the ‘bands’ we’ll run into later. Since u(r) is periodic over the lattice spacing, it can be expressed as a Fourier series.



The G’s are called ‘reciprocal lattice vectors’, again. Note that the equation for un**k**(r) is Hermitian itself. So the un**k**(r), for fixed **k**, and any n, will be orthogonal to each other, and will have their eigenvalues E – k2/2m (which we’re labeling generically with quantum number n). Also, unk only depends on the crystal potential inside the unit cell. It doesn’t matter how many atoms are, or are not, inside that cell (except insofar as it changes Vcrystal).

**Bloch’s Theorem again**

So having taken account of all the discretizing stuff, we can write our wavefunction as:



where all the possibilities that ψ(r) represents are split up into the separate unk(r) and eik·r degrees of freedom. Want to emphasize that u will depend on both the wavevector k, and the ‘band’ n. And of course it is implicit that k is discretized and restricted to the first BZ.

**Example: Hermiticity of u’s Schrodinger equation**

Let’s quickly verify the LHS operator acting on u is Hermitian. So we have:



And want to verify that:



So using IBP, twice on the first term, and once on the second, we can write:



So there.

**Example: Bloch’s theorem applied to free particle in 1D**

Say we have a 1D particle in a crystal of length L, subject to a zero strength potential with period a. What is the Bloch form of the wavefunction?

V(x) = 0 is a periodic potential too, and so Bloch’s theorem ought to apply to the free particle as well. According to Bloch’s theorem, the wavefunction is:



and what is unk(x)? It satisfies,



Of course V(x) = 0, so:



And we can use a simple complex exponential ansatz, u(x) = eiGx,



Now have to impose bounary conditions though,



So our solution is:



It seems that only for the free particle is unk independent of k. Note unk(x) follows the form we said it would, since it is equivalent to (woops forgot to normalize u, whatever):



So all this makes our wavefunction ψ(x) equal to:



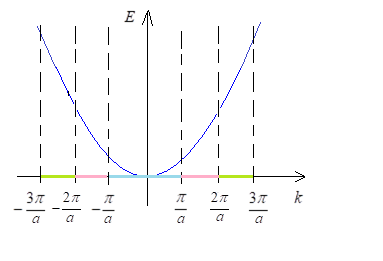
Just to see ψ(x) is right, let’s work on ψ(x) a little more. We’ll note that,



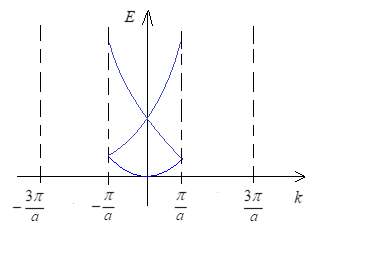
But if you think about it, you’ll see that k+ G0 is all wavevectors periodic over L within the region (-π/a, π/a], and k + G±1 is all wavevectors periodic over L within the region (-2π/a, -π/a] and (π/a, 2π/a], and k + G±2 is all wavevectors periodic over L within region (-3π/a, -2π/a] and (2π/a, 3π/a]. Reasoning similarly, we can see k + Gn for all n covers all wavevectors periodic over L. And so our solution amounts to:



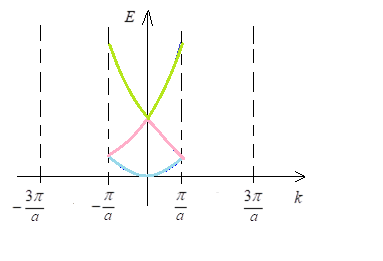
which we will recognize as being the solution for a free particle subject to periodic boundary conditions over the length, L, of the crystal. So the energy spectrum is the familiar free particle spectrum (the k’s are discrete and so curve would be a bunch of dots, not a continuous line, but you know)



(note the reciprocal lattice points are at 2πn/a, n = 0, ±1, ±2, etc.) This plot is called the extended zone scheme. The reduced is when we write it in the usual way, with the bands, by displacing each of the separate curves in the zones by a RLV (2πp/a) sufficient to put the curve inside the Brillouin Zone (BZ) = (-π/a, π/a). For instance, consider the part of the spectrum in the 2nd BZ (the pink regions). We would shift the left part, between (-2π/a, -π/a) rightward by 2π/a, and we’d shift the right part, between (π/a, 3π/a) leftward by 2π/a. And in the 3rd BZ (the green region), we’d shift the left part over to the right by 4π/a, and the right part over to the left by 4π/a. This would give us:



Just to be clear, let me color code the BZ the part of the spectrum the parts of the curve came from.



FWIW, we can represent this spectrum in explicitly band format as:



It’s a bit harder to do this in 2D.

**Example: Bloch’s theorem applied to free particle in 2D**

Say we have a 2D particle in a crystal of size L2, subject to a zero strength potential with period a. What is the Bloch form of the wavefunction? According to Bloch’s theorem, the wavefunction is:



And of course this and the energy would be:

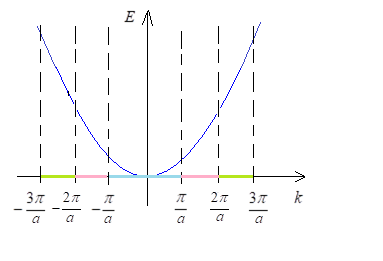


where **n** is some integer vector **n** = n1+ n2. Mathetmatically it seems a little cumbesome to try to write down a formula for each band individually. I guess I’ll just say that for any point k in the 1st BZ, there will be associated with it many different energies, corresponding to each of the bands. We can get these energies by just filling in all of the reciprocal lattice vectors.

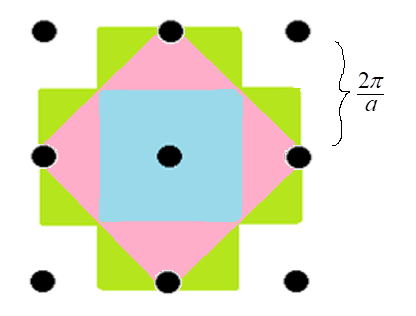


The zeroth (n = 0) band is obtained when n1 = n2 = 0. The first (n = 1) band would be whichever (n1, n2) combination gives the next lowest value of ε(n1,n2)k. The second (n = 2) band would be whichever (n1, n2) combination gives the next lowest value of ε(n1,n2)k after *that*. And so on. The particular (n1, n2) combination associated with the n = 1 band will change depending on what k is. For instance, when k is near the right edge of the 1st BZ, then (n1, n2) will be (-1,0). When k is near the left edge of the 1st BZ, then (n1, n2) will be (1, 0). This would straightforwardly generalize to any kind of lattice structure. But I don’t know a more efficient algorithm to find the nth band energy than to simply find by trial and error the value of (n1, n2) which gives the nth smallest energy for the given value of **k**.

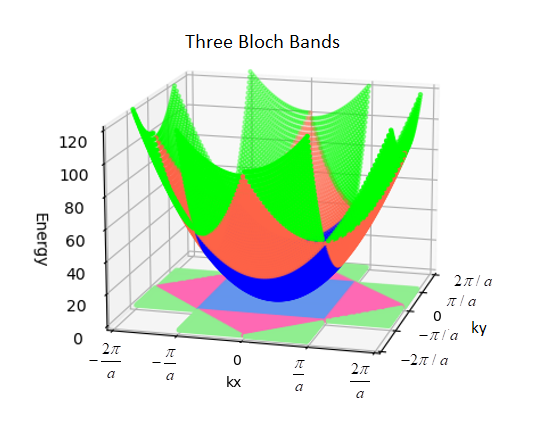
It’s a little harder to visually depict the band structure for a 2D Bravais lattice, but we can easily generalize from our 1D example. We will have our free spectrum,



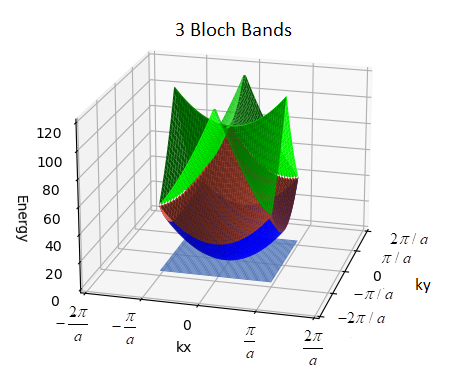
which we can convert to 2D by rotating around the E axis. Now the BZ’s for our 2D cubic lattice would be something like these guys below.



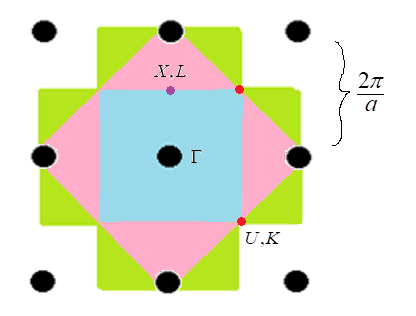
Well here’s a picture of the free particle spectrum within the first three BZ’s.



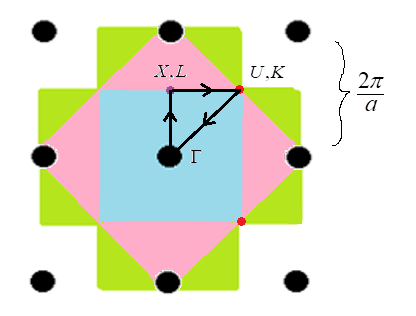
We can translate the parts of the free spectrum that leak out of the 1st BZ (blue region) back into the 1st BZ by doing as we did above. We displace them by the requisite reciprocol lattice vector. So for instance we’d take the part of the spectrum in the 2nd BZ (pink region) and displace the top, left, bottom, right regions by (-2π/a), (2π/a), (2π/a), and (-2π/a). And for the the 3rd BZ, well, figure it out. Then it would look like this (changed plot type a little bit):



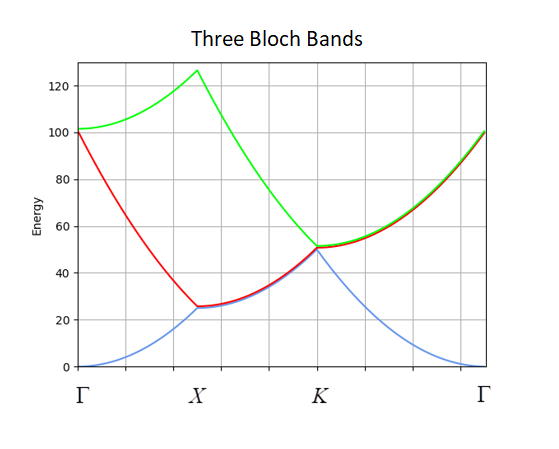
One point of note: we can see that unlike in 1D, where the n+1th band was unambiguously higher in energy than the nth band, that is no longer the case here. We see already that the 1st band is in some parts, specifically near the Bragg planes, lower in energy than the 0th band, for instance. A word on those Greek letter points I see in the energy spectrum diagrams.. Instead of trying to depict a 2D, or 3D energy spectrum, one will often just draw the spectrum along a path in k-space, typically connecting Γ with one of the other points. Γ is the origin. X, L seem to be points in the middle of a single Bragg plane. U, K seem to be points at the middle of the line created by the intersection of two Bragg planes.



For instance, if we plot the band energies from Γ to X to K back to Γ,



We’d get this:



In 3D we can have a place where 3 Bragg planes can intersect. This point is called W. This is illustrated below from a picture I stole for an fcc real space lattice, which corresponds to a bcc momentum space (reciprocal space) lattice, and its following (Wigner-Seitz) unit cell.

Chart, radar chart

Description automatically generated

Seems typical order of path is ΓXWLΓK. Not sure why.