**Crystal Excitations**

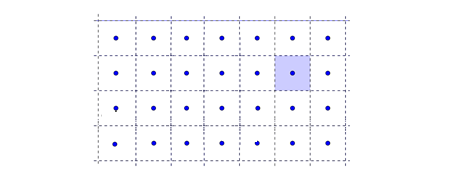
The tight binding approximation works best for tightly bound electrons – usually those in the d and f subshells.

**Tight Binding from Variational Principle (single orbital per site)**

So I guess I’ll start with the most exactest version of the tight binding calculation, where we don’t presume the orbitals on different sites are orthogonal. In this scenario, we are really doing a variational principle calculation (see Quantum Mechanics/Time-Independent/Variational Principle), where we assume the wavefunction is a linear combination of the site orbitals |j>,



And we look to find the coefficients which minimize the energy expectation. Normally the solution is assumed to be of Bloch form, which it kind of must be as we know. And then the wavefunction is normalized, and the minimum energy expectation calculated. But I’m going to do it a little differently. As we saw in the aforementioned file, an equivalent approach is to project the Hamiltonian onto the |j> basis, and solve the matrix equation. This differs from the tight binding calculations we’ve done previously in that we don’t presume this basis is complete or orthonormal. Basically we allow that the wavefunctions have some overlap, and this will introduce a usually small correction to the formula for the energy and eigenfunctions that we missed when we presumed the states were orthogonal.



Okay so let’s say our Hamiltonian is:



Then acting both sides on |ψ>,



then dotting both sides by <m|, but not presuming it’s orthogonal to |n> (and it could be equal to <n|) we have:



I think it’s common to define:



as the contribution to the potential at a given site from all cells surrounding that site. So it would be the crystal potential at that site, minus the site’s own potential, at that site. Note that due to the crystal’s symmetry, ΔVn() should be independent of n. Defining the overlap and potential matrices, we have:



What makes this equation solvable is the feature of Smn and ΔVmn, that they only depend on the displacement between the orbitals. So,



So we can write:



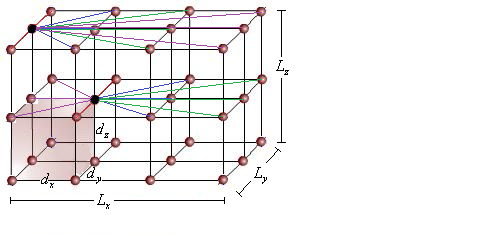
Though the equation may seem formidable, turns out the solutions/eigenfunctions aren’t. They are in fact the discrete analogs to traveling waves.



where **k** is an element of the Brillouin Zone (we need k to be an element of a BZ in order to ensure the coefficients ψ(k)(Rm) have the periodicity of the lattice). If we fill this ansatz into the equation, we get:



where we changed summation variables **R**n → **R**n + **R**m. Now thanks to the periodicity requirement, summing over all possible **R**n is the same as summing over all possible **R**n – **R**m. This means that we can choose our origin to be where we want when summing over all atoms’ positions in the lattice. For instance consider our lattice again, and in particular the two black colored atoms. Let’s just sum over the lattice vectors in their respecitve horizontal planes for instance. Then the same-colored lines constitute the same vectors. In particular, the set of purples is the same thanks to the periodicity of the lattice.



So we can say,



Now define,



and we can write,



So we have:



Let’s flesh out the energy formula a little more. So,



We can write this a little nicerly. Let our origin be at the coordinate Rn, where state |n> is. And let’s call |n+δ> the state that’s at location **R**m – **R**n = **R**δ away from |n>. Then we can say,



and remember δ can be zero. And of course this is independent of our choice of |n>. Now for the potential:



Again let Rδ = Rm – Rn point to the state m = |n + δ>. Then we can say,



So then bringing all the energy terms together, we come to:



I think it’s also common to separate out the δ = 0 term. Then we have:



Again, due to crystal periodicity, this expression will not depend on our choice of location of |n>. Let’s briefly look at the wavefunction. It is,



And this obeys Bloch’s theorem, as can see if we put this in position space,



So there!

**Tight Binding from Variational Principle (multi orbitals per site)**

Would like to generalize to case where each site may have multiple orbitals |jν> which may mix with each other, and those of other sites. We’re considering spin to be just a spectator variable. So now we posit,



And we still say our Hamiltonian is:



Then acting both sides on |ψ>,



Borrowing a definition from above, I’ll write this as:



then dotting both sides by <mμ|, but not presuming it’s orthogonal to |nν> (and it could be equal to <nν|) we have:



Defining the overlap and potential matrices, we have:



Again, these overlaps should be independent of absolute position. So we must have:



And we can write:



The solution to this equation is a little more complicated than it was before. Let’s generalize our ansatz to:



where **k** is an element of the Brillouin Zone (we need k to be an element of a BZ in order to ensure the coefficients ψν(ks)(Rm) have the periodicity of the lattice), and Uνs is a matrix of the same dimensionality as the number of orbitals per site. If we fill this ansatz into the equation, we get:



where we changed summation variables **R**n → **R**n + **R**m. Now thanks to the periodicity requirement, summing over all possible **R**n is the same as summing over all possible **R**n – **R**m. So we can say,



As before, we define,



So we have:



This is clearly an eigenvalue matrix equation for the energies E(s)(**k**). We can write this in matrix form,



where 0 is the matrix with E0ν along its diagaonal (0 elsewhere). And Uνs would be set of s column vectors which diagonalize all that stuff in brackets.



Let’s flesh out the energy formula a little more. So,



We can write this a little nicerly. Let our origin be at the coordinate Rn, where state |n> is. And let’s call |n+δ> the state(s) that’s at location **R**m – **R**n = **R**δ away from |n>. Then we can say,



and remember δ can be zero. And of course this is independent of our choice of |n>. Now for the potential:



Again let Rδ = Rm – Rn point to the state m = |n + δ>. Then we can say,



So then bringing all the energy terms together, we come to:



I think it’s also common to separate out the δ = 0 term. Then we have:



Again, due to crystal periodicity, this expression will not depend on our choice of location of |n>. Let’s briefly look at the wavefunction. It is,



And this obeys Bloch’s theorem, as can see if we put this in position space,



**Tight Binding from Variational Principle (basis?)**

Next question is, what if we had a basis, so that there wasn’t just a single atom in a unit cell? Well our Hamiltonian would still look substantially the same. Now we’d have:



where λ enumerates the p atoms in the basis, and aλ denotes their position within the basis, taking Rj as the origin. Note , Rj, and aλ are all vectors. What about the wavefunction? We could still say something like,



But I guess now ν would enumerate the ‘orbital’ d.o.f. of the molecular Hamiltonian, i.e., the Hamiltonian of the basis. Well we could use the Variational Principle again to get some kind of approximation to these states. For instance, if we had two atoms in the basis, and their eigenstates, irrespective of all other atoms, were |nℓmℓ>1 and |n´ℓ´m´ℓ>2 respectively, with energy levels Enℓm\_ℓ (we’ll presume same atom/same spectrum for simplicity) then maybe to first order we could approximate the combined Hamiltonian’s states as |nℓmℓλ> = |nℓmℓ>1 + λ|nℓmℓ>2, where λ = ± denotes the symmetric and antisymmetric combinations. And our energy spectrum would be something like E(λ)nℓm\_ℓ(k) = Enℓm\_ℓ(k) ± ΔE(12)nℓm\_ℓ(k), where ΔE(12) is some overlap integral 1<nℓmℓ|H|nℓmℓ>2 (see QM/Time-Independent/Variational Principle)Either way, we just get some new set of states |jν>. And the rest would follow as usual, just using the molecular Hamiltonian to define the states, rather than just an atomic Hamiltonian, and using the total number of conduction band electrons of the molecule, rather than the number of either of the individual atoms. For instance, consider GaAs, which I think forms a structure with two atoms per basis. Ga has 3 valence electrons and As has 5 valence electrons. On the left is their band structures if they were alone in the unit cell, and to the right is their structure, within our approximattion, when together.

A diagram of mathematical equations

Description automatically generated

It seems that a qualitatively good picture of the bands can be had by replacing the molecular Hamiltonian with just an averaged atomic Hamiltonian – cause the band structure for two-atoms in a basis guys like Si, looks pretty close to the regular tight-binding approximation for one atom in a basis. Of course this itself looks pretty close to the band structure we get in the nearly free approximation. So this probably just means all of these metals’, semiconductors’ band structures can be depicted qualitatively using the nearly free approximation.