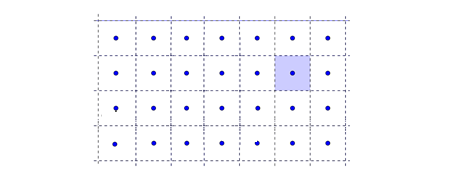
**Crystal Excitations**

**Tight binding model (implicitly in 2nd quantization approach)**

Yeah, let’s look at the tight-binding model, from an implicitly 2nd quantization point of view. Again we assume the crystal potential is a strong periodic potential and almost confines the electrons to their host sites. This model tends to prevail for transition metals with unpaired d-f orbital electrons, like Mn, Cu, Ag, Au, etc. We presume to write the Hamiltonian as:



where Vei(r-Rj) are something like the potentials coming from the positive core of each primitive cell (well I drew the cores at the edges, but if shift the shaded cube over a little bit…).



To make progress, we mentally decompose the sample into a union of the primitive cells (as usual) and then posit a set of orbital basis functions |jν>. These basis functions within each cell would be the basis functions that diagonalize just the cell Hamiltonian,



[where |iν> is the ket corresponding to φν(r-Ri), and energies shouldn’t depend on i since Hcell is the same for each, and ν labels the orbital d.o.f. of the cell eigenfunctions]. Now we’ll recall that if we had separated the cells to infinity, these |iν> would be the basically exact eigenfunctions of the actual Hamiltonian across the cell, i. And the energy levels of the material with these widely separated cells would be just N (# of cells) degenerate copies of εν. But as we bring the cells closer into position, neighboring Hcell,j’s overlap with cell i, etc., making the degenerate energy levels broaden into bands. The outermost (typically highest) ν orbitals will mix/broaden first, and then followed by the inner ones. If mixing is rather weak, then we may expect only mixing between like suborbitals from different sites, but if strong, then different suborbitals will begin to mix, etc. Anyway. We can postulate that the new eigenfunctions will just comprise some linear combination of the old ones. This is the basis for a variational approximation in the previous file. And so far we’ve not assumed anything other than what we had in the previous Variational Principle Tight Binding file. But now we will. So another less good, but usually not too bad assumption, is that the overlap between neighboring cell wavefunctions is so small as to be negligible, and further that the set of orbitals in all cells comprise a complete set, so that the set of all cells’ orbitals comprises an orthornormal basis for the entire sample, at least within the energy subspace we care about (by saying overlap is small, we don’t necessarily mean that one is non-zero only where the other is zero, just that they’re orthogonal). With this in mind, we can project the H onto our tight-binding subspace,



where we also make the usual definition:



And this guy shouldn’t really depend on i, thanks to the crystal’s periodicity. I think we’ll introduce the notation |i´ν´> = |i+δ,ν´>, where δ is telling us where |i´> is relative to |i>. So δ is a vector index, really, just as i and i´ are. So,



Now as we said, ΔVi() shouldn’t depend on i, just δ. So we can say,



[note in that sum δ can be zero too] And, often we’ll assume there are no orbital/spin d.o.f., either, and so we can forget about sums over ν, ν´. We can combine both terms together if want and write:



**Tight binding model reprised (in explicit 2nd quantized notation)**

Now let’s translate all this to 2nd quantized notation. Note that the 2nd quantization technique also assumes that the set of single particle basis functions we’re working with are orthonormal and complete. It is the completeness presumption that makes what we’ll do equivalent to the stuff above, but inequivalent to the tight binding approach in the Variational Principle Tight Binding file. I’ll start all over again, though we could just begin where we left off in the previous section. So we have our H.



And the basis states within each site, |jν>, would satisfy the site/cell Hamiltonian, so that:



where ν labels the orbital dof of the particular site. Spin is just a spectator variable – but see QM/Identical Particles/2nd Quantization-Tight Binding if want to see how spin is involved. We can associate creation and annihilation operators with each orbital. Then we have, for the 2nd quantized H (see QM folder/Identical Particles/2nd Quantization):



where have again defined:



Like we said before, ΔViν;i´ν´ shouldn’t depend on i, but rather the separation betweeen |i> and |i´>, which we’ll parameterize with the parameter δ. We’ll say,



So we can write:



[note δ can be zero too] ΔVδ=0 is the site energy correction from the other potentials, and ΔVδ≠0 is called a hopping term, meaning that the e- can hop from site to site. Note the kinetic energy operator was included in H0, as we saw, so the hopping term doesn’t serve the purpose of ‘including’ KE in the Hamiltonian. The hopping refers to there being Vcrystal(r) overlap between adjacent site’s wavefunctions…and this alters the form of the wavefunction from a localized to delocalized state, and gives the energy band curvature, which gives the electron states a mean velocity (see Crystal Excitations Properties file) whereas before it wouldn’t have had a mean *velocity*. If we want, we can combine both terms, and write:



Okay let’s look at solving this guy. But this time we won’t presume no mixing between orbitals. The standard procedure is to switch to Fourier operators ckν, c†kν:



where **k** spans a BZ, i.e. kx = 2πnx/Lx ∈ (-π/dx, π/dx] and similarly for other guys. The inverse transformation is:



and so,



Then inserting this definition into the equation for H and we have:



Now let’s define,



We’ll recall a similar definition in the previous file. And then we can write:



Now if we presumed the left over crystal potential term, ΔVνν´(**k**) were diagonal in its νν´ indices, we’d be done. Cause then we’d have:



and this form would clearly evince that the energy levels are:



But let’s say ΔVνν´ is not diagonal in its νν´ indices, which would imply that different orbitals are mixing because the crystal potential is strong enough to do so. Then we’ll have:



Now let’s introduce a new set of creation / annihilation operators:



where Uνs is an orthonormal matrix, whose columns are eigenvectors of E0δνν´ + ΔVνν´(**k**), with eigenvalues Es(**k**), so that:



The inverse transformation would be:



So,



Now plug this in,



And so finally we have:



This form evinces that the Es(k) are the energy levels of course. So the energies/eigenvectors are:



where 0 is the matrix with E0ν diagonals, and Δ(**k**) is the matrix with elements ΔVνν´(**k**). We’ll observe this is the same thing we got in the previous file except that here the overlap matrix Smμ;nν = <mμ|nν> has vanished. And this is because we presumed the orbitals formed a complete orthonormal basis. Note s will have the same dimensionality as ν, and there will be s energy bands, each parameterized by k. What are the eigenfunctions? These should be:



where |0> is the vacuum state – no particles. Now let’s put this in terms of our familiar basis that we started out with. First gotta solve for c†ks. So,



And in position space, therefore, we have:



We can put this in Bloch form,



and we can see clearly that uks is periodic.