**Crystal Excitations**

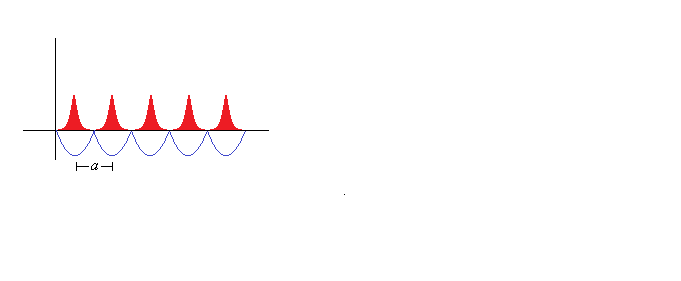
Now we’ll take a look at various tight-binding models. These do a good job of describing the outer bands of transition metals (Group III) like Fe, Mn, and maybe to a lesser extent Cu, Ag, Au. In such metals the outer electrons lie in the d orbitals, which overlap a good amount with neighboring atoms, but not so much as to completely delocalize the electrons in these orbitals, like happens in the Alkali metals (Group I). What follows are a bunch of examples I did at one time, not necessarily directly applying the formulas in the previous two files, but it amounts to the same thing. By the way, in last example, I’m going to kind of presume the orbital index, ν, refers to spatial orbitals, and that spin is a spectator variable [see Quantum Mechanics/Independent Particles/2nd Quantization-Tight Binding for treating spin]. One could consider these examples as being relevant to the case of tight binding as applied to atomic s-orbitals in 1D (first example) and 3D (last example).

**Example: 1D**

Now let’s take it from the other end and consider a perturbative approach based on approximately locallized states, rather than free states. So consider the extreme case of widely separated cells at positions Rn. And say the Hamiltonian of the electron within the cell, excluding influences from all other cells, is:



And say it has a ground state |n> = φn(x) = φ0(r-Rn), and energy E0. The ground state wavefunctions (red) of the wells (blue) will look something like,



So in the limit of widely separated, therefore non-interacting, cells, the ground state of the crystal will be N-fold degenerate corresponding to any of the N linearly independent combinations of φ0(r-Rn) that we can make.

As we bring the cells (potential wells) together these states will mix/overlap and the N fold degenerate energy levels E0 will broaden into a band. We presume these individual ground states will still form an approximate orthonormal basis for the true ground state and N-1 lowest lying excited states. So now our H is (well, it was always this, but, *per* *cell*, we could always neglect the potentials of all the other cells when they were far away; now we can’t since they’re close):



Projecting this onto our approximate basis (recall a better way to do this is with the variational principle – see variational principle in QM folder, but this will still give us good results, and basically match the variational way to within 0th order of the overlap S = <m|n> … which we pretty much always take to be super small anyway….and doing it *this* way matches up with the 2nd quantized tight binding model)



where we define,



which is the potential felt at site n stemming from all the *other* sites. Now dot both sides with <m|,



where,



As we’ve said before, ΔVmn should only depend on the site separation, so it should be a function only of |m-n|. It’s common to presume only nearest neighbors have appreciable interaction, so δ restricted to ±1, well, and also 0. So,



Then we have:



Now typical approach to solving a difference equation is same as for a differential equation. Let’s say ψm = Aeiλm, but must impose periodicity. So that:



(note there are/can be only N distinct solutions because the dimension of our approximate basis is N). So anyway, filling this into our Schrodinger equation,



So our eigenstates, eigenenergies are:



a more fitting way to write this, in accord with the general form we expect from Bloch’s theorem the wavefunction to take, is by defining k = λ/a. Then we have:



And noting that ma = Rm, the position of the mth well, and that Na = L, the length of our 1D crystal, we have:



The wavefunction can be put in Bloch form by projecting |ψk> against <r|, and factoring out eikr. Then we have:



So observe how the previously N-fold degenerate level has been perturbed by the n.n. interaction, into a band. We may imagine the first excited states of the cells behave similarly, and generate their own band above this one. If we were to find that the two bands overlap, we’d probably have to go back and redo the whole thing from the beginning, expanding our basis to include both sets of states. We’ll tackle such a situation in the last example.

**Comparison with Exact Solution of Dirac Comb Model (negative potential bound state)**

So before moving on, let’s take a second to compare this result to the exact result for our 1D Dirac Comb example (solved in previous file). Ostensibly, the tight binding approximation would work very well for it, for the ground state at least, where the individual wavefunctions are tightly bound to the delta potential. Let’s compare. Tight binding says:



where,



And according to the solution to the bound state for the single Dirac delta function potential (see QM folder/Dirac Delta potential) we have these (where V < 0):



So these matrix elements work out to be:



so the Tight Binding approximation to the ground state spectrum of the entire crystal would be:



But denoting Eδ = -(1/2)mV2/ℏ2, and borrowing terminology from the Dirac Comb file: Ed = ℏ2/2md2 (which for us would be ℏ2/2ma2), and E´ = E/Ed, E´δ = Eδ/Ed, and r = -√|E´δ|, we can say:



and so write the energy spectrum equation, upon division of both sides by Ed, as:



Now compare this to what we found in the large separation limit in the Dirac Comb model file:



So they agree, at least out to order er. We didn’t expand our solution in the Dirac Comb model past this point, so whether it would also agree at the e2r level I don’t know. But this term would shrink to zero fast as d (i.e., a) → ∞. Below is a comparison between the exact Dirac Comb result (purple) and the tight binding result (red).

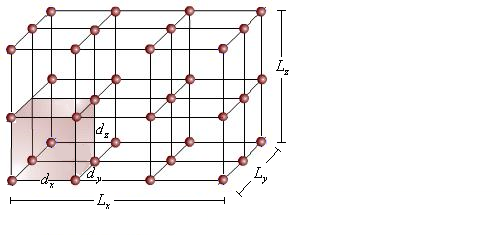
Chart, line chart

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Agreement is pretty good even though r is not large (meaning the separation is not large).

**Example: 3D orbital band structure (1 non-degenerate level mixing)**

Now we’ll upgrade our calculation to 3D. Let’s consider the following lattice.



And recall the tight binding model we derived in the Interactions file, which is basically just a 3D upgrade to the one above (along with including more orbital d.o.f., ν, within the cell). We’ll just start with it.



where |iν> is the set of eigenkets on the ith cell. Obviously i labels the position (Ri) of the cell, and ν the individual basis functions, i.e., eigenfunctions of that single cell’s Hamiltonian. And



(where δ includes zero) Note this shouldn’t depend on i, thanks to periodicity of the potential. Now we can make approximations. Let’s presume that ΔV is diagonal in the orbital indices. So we’re saying that different energy levels do not mix. So,



So then we basically have a 3D copy of the simplified problem we ended up with in previous example.



We can guess the wavefunction, certainly with the previous example as a guide, as being an inverse lattice Fourier transform of the unperturbed basis. So we’ll write:



[this wavefunction is unnormalized if there is overlap between |js>’s, but we presumed there to be none given our S supposition] To evince the Bloch form of the wavefunction, we can write it in position space:



where ν would label the orbital being used. And so the periodic function ukν(r) ought to be:



And we see that ukν(**r**) does depend on k itself in general. So observe that uks(r) is not the sum of all the φν(r-Ri) of each base, but rather the sum of all the φν(r-Ri)eik(r-Ri) of each base. So the only difference is that instead of adding the basis functions together, we add the basis function × a phase factor. Just to check that u has cell periodicity…



Good. So we have:



Alright well let’s find the energy. Plugging this in we have:



where z is the # of cells that appreciably overlap with the given cell. z would increase with # of near cells, width of orbitals, and or width of potential. And so we may infer that:



(the sum includes δ = 0, and all z near neighbors) Let’s use definite values. We’ll say that z only comprises δ = 0 and nearest neighbors. And we’ll say ΔVδν is the same for all nearest neighbors. So,



Could represent pictorally by, say:

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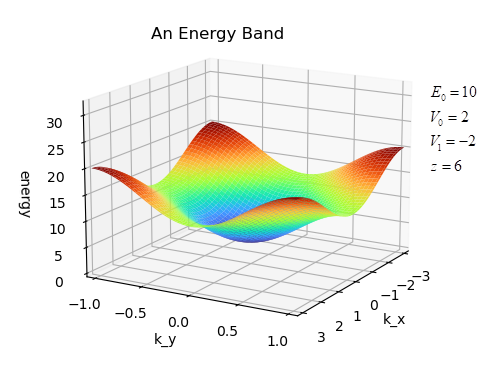
(we only drew circles for ν = 1, but all the other ν = 2, 3, 4, … would have analogous relationships) and this gives us:



which is:



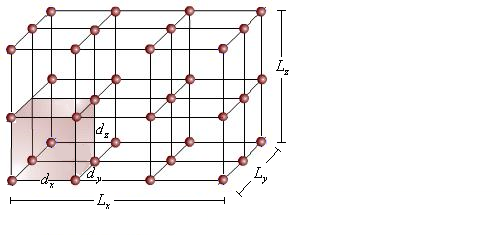
Note each orbital broadens into its own band, according to our presumption that there is no mixing between onsite orbitals. And we’d get something like this below, at least in 2D (getting rid of kz terms),



Might note that that the Fermi surface associated with these bands is spherical (or well, circular) for low filling. But for medium filling, electrons would reside in the yellow parts, which would comprise both the middle, and the edges. Observe that the band width is zΔV1 approximately. If we include more n.n. (increase z), then the width increases, and the likelihood of overlap with other bands increases. We’ll note that in general, when we have more than one level per atom; then when we apply a tight binding model, each of these k distinct levels will broaden into k distinct bands, just like in the Kronig Penny model. And transitions between electronic levels will become transitions between electronic bands. So that is how the periodic lattice affects the single particle energy levels. Also, if the overlap integrals above are very tiny, or if they are non zero for only small δ, then the width of the band will be very small. That is to say, the bandwidth will by tiny in comparison to the average energy of the band. In that case we basically have straight line bands, which is the independent atom electron model again.

**Example: 3D orbital band structure (2 non-degenerate orbitals mixing)**

Let’s do another example within the 2nd quantized formalism (see 2nd quantization file in QM folder, or the previous Tight Binding 2nd quantization file)



Recall we started with:



And broke it down into the 2nd quantized form,



where E0ν is the site energy of the orbital |jν>, and,



Then we solved this model by introducing the Fourier transformed creation/annihilation operators,



to diagonalize the spatial part and come to:



where,



(and δ includes 0). Then made an orbital change of variables to diagonalize the orbital mixing.



and we finally came to:



where,



and 0 is the diagonal matrix with entries E0ν. Okay, so now let’s just jump into an example. We need to get the eigenvectors and eigenvalues of:



(calling E0ν = εν) Now let’s say that now we’re concerned with just two orbitals mixing, so that ν = 1,2. Say these are characterized by states |jν> = φ1,2(r – Rj), and have distinct energies ε1,2 such that ε1 < ε2, but otherwise arbitrary. Let’s say ΔVδνν´ only matters for δ = 0, and δ = (±dx, ±dy, ±dz), i.e. for self and nearest neighbors only. For simplicity, let’s say that ΔVδ=0;νν´ = ΔV0δνν´. Let’s also say that in the latter case, ΔVδνν´ is isotropic in δ, so that it doesn’t therefore depend on the direction of δ. And to make it easy, I’m also going to say diagonal elements are all equal, and off-diagonal elements are all (separately) equal,



Pictorally,

A diagram of a mathematical equation

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(and implicitly (ν = 3, ν = 4) would follow a similar coupling, as well as (ν = 5, ν = 6), etc.) Then we can say (restricting our attention to ν,ν´ ∈ {1,2}),



which we can write as:



where z = number of nearest neighbors = 6. Written out as a matrix, we have:



We don’t need to work the eigenvalues/vectors out exactly. Let’s just use PT, to second order in V0. So recall from QM that:



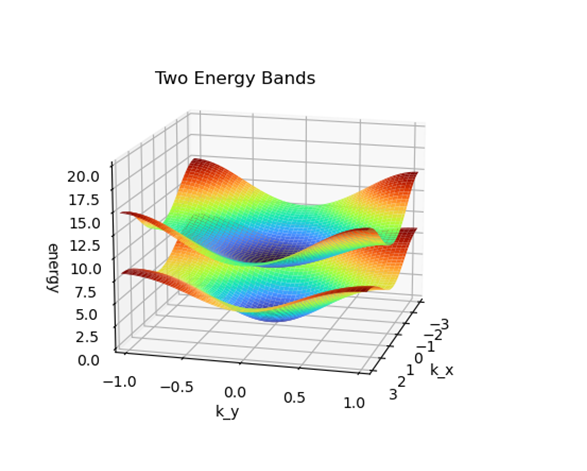
And our unperturbed eigenenergies are ε1,2 and eigenkets are (1 0) and (0 1). So,



And therefore,



where s = 1, 2 are the top, bottom energies in the box. I plotted these below in 2D (getting rid of all the kz terms), for ε1,2 = 5,10, ΔV0 = 0, ΔV1 = -1, ΔV2 = 0.50 (in retrospect, ΔV2 should be negative, but it doesn’t change shape really), z = 6. Also, dx = 1, dy = 3.



Let’s get the eigenstates too. We’ll recall from previous file that:



And recall U is the matrix of eigenvectors of W.



We can work these out perturbatively using (this generic ψ below, not to be confused with ψ above),



So we have:



We need to normalize these too, but they are, up to first order. So U is:



and we have:



where top row refers to ground state band (s = 1, say), and bottom row (s = 2) to the excited band. Anyway, so the energy levels develop into bands, all the same.