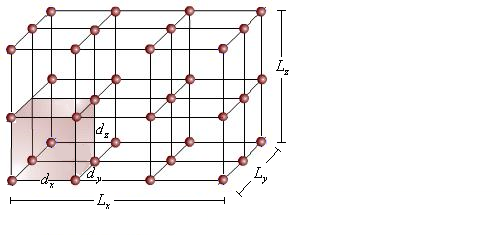
**Crystal Excitations**

In last file we did mixing between two onsite orbitals. Now I’ll upgrade to mixing between three onsite orbitals. And we’ll have in mind the specific application to the three p-orbitals. By the way, I’m going to kind of presume the orbital indicex, ν, refers to spatial orbitals, and that spin is a spectator variable [see Quantum Mechanics/Independent Particles/2nd Quantization-Tight Binding for treating spin].

**Example: 3D band structure (3 degenerate orbitals mixing)**

So in the previous example, we just did mixing between two generic degenerate orbitals. But the example wasn’t very realistic per se´. In metals, the group 1,2 elements have just a single orbital (though electron can be spin up/down), and unless there is a spin-orbit interaction, these two electron states within the orbital shouldn’t mix. But the group 13-17 guys have three p orbitals, and there could be realistic mixing between those bands. So let’s do that. We’ll presume the orbitals are degenerate to start with. We’ll also specialize to a cubic lattice: dx = dy = dz = d.



Recall we start with:



And break it down into the 2nd quantized form,



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



Then we solve 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 we’ll go back to:



which we have to diagonalize to get the energies. Recall from Quantum Mechanics/Time-Independent/H atom file that we found the the hydrogen atom wavefunctions to be:



And also from Quantum Mechanics/Time-Independent/L eigenfunctions file that we found the ℓ = 1 spherical harmonics to be:

Chart, bubble chart

Description automatically generated

So our orbitals will be (we’ll choose n = 2, Z = 1 for simplicity), and ignore spin d.o.f.:



And I’ll also note that rcosθ = z, rsinθcosφ = x, and rsinθsinφ = y,



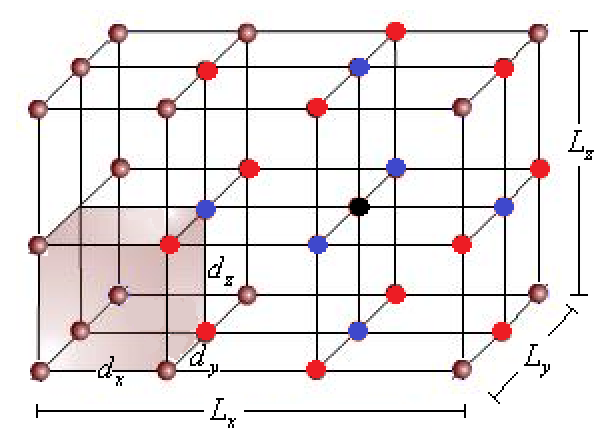
Note these orbitals are all degenerate. And so any linear combination of them is degenerate as well. There is a favored linear combination though, that makes the ensuing overlap integrals easier to intuit. So we’ll add the mℓ = 1, -1 guys together (and divide by -√2), and then subtract the mℓ = 1, -1, guys from each other (and divide by i√2). And then also rename them φν, in accordance with our terminology.



And then on each site, the orbitals will be:



where **R**m = Xm + Ym + Zm. Now we need to know the overlap integrals. We’ll do it for nearest neighbors (blue guys) and next nearest neighbors (red guys).



The overlap integrals for the same site (black) orbitals themselves is given by:



For the nearest neighbors, the integrals depends on the relative orientations of the neighboring orbitals. If they are both parallel to **δ**, then this is σ-bonding, and we get ΔV1 > 0 (should be positive, roughly, because potential is negative, but overlap of orbitals is negative too, because in region where overlap is greatest, they have opposite sign – see below). And if they are both perpendicular to **δ**, then that’s π-binding, and we get ΔV2 < 0 (should be negative, roughly, because potential is negative, but overlap of orbitals is positive too, because where the orbitals mostly overlap they have same sign – see below). But if the oribitals themselves are not aligned with each other, then that gives 0. Illustrative orientations and bonds are given below (φx is illustrated below: red is positive values, and blue negative values),

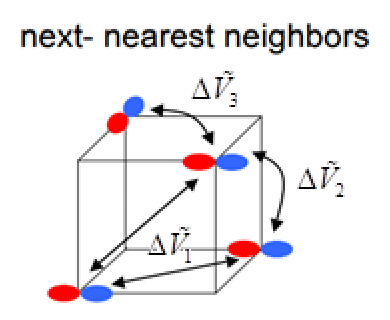
Diagram

Description automatically generated

We find:



Apropos next nearest neighbors, we have a somewhat similar situation. If the orbitals are parallel and in the plane of **δ**, then we get Δ1 > 0 (should be positive for same reason ΔV1 was positive). If the orbitals are not parallel to each other, but are still both in the plane of **δ**, then we get Δ3(the sign of this quantity is positive whenever the orbital overlap is mostly negative – i.e. a positive end next to a negative end – and is negative whenever the orbital overlap is mostly positive; we can factor out the appropriate sign and write Δ3 → Δ3sgn(±d)sgn(±d), where the latter Δ3 is taken positive). And this is the only case where we have coupling between *different* orbitals. And last, if they are parallel and perpendicular to **δ**, then that’s Δ2 < 0 (should be negative for same reason ΔV2 was negative). For example (pictures stolen from Solid State Theory, by Manfred Sigkrist).



We find,



Pictorally, very roughly, looks something like,

A diagram of a mathematical equation

Description automatically generated with medium confidence

So level mixing is diagonal, basically, for nearest neighbors, but completely general-ish for next nearest neighbors. Levels 4,5,6 would be similarly connected. Well, restricting our attention to levels 1,2,3. So,



Altogether, this looks like,



Going to use perturbation theory to get these eigenvalues/vectors. What should I consider the perturbation? I guess I’ll say that Δ1,2,3, i.e., a next nearest neighbor coupling, is a perturbation. Then the unperturbed eigenvectors are just |ψ> = (1 0 0), (0 1 0), (0 0 1). And the unperturbed eigenvalues are:



So then the perturbed eigenvalues are:



And V is:



I don’t really want to work that out per se´. Well, the energies, perturbatively, are:



and,



and finally,



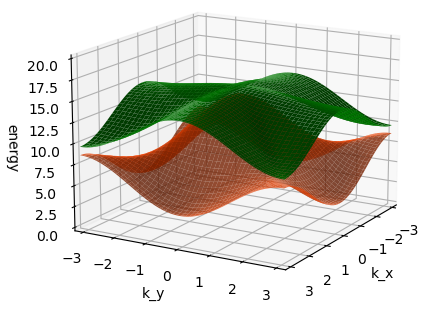
Can’t really plot these in 3D. So going to drop down to 2D. I feel like E3 wouldn’t really show up in 2D. So I’m going to just plot the first two bands, E1,2. I’m doing it in separate graphs, because Python doesn’t do graph overlap very well. Using the following values, ε0 = 10, ΔV0 = 0, ΔV1 = 2, ΔV2 = -0.5, Δ1 = 0.4, Δ3 = 0.3.

Chart, surface chart

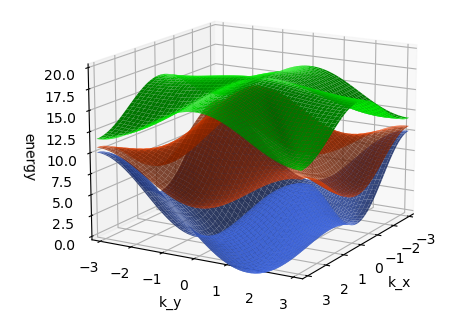
Description automatically generated Chart, surface chart

Description automatically generated

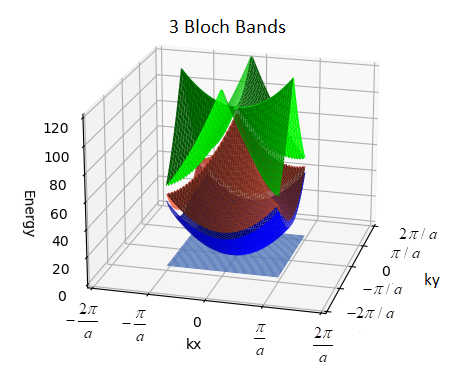
Well here’s them together, without the colormap.



I’ll combine these with the s-orbital plot (never mind the energy scale, and don’t know why the plot looks off-center from the origin – Python has some issues) from the previous file.



These bear a passing resemblance to the analogous bands of the nearly free model, in 2D, reproduced below. Same general features, just softer, and better near the band edges too.



Let’s take a quick look at the eigenvectors. 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:



and,



and finally,



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 next row (s = 2) to excited band above it, and final row (s = 3) to the last excited band.