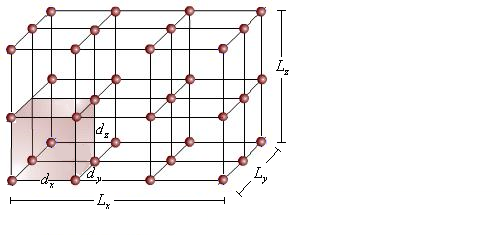
**Crystal Excitations**

Guess we can look at a few approximate techniques. This by no means runs the gamut. But for our purposes, we don’t really need to get the best estimates for the energies and wavefunctions – just understand the general features. 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]. And I’m doing a kind of artificial example where we have 2 orbitals on site. So this doesn’t really compare to anything physical, such as s (1 orbital) mixing or p (3 orbitals) mixing.

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

Let’s do another 3D example. This time I’ll explore what happens when we have onsite mixing between two degenerate orbitals. This kind of thing can happen in the p, d, f bands, although obviously these guys comprise more than just two orbitals, but rather 3, 5, 7.



Again we’ll do it within the 2nd quantization 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:





Again, we’ll say that we’re concerned with just two orbitals mixing, so that ν = 1,2. Say these are characterized by states |jν> = φ1,2(r – Rj). But now we’ll presume degenerate energies ε1 = ε2 = ε0. Otherwise the same. 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, it looks like this (the ν = 1,2 orbitals are mixing because they share the same energy; same with the ν = 3,4 orbitals):

A diagram of a mathematical equation

Description automatically generated

(and similar situation would prevail for orbitals ν = 3,4) Then we can say (restricting our attention to ν,ν´ ∈ {1,2}),



which we can write as:



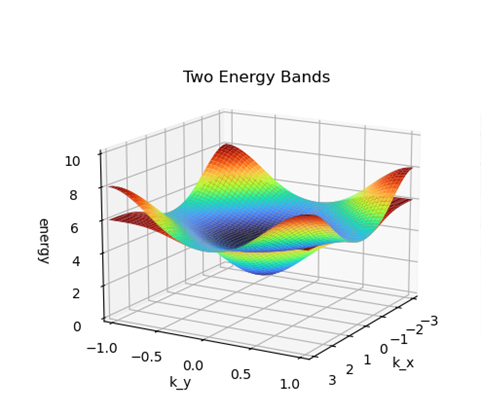
where z = number of nearest neighbors = 6. Written out as a matrix, we have:



Have to use degenerate perturbation theory to get these eigenvalues/vectors. Well, this amounts to just finding the eigenvalues/vectors. The eigenvalues are clearly,



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 ε0 = 5, ΔV0 = 0, ΔV1 = -0.5, ΔV2 = 0.25 (in retrospect, ΔV2 should be negative, but doesn’t change the shape really), z = 6. Also, dx = 1, dy = 3.



Basically the same shape as before, except that the wiggles are modulated by the energy difference of the unperturbed states, roughly. So wiggle amplitude is larger for the degenerate case than for the non-degenerate case. And we can see that the bands overlap except near the edges. We’ll also find this to be the case when we look at (but don’t calculate) the bands of d-orbitals; some of them tend to overlap near the center of the band, but diverge approaching the edges. And our eigenvectors are (first corresponds to top eigenvalue, second to bottom):



And therefore,



And so we have:



where top row refers to ground state band (s = 1, say), and bottom row (s = 2) to the excited band.