I. ELECTRONS IN A LATTICE

A. Degenerate perturbation theory

To carry out a degenerate perturbation theory calculation we need to concentrate only on the part of the Hilbert space that is spanned by the degenerate states. Let's look at p near $k/2$. Then $|p\rangle$ and $|p-k\rangle$ have similar energy eigenvalues. In fact, let's just write

$$p = k/2 + \delta \tag{1}$$

Let's write the hamiltonian just as it pertains to these two states:

$$H_{eff} = \begin{pmatrix} \frac{(k/2+\delta)^2}{2m} & V_0 \\ V_0 & \frac{(-k/2+\delta)^2}{2m} \end{pmatrix} \approx \begin{pmatrix} \frac{(k/2)^2+k\delta}{2m} & V_0 \\ V_0 & \frac{(k/2)^2-k\delta)}{2m} \end{pmatrix} \tag{2}$$

We can write this in terms of Pauli matrices and the identity:

$$H_{eff} \approx \mathbf{1}\frac{k^2}{8m} + \sigma^z \frac{k\delta}{2m} + V_0\sigma^x \tag{3}$$

And the energy eigenstates are:

$$E_\pm = \frac{(k/2)^2}{2m} \pm \sqrt{((k\delta)^2/4m)^2 + V_0^2} \tag{4}$$

And amazingly, when $\delta = 0$ there is a gap - V_0 between the two possible states. The way to think about it is that we had a degeneracy which we can see by moving the right moving dispersion by a k to the left, and then there is this crossing. It gets resolved via this analysis.

What about other places in the band? Actually, these degeneracies are going to plague us in every point in the dispersion that is related to another point with the same energy by some momentum which is an integer multiple of a reciprocal lattice vector $n\vec{k}$:

$$\frac{p^2}{2m} = \frac{(p+n\vec{k})^2}{2m} \tag{5}$$

will give momenta that exhibit a gap. You may wonder why this is true given that hte hamiltonian (**??**) doesn't have terms that connect these momenta directly for $|n| > 1$.

The first order answer is that the potential will always have components at haigher momenta, since no potential is a simple harmonic. For instance, one can consider a square potential well that repeats. If we want to know the periodic part of the potnetial we need a Fourier series:

$$V(x) = \sum_n -V_0\Theta(|x-n|-d) \tag{6}$$

with $d < 1/2$ and $\Theta(x)$ the Heaviside function. We would like to write it in terms of harmonic functions -sum of reciprocal lattice vectors. No problem. That is really just a Fourier series:

$$V(x) = \sum_n e^{i2\pi xn} V_n \tag{7}$$

with

$$V_n = \int_{-0.5,0.5} dx e^{-i2\pi xn} V(x) \tag{8}$$

In our case, this reduces to:

$$V_n = \int_{-0.5,0.5} dx e^{-i2\pi xn} V(x) = \frac{e^{2\pi ind} - e^{-2\pi ind}}{2\pi in} = \frac{\sin(2\pi nd)}{2\pi n} \tag{9}$$

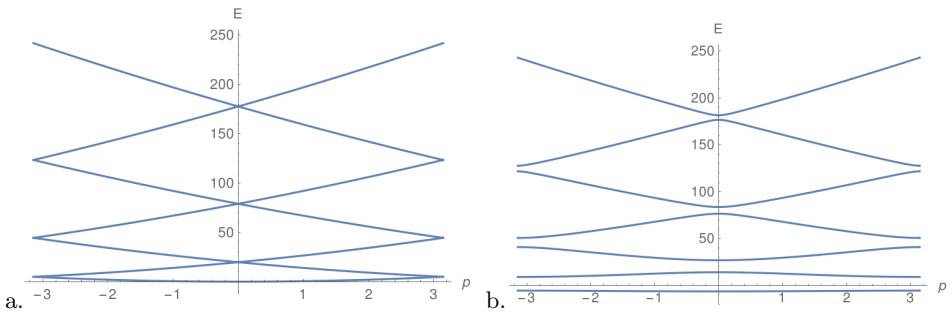

FIG. 1. A 1d band structure in the folded zone representation with $a = 1$ lattice constant. (a) No periodic structure. (b) A periodic structure with harmonics falling of as $1/n$ with n the harmonic.

So clearly every resonating vector can participate.

The second order answer is that even when there is no direct term connecting the momenta, higher order terms in perturbation theory will emerge to give this connection. For instance, In second order perturbation theory, we expect terms that follow the effective hamiltonian:

$$H_{eff} = H_0 + \hat{V}\frac{1}{E_0 - \hat{H}_0}\hat{V}. \tag{10}$$

This alows for instance for a term such as:

$$H_{eff}\left|p\right\rangle = \frac{p^2}{2m}\left|p\right\rangle + \frac{V_0^2}{p^2/2m - (p-k)^2/2m}\left|p-2k\right\rangle. \tag{11}$$

This leads to suppressed gaps, but nontheless opens a gap to the second Brillouin Zone.

B. Effective mass

If we look a the bottom of the second band, it looks like a quadratic dispersion. W ecan even expan the square root

$$E_{\pm} = \frac{(k/2)^2 + \delta^2}{2m} \pm \sqrt{((k\delta)^2/4m^2) + V_0^2} \approx \frac{k^2}{8m} + V_0^2 + \frac{\delta^2}{2(4m^2V_0/k^2)} \tag{12}$$

The expression underneath δ^2 is the effective mass. The effective curvature of the bottom of the band. Or the top of the valence band for that matter. For the conduction band we have:

$$\frac{1}{m^e_{eff}} = \frac{1}{m} + \frac{k^2}{4m^2V_0}. \tag{13}$$

The top of the valence band can accomodate holes, and they too will have an effective mass. The value will be given with the minus choice for the square root:

$$\frac{1}{m^e_{eff}} = \frac{1}{m} - \frac{k^2}{4m^2V_0}. \tag{14}$$

C. Brillouin zones

Now the meaning of the BZ's becomes clear. The 1st Brillouin zone is where a gap opens due to single reciprocal lattice vectors. But then there is a second BZ - which is out the first BZ, but contained within the lines where a gap opens due to a second order scattering by the lattice potential. And so forth.

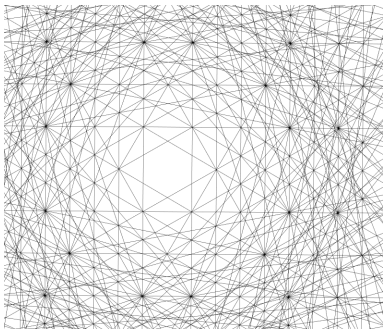

FIG. 2. The Brillouin zone boundaries of a triangular lattice.

D. 1d example rehashed in the spirit of Bloch theorem

We could have done something a bit different. We could have just took the ansatz that Bloch theorem gives us, and plugged it into the Schroedinger equation. This results in:

$$Ee^{ipx}\sum_n e^{iknx}\psi_n = \sum_n \left(\frac{(p+nk)^2}{2m} + V(x)\right) e^{ipx}\sum_n e^{iknx}\psi_n \tag{15}$$

With $V(x)$ expanded in Fourier series $V(x) = \sum_n e^{ikxn}V_n$, we then get the following

$$Ee^{ipx}\sum_n e^{iknx}\psi_n = \sum_n \left(\frac{(p+nk)^2}{2m} + \sum_m e^{ikxm}V_m\right) e^{ipx}\sum_n e^{iknx}\psi_n \tag{16}$$

But identifying the same terms on the two sides of the equation, we find a simple matrix relation:

$$E\psi_n = \frac{(p+nk)^2}{2m} + \sum_m V_m\psi_{n-m}. \tag{17}$$

This is just an effective hamiltonian, $E\psi_n = \sum_m H_{nm}\psi_m$, with:

$$H_{nm} = \frac{(p+nk)^2}{2m_e}\delta_{nm} + V_{n-m} \tag{18}$$

Where I added an e subscript to the mass. Not to get confused with the matrix index!

E. 2d example

Let's do an example in 2d - maybe even the most complicated bravais lattice - the triangular one. The reciprocal lattice vectors of the triangular lattice are $\vec{k}_1 = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right)$ and $\vec{k}_2 = \frac{4\pi}{\sqrt{3}a}\hat{y}$. This sugests that the first gaps will open at:

$$\vec{p} = \pm\frac{1}{2}\vec{k}_i + \lambda\vec{a}_j \tag{19}$$

with $j \neq i$. This gives this parallelogram. But wait! This doesn't look like it has the symmetry of the lattice. It should have some symmetry for rotation by $2\pi/3$. But that is not the case. What are we missing? We can also use $-\vec{k}_1 - \vec{k}_2$ to open gaps. And indeed, in a triangular lattice, there will be Fourier components corresponding to this combination, due to symmetry. This makes the gaps appear at a momentum hexagon, as we suspected the symmetry should be. These are the borders of the first Brillouin zone.

But gaps will open at higher momenta as well. Fig. 2 gives the boundaries of the triangular lattice Brillouin zones.

F. Tight binding apprximation.

To be completely honest, it is rare that we use the weak scattering limit. We much rather think in terms of atomic orbitals, or similar states that are localized at hte site of the atoms, which combine to give us a band. Consider, for instance, the set of wave functions:

$$\psi_n(\vec{r}) = \psi(\vec{r} - \sum_\alpha n_\alpha \vec{a}_\alpha) \tag{20}$$

with α being lattice directions, and $\psi(\vec{r})$ describing an orbital localized on an atom. In the spirit of Bloch theorem, we can try to write a plane wave out of such an orbital. For the sake of simplicity, let's stick in 1d.

$$|k\rangle = \psi_k(x) = \sum_n e^{ikna}\psi(x - na) \tag{21}$$

What's the problem with these plane waves? Mostly, that they are not really good plane waves! On the one hand, they do have the bloch form:

$$\psi_k(x + a) = \sum_n e^{ikna}\psi(x + a - na) = \sum_n e^{ik(n+1)a}\psi(x - na) = e^{ika}\psi_k(x) \tag{22}$$

On the other hand, they are not orthogonal at different k!

$$\langle k' | \, k\rangle = \sum_{n,m} e^{i(mk-nk')a} \int dx \psi(x - ma)\psi^*(x - na) = \sum_{n,m} e^{i(mk-nk')a} M_{nm} \tag{23}$$

unless $M_{nm} = \delta_{nm}$ this is not proportional to $\delta(k - k')$. And M_{nm} is the overlap matrix:

$$M_{nm} = \int dx \psi(x - ma)\psi^*(x - na) \tag{24}$$

It is a positive definite matrix. Which suggests how we can proceed. Let's find a superposition of the $\psi(x-na)$ which are orthogonal:

$$\phi_n(x) = \sum_m \alpha_{nm}\psi(x - na) \tag{25}$$

Then:

$$\int dx \phi^*_m(x)\phi_n(x) = \sum_{k,\ell} \alpha^*_{nk}\alpha_{m\ell} \int dx \psi(x - \ell a)\psi^*(x - ka) = \alpha_{m\ell}M_{\ell k}\alpha^*_{nk} = \alpha M \alpha^\dagger \tag{26}$$

But with M hermitian, we can assume that α irs also hermitian, and get:

$$\alpha = M^{-1/2} \tag{27}$$

If we do this we get:

$$|k\rangle = \psi_k(x) = \sum_n e^{ikna}\phi_n(x) = \sum_n e^{ikna}(M^{-1/2})_{nm}\psi(x - ma) \tag{28}$$

Plug it into the hamiltonian, and we also get the result from the problem set, which is:

$$\epsilon_k \approx \sum_{nm} e^{ik(m-n)a}(M^{-1/2})_{nk}H_{k\ell}M^{-1/2}_{\ell m} \tag{29}$$

The functions $\phi_m(x)$ are called the Wannier functions. They are actually orthonormal, and take the form of local orbitals centered about the m'th atom. This is the essence of Eq. 26.

G. Lattice Symmetries

Crystals are clearly highly symmetric objects. The way that Bravais lattices distinguish themselves from each other is by symmetry groups of the lattice.

A square lattice, for instance, could be rotated by $\pi/2 = 2\pi/4$. If the lattice is symmetric by roatations by $2\pi/n$, then we say it possesses C_n symmetry. C_n is the symmetry group which is generated by application of rotations by $2\pi/n$. It has n elements therefore, and is Abelian. The rotations must be about a particular point. Therefore these kind of symmetries are called 'point-group symmetries'.

What other symmetries could we expect? How about mirror? We can have reflections about particular axes. For a square lattice we have reflections by an axis that is at angle $\nu\pi/4$ with $\nu = 0, 1, 2, 3$ to the x axis. This is the reflection group R_4.

Usually, these groups combine to give us the Dehidral group, D_n which has both reflections and rotations.

There is another important point group - inversion. $\vec{r} \to -\vec{r}$. Indeed, this is contained within the reflection group. Sometime, however, inversion may be present, but not the individual mirror reflections that give rise to it.