# I. ELECTRONS IN A LATTICE

Ultimately we want to think about electrons on a lattice of atoms. This gives rise to one most important aspect of solid state systems: band structures. Let's see in various ways how these come about.

## A. Periodic potentials in 1d

Electrons in a lattice move through a periodic array of atoms. A periodic lattice can have a hamiltonian:

$$\hat{\mathcal{H}} = \frac{\vec{p}^2}{2m} + V(\vec{r}) \tag{1}$$

with $V(\vec{r})$ periodic. So there exist lattice unit vectors, which form the crystal basis: $\hat{a}_i$ with $i = 1, \ldots, d$ such that:

$$V(\vec{r}) = V(\vec{r} + \vec{a}_i). \tag{2}$$

How would we construct a potential like that? It is a periodic function, so might as well do a FT. Or at least try to write it in terms of harmonics. Let's start simple. 1d. If $V(x) = v(x + a)$, then we can definitely write:

$$V(x) = \sum_n V_n e^{iknx} \tag{3}$$

with $k = 2\pi/a$. For instance, $V(x) = V_1 \cos(kx)$ has the write form.

## B. 1d example: Weak periodic potential

Let's start with a 1d system where electrons can move through a simple and weak periodic potential:

$$\hat{\mathcal{H}} = \frac{p^2}{2m} + 2V_0 \cos \frac{2\pi x}{a}. \tag{4}$$

The potential minimia are a crude approximation for the attractive potential that atoms apply to electrons. Typically, the potential will take more harmonics to have an honest description. Let's bear that in mind, and push on the simple potential.

How do we start on this problem? Let's just do perturbation theory. Start with:

$$|p\rangle = \frac{1}{\sqrt{L}} e^{ipx} \tag{5}$$

with $L$ being the size of the system. We break the hamiltonian to the pieces:

$$H = H_0 + V \tag{6}$$

with $H_0 = p^2/2m$ and $V = 2V_0 \cos \frac{2\pi x}{a} = V_0(e^{ikx} + e^{-ikx})$ with $k = 2\pi/a$.

If we ignore $V$, then $|p\rangle$ are the eigenstates. If we include $V$, we have a first order correction for the wave function:

$$|\tilde{p}\rangle = |p\rangle + \frac{1}{E_0 - \hat{H}_0} \hat{V} |p\rangle = |p\rangle - \frac{2V_0}{\Delta E_+} \left|p + \frac{2\pi}{a}\right\rangle - \frac{2V_0}{\Delta E_-} \left|p - \frac{2\pi}{a}\right\rangle \tag{7}$$

with $\Delta E_\pm = \frac{(p \pm \frac{2\pi}{a})^2 - p^2}{2m}$. If we write these as a wave function, we can write:

$$\psi_p \approx \frac{1}{\sqrt{L}} e^{ipx} \left(1 - \frac{V_0}{\Delta E_+} e^{ikx} - \frac{V_0}{\Delta E_-} e^{-ikx}\right) \tag{8}$$

Similarly, there is an energy shift:

$$\tilde{E} = E_0 + \langle p| \hat{V} \frac{1}{E_0 - \hat{H}_0} V |p\rangle \tag{9}$$

which in our case is:

$$\tilde{E} = \frac{p^2}{2m} - \frac{V_0^2}{\Delta E_+} - \frac{V_0^2}{\Delta E_-}. \tag{10}$$

Looks simple enough. What can go wrong? Degeneracies. This works okay as long as $\Delta E_\pm$ obey:

$$|\Delta E_\pm| \ll |V_0|. \tag{11}$$

Clearly this is not always the case... In particular, looking at $p = \pm k/2$ we see that $\Delta E_\mp \to 0$. What do we do then? In that case, we need to rely on degenerate perturnation 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

$$p = k/2 + \delta \tag{12}$$

[DRAW on diagram] Let's write the hamiltonian just as it pertains to these two states:

$$H_{eff} = \begin{pmatrix} \frac{(k/2+\delta)^2}{2m} & V_0 \\ V_0 & \frac{(-k/2+\delta)^2}{2m} \end{pmatrix} \approx \begin{pmatrix} \frac{(k/2)^2+k\delta}{2m} & V_0 \\ V_0 & \frac{(k/2)^2-k\delta)}{2m} \end{pmatrix} \tag{13}$$

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

$$H_{eff} \approx \mathbf{1}\frac{k^2}{8m} + \sigma^z \frac{k\delta}{2m} + V_0 \sigma^x \tag{14}$$

And the eigenenergies are:

$$E_\pm = \frac{(k/2)^2}{2m} \pm \sqrt{(k\delta/2m)^2 + V_0^2} \tag{15}$$

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.

Some terminology. The wave vector $k$ is called the recirocal lattice vector. Multiplied by the lattice constant it gives $2\pi$. The region between the two momenta where the first gap occurs is called the Brillouin zone. In 1d it is simply $-\frac{k}{2} < p < \frac{k}{2}$.

### C.   Bloch Theorem in 1d

We can already see that wave functions can not be classified based on momentum when a periodic potential is present, since momentum is not a good quantum number. There is no translational invariance! According to Bloch, though, ther is something close: Crystal momentum. The statement of Bloch theorem is that the wave functions in the lattice have the form:

$$\psi(x) = e^{ipx} \cdot u_p(x) \tag{16}$$

where $u_p(r)$ is a periodic spatial function with the same periodicity as the underlying lattice. The momentum $p$ is called the 'crystal momentum', and it only makes sense to define it upto reciprocal lattice vectors - $-k/2 < p < k/2$. Why? Because we can expand the whole thing in terms of reciprocal harmonics:

$$u_p(x) = \sum_n u_p(n) e^{inkx} \tag{17}$$

The different coefficients $u_p(n)$ encode the wave function in terms of the different momentum components that are connected to $p$ by adding an integer number of reciprocal lattice vectors.

Therefore, generically, there will be several bands present. Indeed, if we start with a free electron, its momentum can be anything. The periodic potential distorts its $p^2/2m$ dispersion to introduce band gaps. By shifting the high-energy bands by integer times the reciprocal momentum $k$, we can shift all those bands to the first Brillouin zone.

But the price we pay is that for each $-k/2 < p < k/2$ crystal momentum there are several energy eigenstates - one from each band. This is refered to as the 'folded band' picture, and in it, the eigenstates become:

$$\psi_p^m(x) = e^{ipx} \cdot u_p^m(x) \tag{18}$$

with $m$ being the band index, and $|p| < k/2$.

Note that Eq. (8) is consistent with the Bloch theorem expression, and so is the degenerate perturbation theory expansion of it.

### D. Effective mass

Let's go back to the results of our degenerate perturbation theory. If we look a the bottom of the second band, about $p \sim k/2$, it looks like a quadratic dispersion. We can even expand the square root

$$E_\pm = \frac{(k/2)^2 + \delta^2}{2m} \pm \sqrt{((k\delta)^2/4m^2) + V_0^2} \approx \frac{k^2}{8m} + V_0^2 + \frac{\delta^2}{2(4m^2 V_0/k^2)} \tag{19}$$

The expression underneath $\delta^2$ 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:

$$\frac{1}{m_{eff}^e} = \frac{1}{m} + \frac{k^2}{4m^2 V_0}. \tag{20}$$

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:

$$\frac{1}{m_{eff}^e} = \frac{1}{m} - \frac{k^2}{4m^2 V_0}. \tag{21}$$

### E. Higher-order gaps

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 $n\vec{k}$:

$$\frac{p^2}{2m} = \frac{(p + n\vec{k})^2}{2m} \tag{22}$$

will give momenta that exhibit a gap. You may wonder why this is true given that hte hamiltonian (4) 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:

$$V(x) = \sum_n -V_0 \Theta(d - |x - n|) \tag{23}$$

with $d < 1/2$ and $\Theta(x)$ the Heaviside function $\Theta(|x|) = 1$, $\Theta(-|x|) = 0$. 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:

$$V(x) = \sum_n e^{i2\pi x n} V_n \tag{24}$$

with

$$V_n = \int\limits_{-0.5}^{0.5} dx e^{-i2\pi x n} V(x) \tag{25}$$
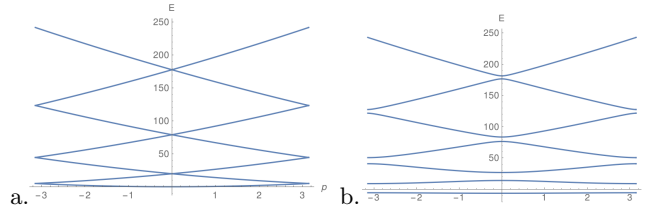
FIG. 1. A 1d band structure in the folded zone representation with $a = 1$ lattice constant. (a) No periodic structure. (b) A periodic structure with harmonics falling of as $1/n$ with $n$ the harmonic.

In our case, this reduces to:

$$V_n = \int_{-0.5}^{0.5} dx e^{-i2\pi x n} V(x) = -V_0 \left( \frac{e^{2\pi ind} - e^{-2\pi ind}}{2\pi in} \right) = -V_0 \frac{\sin(2\pi nd)}{\pi n} \qquad (26)$$

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:

$$H_{eff} = H_0 + \hat{V} \frac{1}{E_0 - \hat{H}_0} \hat{V}. \qquad (27)$$

This alows for instance for a term such as:

$$H_{eff} |p\rangle = \frac{p^2}{2m} |p\rangle + \frac{V_0^2}{p^2/2m - (p-k)^2/2m} |p - 2k\rangle + \dots. \qquad (28)$$

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

## F.   Brillouin zones

Now the meaning of the BZ's becomes more palpable. 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.

## G.   Lattice vectors and reciprocal lattice in more than 1d

How about 2d? Let's say $\hat{a}_1 = \hat{x}$ and $\hat{a}_2 = \frac{\sqrt{3}}{2}\hat{y}$... you think that's it? Forget it! $+\frac{1}{2}\hat{x}$. It is a unit vector! How do we write it in terms of harmonics? definitely we can write:

$$V(\vec{r}) = \sum_{\vec{n}} V_{\vec{n}} e^{i\vec{k_1} \cdot \vec{r} n_1 + i\vec{k_2} \cdot \vec{r} n_2} \qquad (29)$$

What $\vec{k}$'s should we have? Let's satisfy the condition of periodicity. For once:

$$V(\vec{r} + \vec{a}_i) = \sum_{\vec{n}} V_{\vec{n}} e^{i(n_1 \vec{k_1} + n_2 \vec{k_2} \cdot (\vec{r} + \vec{a}_i))} = \sum_{\vec{n}} V_{\vec{n}} e^{i(n_1 \vec{k_1} + n_2 \vec{k_2} \cdot \vec{r})} \qquad (30)$$

Which implies:

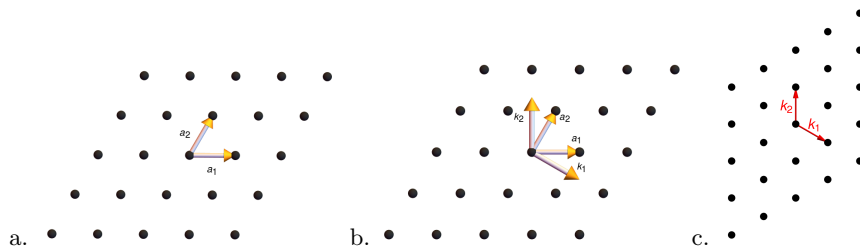$$\vec{k}_i \cdot \vec{a}_j = 2\pi \ell_{ij} \qquad (31)$$

FIG. 2. (a) The lattice base vectors of a triangular lattice. (b) Same as (a) with the reciprocal lattice vectors (divided by $2\pi$ to fit in the figure) included. Note that $k_i$ are perpendicular to lattice planes. (c) The reciprocal lattice. These are the momenta that participate in the Bloch wave function, multiplying the crystal momentum.

with some integers $\ell_{ij}$. There are many solutions. But let me advertize one simple one:

$$\vec{k}_i \cdot \vec{a}_j = 2\pi \delta_{ij} \tag{32}$$

How do we construct these? Mostly, we want $\vec{k}_1 \cdot \vec{a}_2 = 0$, and numbers reversed. We need vectors that only have projections on one basis vector. So it needs to be normal to all others.

With our example, in 2d, we can just play a trick:

$$\vec{k}_i = 2\pi N_i \hat{z} \times \vec{a}_{3-i} \tag{33}$$

so

$$\vec{k}_2 = 2\pi N \hat{y} \tag{34}$$

which then implies $N = \frac{2}{\sqrt{3}}$, and, likewise:

$$\vec{k}_1 = 2\pi \left( \frac{\sqrt{3}}{2} \hat{x} - \frac{1}{2} \hat{y} \right) \cdot \frac{2}{\sqrt{3}} \tag{35}$$

These momenta are the 'reciprocal lattice vectors'. You can see that they are just the rotated lattice vectors - by 90 degrees. Now that we have them, we can construct a potentil with these lattice constants. The trivial way would be:

$$V_1(x,y) = V_0(\cos(\vec{k}_1 \cdot \vec{r}) + \cos(\vec{k}_2 \cdot \vec{r})) \tag{36}$$

Check out the figure - looks like a triangular lattice! We could even make it nicer by adding the vector that completes the triangle:

$$V_2(x,y) = V_0(\cos(\vec{k}_1 \cdot \vec{r}) + \cos(\vec{k}_2 \cdot \vec{r}) + \cos((\vec{k}_1 + \vec{k}_2) \cdot \vec{r})) \tag{37}$$

Looks better! For a comparison see Fig. 3.

In 3d there is even more of a suggestive way of getting the reciprocal vectors. Cross products anyone?

## H. Bloch theorem

Now we can also extend the Bloch prescription for solutions of the periodic potential hamiltonian to higher dimensions. Once again, we write the wave function in terms of a non-periodic phase times a periodic function:

$$\psi(\vec{r}) = e^{i\vec{p}\cdot\vec{r}} \cdot u_{\vec{p}}(\vec{r}) \tag{38}$$

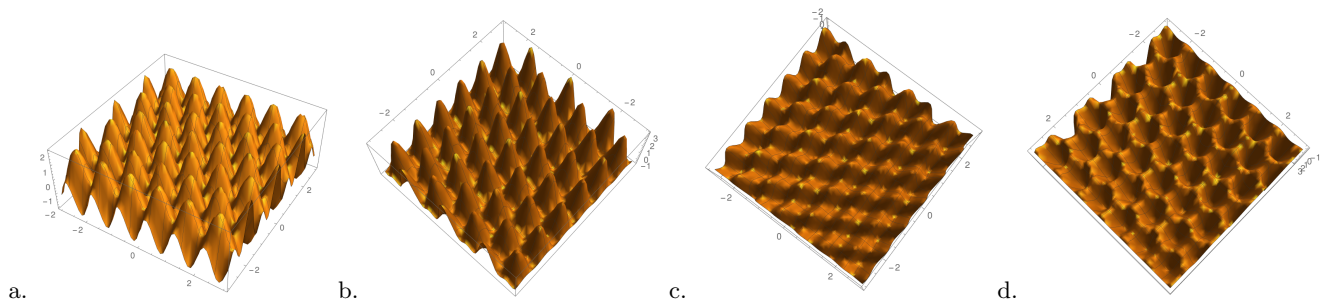a.        b.        c.        d.

FIG. 3. Potentials (a) $V_1$ and (b) $V_2$ from above. Differences between the two potentials are more apparent when we look from below.

where, again, $u_{\vec{p}}(\vec{r})$ is a periodic spatial function with the same periodicity as the underlying lattice. $\vec{p}$ is the 'crystal momentum', and the expansion in terms of reciprocal harmonics takes the form:

$$u_{\vec{p}}(\vec{r}) = \sum_{n,m,\ell} u_{\vec{p}}(n,m,\ell)e^{i(n\vec{k}_1 + m\vec{k}_2 + \ell\vec{k}_3)\cdot\vec{r}} \tag{39}$$

so that shifiting $\vec{p}$ with a reciprocal lattice vector $\vec{k}_i$ will only relabel the Fourier components of $u_{\vec{p}}$.

BTW, $n$, $m$, $\ell$ are the Miller indices, and they mark crystal planes. So you can use them to describe lattice termination.

## I.    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:

$$Ee^{ipx}\sum_n e^{iknx}\psi_n = \sum_n \left(\frac{(p+nk)^2}{2m} + V(x)\right)e^{ipx}\sum_n e^{iknx}\psi_n \tag{40}$$

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

$$Ee^{ipx}\sum_n e^{iknx}\psi_n = \sum_n \left(\frac{(p+nk)^2}{2m} + \sum_m e^{ikxm}V_m\right)e^{ipx}\sum_n e^{iknx}\psi_n \tag{41}$$

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

$$E\psi_n = \frac{(p+nk)^2}{2m} + \sum_m V_m\psi_{n-m}. \tag{42}$$

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

$$H_{nm} = \frac{(p+nk)^2}{2m_e}\delta_{nm} + V_{n-m} \tag{43}$$

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

## J.    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:

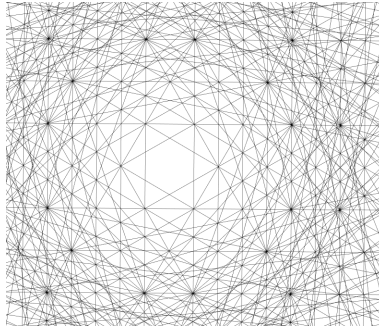$$\vec{p} = \pm\frac{1}{2}\vec{k}_i + \lambda\vec{a}_j \tag{44}$$

FIG. 4. The Brillouin zone boundaries of a triangular lattice.

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. 4 gives the boundaries of the triangular lattice Brillouin zones.