# Lecture II : Fundamental concepts in solid state

I. PERIODICITY AND CRYSTALS

A *crystal* is a periodic repetition of a set of nuclei in space. It is completely specified by the positions of the nuclei, known as the *basis* in one repeat unit and the translation vectors.

$$\text{Crystal structure} = \text{Bravais lattice} + \text{basis}$$

where the term *Bravais lattice* refers to the lattice generated by the periodic repetition of a single nuclear position.
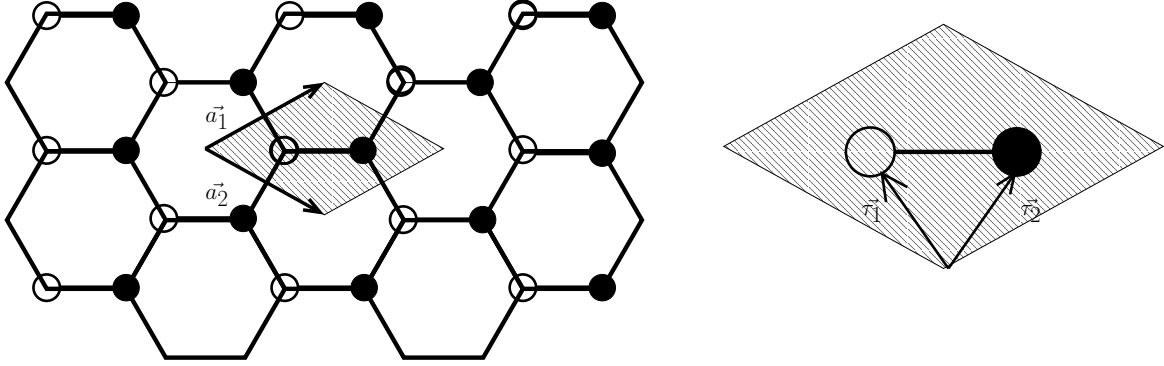
In the figure above, we see a lattice of black and white atoms. These could be B and N atoms respectively for a BN-sheet. Using one of the equivalent unit cells (hashed area) and combinations of the unit vectors, $\vec{a}_1$ and $\vec{a}_2$, we can generate the entire lattice.

A general translational vector in a periodic lattice can be written as the sum of integer multiples of unit vectors,

$$\vec{T}(\vec{n}) = \vec{T}(n_1, n_2, n_3) = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \tag{1}$$

where the three unit vectors $\vec{a}_i$ need not be orthonormal. In fact, in the figure above, we see that the two unit vectors spanning the space are not orthonormal.

The lattice vectors do not say anything about how many atoms there are in the unit cell and where they are located. This information is given by the *basis vectors*, which are denoted by $\vec{\tau}_1$ and $\vec{\tau}_2$ in the above picture. While there are at most three lattice vectors for each unit cell, each unit may contain an arbitrary number of atoms in its basis.

II. RECIPROCAL SPACE

Solids are obviously finite materials with bounding surfaces. However, for practical purposes, we treat them as infinite systems satisfying specific boundary conditions[1], which impose periodicity in all three dimensions,

$$\Psi(\vec{r}) = \Psi(\vec{r} + N_1\vec{a}_1) = \Psi(\vec{r} + N_2\vec{a}_2) = \Psi(\vec{r} + N_3\vec{a}_3) \tag{2}$$

where N_i are the numbers of unit cells in each of the three directions along the lattice vectors. Such boundary conditions are referred to as *Born-von Karman* boundary conditions.

The long-range periodicity described above is not the only kind of periodicity we have in a crystal. The crystal has another symmetry on a much shorter scale, namely the lattice vectors. Any function defined for a crystal, such as the electron density, is bound to be periodic, repeating itself with the same translation vectors as those that span the lattice. Thus,

$$f(\vec{r} + \vec{T}(n_1, n_2, n_3)) = f(\vec{r}). \tag{3}$$

where $\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ is a translation vector.

Such periodic functions lend themselves easily to Fourier transform. Under certain conditions, it becomes more advantageous to deal with the Fourier components of such systems rather dealing with them in real space. The forward Fourier transform is conventionally defined as

$$f(\vec{q}) = \frac{1}{\Omega_{\text{crystal}}} \int_{\Omega_{\text{crystal}}} d\vec{r} f(\vec{r}) \exp(i\vec{q} \cdot \vec{r}). \tag{4}$$

where Ω_{crystal} is the volume of the crystal. The Born-von Karman conditions set constraints on the allowed wavevectors, $\vec{q}$, which we may use while determining the Fourier components. This may easily be seen by adding a translation vector, $N_i \vec{a}_i$ to $\vec{r}$ in Eq. 2 and making use of Eq. 4,

$$f(\vec{q}) = \frac{1}{\Omega_{\text{crystal}}} \int_{\Omega_{\text{crystal}}} d\vec{r} f(\vec{r} + N_1\vec{a}_1) \exp(i\vec{q} \cdot (\vec{r} + N_1\vec{a}_1)) = \frac{\exp(i\vec{q} \cdot (N_1\vec{a}_1))}{\Omega_{\text{crystal}}} \int_{\Omega_{\text{crystal}}} d\vec{r} f(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) \tag{5}$$

Comparing Eq. 4 and Eq. 5, we see that $\exp(i\vec{q} \cdot (N_1\vec{a}_1)) = 1$. The same argument may be applied to the directions of the other two lattice vectors, yielding the following restriction on the wavevectors $\vec{q}$.

$$\vec{q} \cdot \vec{a}_i = \frac{2\pi n_i}{N_i} \quad \text{where} \quad n_i = 0, 1, 2, \cdots, N_i - 1 \tag{6}$$

We thus have the familiar situation that periodicity causes the wavevectors to be quantized. Next, we make use of the periodicity on the scale of the lattice constants. For a function f having this sort of periodicity, Eq. 4 may be written as

$$f(\vec{q}) = \frac{1}{\Omega_{\text{crystal}}} \sum_{n_1, n_2, n_3} \int_{\Omega_{\text{cell}}} d\vec{r} f(\vec{r} + \vec{T}(n_1, n_2, n_3)) \exp[i\vec{q} \cdot (\vec{r} + \vec{T}(n_1, n_2, n_3))]$$

$$= \frac{1}{N_{\text{cell}}} \sum_{n_1, n_2, n_3} \exp\left[i\vec{q} \cdot \vec{T}(n_1, n_2, n_3)\right] \frac{1}{\Omega_{\text{cell}}} \int d\vec{r} f(\vec{r}) \exp(i\vec{q} \cdot \vec{r})$$

$$= \frac{1}{N_{\text{cell}}} \prod_i \sum_{n_i} \exp[i\vec{q} \cdot (n_i\vec{a}_i)] \frac{1}{\Omega_{\text{cell}}} \int d\vec{r} f(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) \tag{7}$$

where we make use of the fact that the integral over the volume of the crystal can be broken down into integrals of identical crystals. Consider one of the sums over $\{n_i\}$:

$$\sum_{n_i=0}^{N_i-1} \left(e^{i\vec{q} \cdot \vec{a}_i}\right)^{n_i} = \frac{1 - e^{2\pi \frac{integer}{N_i} N_i}}{1 - e^{2\pi i \frac{integer}{N_i}}} \tag{8}$$

by Eq. 2 and the use of a geometric series. Eq. 8 gives zero unless

$$e^{\vec{q} \cdot \vec{a}_i} = 1 \Rightarrow \vec{q} \cdot \vec{a}_i = 2\pi m \tag{9}$$

where m is an integer. Thus, periodicity at this small scale implies a new selection rule for the allowed wavevectors, $\vec{q}$. The space spanned by the allowed, discrete set of $\{\vec{q}\}$ that satisfy Eq. 9 is called the *reciprocal lattice*. They are referred to as a lattice because just like lattice vectors, they define a regular array of atoms with a well-defined periodicity. Any point in the reciprocal lattice can be expressed in terms of a set of minimal set of $\vec{q}$'s which are defined by

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}. \tag{10}$$

An arbitrary point on the lattice is then given by

$$\vec{G}(m_1, m_2, m_3) = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 = \sum_j m_j \vec{b}_j. \tag{11}$$

which satisfies

$$\vec{G} \cdot \vec{a}_i = 2\pi m_i \tag{12}$$

One way to satisfy Eq. 10 is to construct $\vec{b}_i$'s such that they obey

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)} \tag{13}$$

The term on the denominator is numerically equal to the volume of the unit cell in real space. Rewriting Eq. 4 for valid $\{\vec{G}\}$ as defined in Eq. 11 yields

$$f(\vec{G}) = \frac{1}{N_{cell}} \underbrace{\prod_i \sum_{n_i}}_{N_1 \times N_2 \times N_3} \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} d\vec{r} f(\vec{r}) e^{i\vec{G}\cdot\vec{r}}$$

$$= \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} d\vec{r} f(\vec{r}) e^{i\vec{G}\cdot\vec{r}}. \tag{14}$$

A. An example : Face-centered cubic lattice and its Brilliouin zone

A *face-centered cubic* (fcc) lattice is one where the atoms are located on tha corners of a cube as well as on the face diagonals. The primitive unit cell is tus given by the following lattice vectors :

$$\vec{a}_1 = a(\frac{1}{2}, \frac{1}{2}, 0)$$
$$\vec{a}_2 = a(\frac{1}{2}, 0, \frac{1}{2}) \tag{15}$$
$$\vec{a}_3 = a(0, \frac{1}{2}, \frac{1}{2})$$

Using the definition in Eq. 13, we find that the reciprocal lattice vectors are

$$\vec{b}_1 = \frac{2\pi}{a}(1, 1, -1)$$
$$\vec{b}_2 = \frac{2\pi}{a}(1. -1, 1) \tag{16}$$
$$\vec{b}_3 = \frac{2\pi}{a}(-1, 1, 1)$$

Note that the reciprocal vectors that belong to the fcc lattice define a *body-centered cubic* (bcc) lattice in the reciprocal space.

B. The Brilliouin Zone

From Eq. 14, one easily sees that there is a certain periodicity also in the reciprocal space, that is

$$f(\vec{G} + m_i\vec{b}_i) = f(\vec{G}). \tag{17}$$

Thus it makes sense to define a *unit cell* also in reciprocal space beyond which f repeats itselsd. Such a unit cell is already widely used in literature and it is called the *Brillioun zone*. The *Brilliouin zone* is defined by the area surrounded by the planes that are perpendicular bisectors of the vectors from the origin to the reciprocal lattice points.
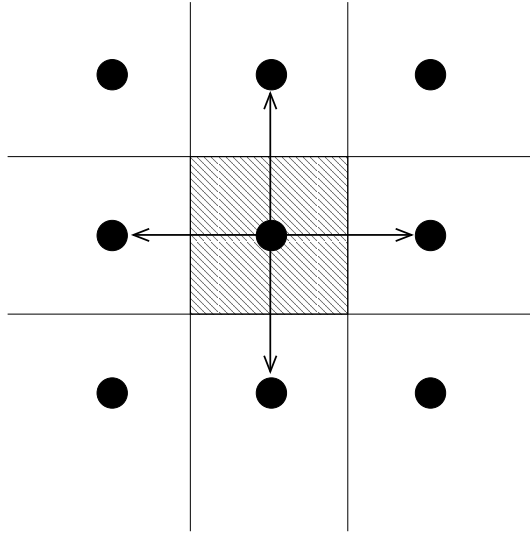
C. Bloch's theorem

In a single-electron picture, the Hamiltonian is invariant under lattice translations. Thus the Hamiltonian commutes with the translation operator

$$[\hat{H}, \hat{T}_{\vec{n}}] = 0 \quad \text{where} \quad \hat{T} = \vec{n}_1\vec{a}_1 + \vec{n}_2\vec{a}_2 + \vec{n}_3\vec{a}_3. \tag{18}$$

From elementary quantum mechanics, e remember that operators that commute share a common set of eigenfunctions. Such a common set may thus be found also for $\hat{H}$ and $\hat{T}_n$. Let's consider in particular, $\vec{n} = (1, 0, 0)$. The Born-von Karman conditions require that the eigenfunctions remain unchanged if the translation operator is applied N_1 times

$$\hat{T}_{\vec{n}}\psi(\vec{r}) = (t_{\vec{n}})^{N_1}\psi(\vec{r}) = \psi(\vec{r}) \tag{19}$$

where $t_{\vec{n}}$ is the eigenvalue of the translation operator $\hat{T}_{\vec{n}_1}\psi(\vec{r})$. The requirement

$$(t_{\vec{n}})^{N_1} = 1 \tag{20}$$

is satisfied for e^{ik} where k is, at this point, just a real number. Eq. 20, on the other hand, dictates that

$$e^{ikN_1} = 1 \quad \Rightarrow \quad kN_1 = 2\pi n_1 \quad \Rightarrow \quad k = \frac{2\pi n_1}{N_1} \tag{21}$$

The same relation may be written by a general, three dimensional $\vec{k}$ restricted to the first Brillioun zone

$$\vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3 \tag{22}$$

We finally arrive at Bloch's theorem which states that the eigenfunctions of a lattice-periodic Hamiltonian must satisfy

$$\hat{T}_{\vec{n}}\psi(\vec{r}) = e^{i\vec{k}\cdot\hat{T}_{\vec{n}}}\psi(\vec{r}). \tag{23}$$

Bloch's theorem states that eigenstates of a periodic Hamiltonian pick up a phase when translated by a translation vector and may thus be labeled by the wavevector that characterizes the phase factor. In particular, Eq. 23 by wavefunctions written as

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r}) \tag{24}$$

where $u_{\vec{k}}(\vec{r})$ is a lattice periodic function with

$$u_{\vec{k}}(\vec{r} + \vec{T}_{\vec{n}}) = u_{\vec{k}}(\vec{r}). \tag{25}$$

Eq. 24 is an equivalent statement of Bloch's theorem. Let's illustrate this with the following picture in one dimension.
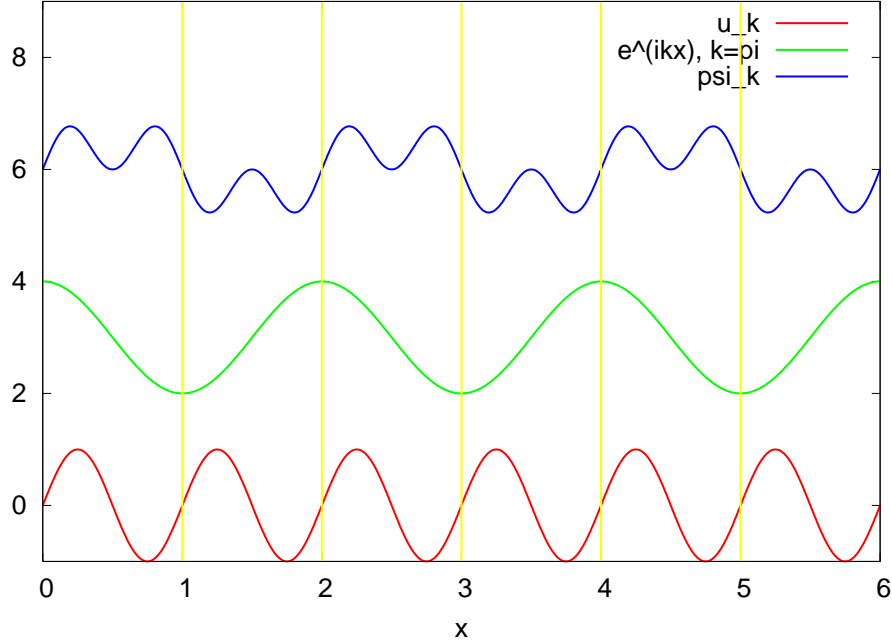
The bottommost line is a lattice periodic wavefunction of period $a = 1$ in some units. The line in the middle is the phase factor e^{ikx} for $k = \pi/2a$ and the topmost curve is the wavefunction that is their product (its real part to be more precise). As you see, unlike the electron density, the wavefunction *need not* have the periodicity of the lattice. It is still required however to obey the Born-von Karman boundary conditions.

The ability provided by the Bloch theorem to break down the wavefunction into a lattice-periodic function $u_{\vec{k}}$ and a phase factor allows us to work with a reduced, wavevector-dependent Hamiltonian. Applying the real Hamiltonian $\hat{H}$ of the system on to the wavefunction given in Eq. 31, we have[2]

$$\hat{H}\psi_{i,\vec{k}}(\vec{r}) = \epsilon_{i,\vec{k}}\psi_{i,\vec{k}}(\vec{r})$$
$$\hat{H}e^{i\vec{k}\cdot\vec{r}}u_{i,\vec{k}}(\vec{r}) = \epsilon_{i,\vec{k}}e^{i\vec{k}\cdot\vec{r}}u_{i,\vec{k}}(\vec{r}) \tag{26}$$

Multiplying the second line in Eq. 26 by $e^{-i\vec{k}\cdot\vec{r}}$, we have

$$e^{-i\vec{k}\cdot\vec{r}}\hat{H}e^{i\vec{k}\cdot\vec{r}}u_{i,\vec{k}}(\vec{r}) = \epsilon_{i,\vec{k}}u_{i,\vec{k}}(\vec{r})$$
$$\hat{H}_{\vec{k}}u_{i,\vec{k}}(\vec{r}) = \epsilon_{i,\vec{k}}u_{i,\vec{k}}(\vec{r}) \tag{27}$$

where $\hat{H}_{\vec{k}} = e^{-i\vec{k}\cdot\vec{r}}\hat{H}e^{i\vec{k}\cdot\vec{r}}$. It is therefore possible to scan the Brillioun zone by writing and solving a new Hamiltonian for each wavevector. Each $\hat{H}_{\vec{k}}$ will yield a spectrum of eigenvalues and in the limit of large crystal dimension, these eigenvalues will merge into a continuous graphical representation of eigenvalues, which is called the *band structure*. The band structure is a very important tool for deciding upon the electronic properties of a crystal.

III. AN EXAMPLE : TIGHT-BINDING MODEL FOR ATOMS ON A CHAIN

In order to illustrate the arguments we have introduced above, let's see a very simple one-dimensional example [3]. Assume that we have a one-dimensional arrangement of infinitely many atoms on a chain and assume Born-von Karman boundary conditions with a period of N atoms.

We are going to employ what is known as the *tight-binding model* where the variational wavefunction is an expansion in terms of atomic orbitals located on different atoms. The character of orbitals to be included in the expansion depends on the species included. For a carbon chain, for instance, it is usually sufficient to take the $2s$ and the $2p$ orbitals since the $1s$ orbitals do not contribute to bonding. However, here we shall only consider the $1s$ orbitals to illustrate the idea.

Let us go through the steps of the calculations one by one :

1. Start with the atomic orbitals centered on each atom :

$$\phi_l(x - na) \tag{28}$$

where l is the orbital label (in three dimensions, $l = 2s, 2p_x, 2p_y, 2p_z$ etc.), x is the coordinate variable, na is the location of the nth atom and a is the lattice constant.

2. Construct $k-$dependent functions from the orbitals in Eq. 28 to be used as a basis.

$$\chi_{kl}(x) = \frac{1}{\sqrt{N}} \sum_n e^{ikna} \phi_l(x - na) \tag{29}$$

where N is the number of atoms in the Born-von Karman cell. The normalization constant should be self-explanatory.

3. Check to make sure that χ_{kl} obey Bloch's theorem.

$$\chi_{kl}(x + n'a) = \frac{1}{\sqrt{N}} \sum_n e^{ikna} \phi_l(x - (n - n')a) \tag{30}$$

Define a new variable for the summation $n'' = n - n'$ and substitute into Eq. 30.

$$\chi_{kl}(x + n'a) = \frac{1}{\sqrt{N}} \sum_{n''} e^{ik(n' + n'')a} \phi_l(x - n''a)$$

$$= \frac{1}{\sqrt{N}} e^{ikn'a} \sum_{n''} e^{ikn''a} \phi_l(x - n''a)$$

$$= e^{ikn'a} \chi_{kl}(x). \tag{31}$$

4. Construct the variational wavefunction — do not forget that k is a good quantum number for this wavefunction.

$$\Psi_k(x) = \sum_l c_{kl} \chi_{kl}(x) \sum_{ln} c_{kl} e^{ikna} \phi_l(x - na) \tag{32}$$

5. Construct the variational equations to find the coefficients

$$\sum_{lm} \left[\langle \chi_{km} | \hat{H} | \chi_{kl} \rangle - \varepsilon_k \langle \chi_{km} | \chi_{kl} \rangle \right] c_{kl} = 0 \tag{33}$$

6. Look at the overlap term n Eq. 33. Substitute Eq. 29 :

$$\langle \chi_{kl} | \chi_{km} \rangle = \frac{1}{N} \sum_{nn'} e^{ik(n - n')a} \langle \phi_l(na) | \phi_m(n'a) \rangle$$

$$= \frac{1}{N} \sum_{nn'} e^{ik(n - n')a} \langle \phi_l(0) | \phi_m(na - n'a) \rangle \tag{34}$$

where $|\phi_m(na)\rangle$ refers to an orbital centered on the nth atom located at $x = na$. Now let $n'' = n - n'$

$$\langle \chi_{kl} | \chi_{km} \rangle = \frac{1}{N} \sum_{n'n''} e^{ikn''a} \langle \phi_l(0) | \phi_m(n''a) \rangle$$

$$= \sum_n e^{ikna} \langle \phi_l(0) | \phi_m(na) \rangle \tag{35}$$

Eq. 35 is the most general expression for a general set of orbitals. In this simple example, we only consider one kind of orbital, namely $l = 1s$ and as a result the sum over l in Eq. 35 reduces to a single term.

Next, we assume that the overlap between the orbitals on neighboring atoms is so small that the inner product of orbitals in Eq. 35 is nonzero only when $n = 0$, i.e. when both orbitals are on the same atom. This is not necessary but makes our job easier. Thus,

$$\langle \phi(0) | \phi(na) \rangle = \delta_{n,0} \tag{36}$$

7. Similarly for the matrix element of the Hamiltonian,

$$\langle \chi_{kl}|\hat{H}|\chi_{km}\rangle = \sum_n e^{ikna}\langle\phi(0)|\hat{H}|\phi(na)\rangle \tag{37}$$

This time, we assume that the Hamiltonian matrix element does not only remain on-site but extends to neighbors. This amounts to

$$\langle\phi(0)|\hat{H}|\phi(na)\rangle = \varepsilon_s\delta_{n,0} + t\delta_{n,\pm1}. \tag{38}$$

This particular approximation is refered as the *nearest-neighbor approximation.*

8. Substitute Eq. 36 and Eq. 38 into Eq. 33 to get

$$\sum_n e^{ikna}\left(\varepsilon_s\delta_{n,0} + t\delta_{n,\pm}\right) = \varepsilon_k\sum_n e^{ikna\delta_{n,0}}. \tag{39}$$

Note that even though the original equation started out as a matrix equation to determined the coefficients, the simplicity of the single-orbital assumption turned it into a single equation.

9. Finally, we obtain the following analytic equation for the energy eigenvalues

$$\varepsilon_k = \varepsilon_s + 2t\cos ka \tag{40}$$

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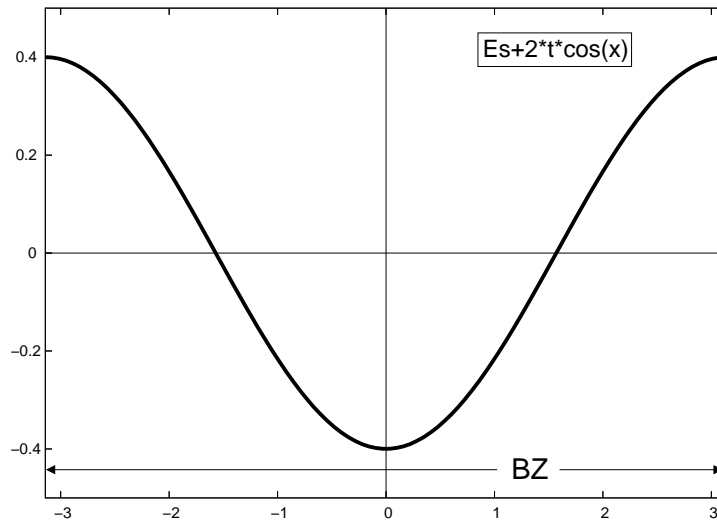
[1] This is a good approximation unless the system size is so small that surface effects cannot be neglected
[2] The new index i designates each eigenfunction in the spectrum of a given $\vec{k}$
[3] Adapted from Kaxiras